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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 synthetization of exfoliated graphite intercalation 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 (H_2O_2, HNO_3 and $KClO_3$) previously mixed with H_2SO_4. 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 H_2SO_4/HNO_3.

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 (H_2O_2, HNO_3 e $KClO_3$), previamente misturados com H_2SO_4. 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 H_2SO_4/HNO_3.

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

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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 HSO_4^- and H_2SO_4 molecules [1, 4, 13]. Different chemical reactions have been proposed as model for the synthetiza-

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tion's process of those materials, among which [1, 13]. 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.

$$24nC + O_x^{z} + H_2SO_4 \rightarrow C_{24n}^{\ +} \cdot HSC_4^{\ -}(m-1)H_2SO_4 + HO_x^{(z-1)} \quad (1)$$

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-ElHAMID 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_2O_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 ^{o}C;

Samples of 0.5 g of each type of graphite were oxidized in three different mixtures, using three different oxidizing reagents: H_2O_2, HNO_3 and $KClO_3$. Each reagent was previously mixed until homogenization with H_2SO_4. The proportions used are shown in Table 1.

Table 1: Proportions of mixtures of graphite with oxidants and acids.

MATERIALS	**$C/H_2O_2/H_2SO_4$**	**$C/HNO_3/ H_2SO_4$**	**$C/KClO_3/H_2SO_4$**
PROPORTIONS	0.5 g : 5 mL : 40 mL	0.5 g : 5 mL : 40 mL	0.5 g : 0.2 g : 40 mL

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 ^oC 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 $2\Theta \approx 26.6^o$ 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_2O_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.

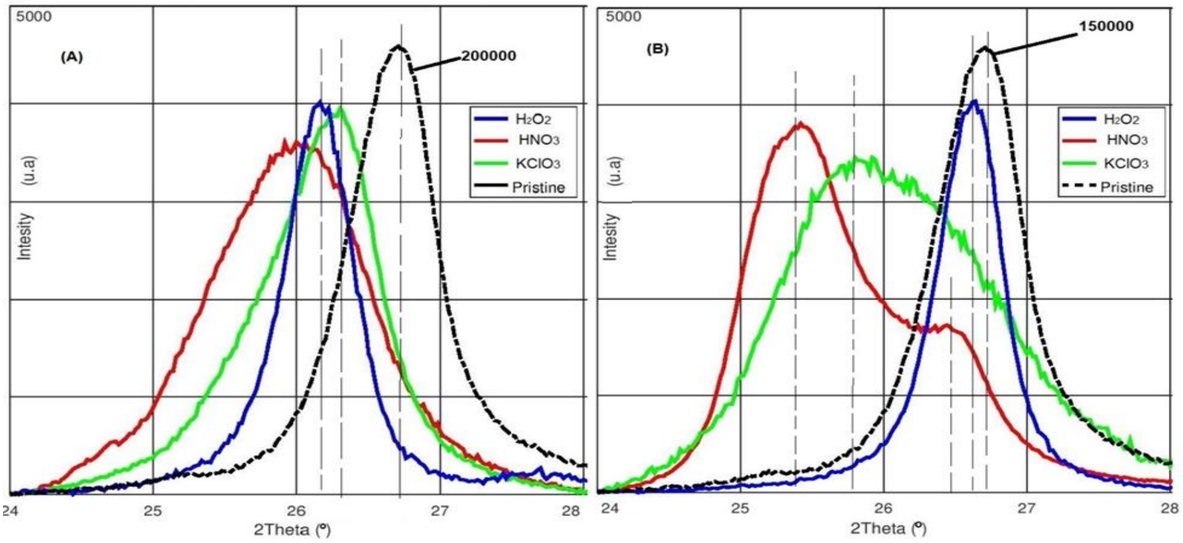

Figure 1: Diffractograms of the samples of (a) graphite type A and (b) graphite type B, oxidized using H_2O_2 (blue), HNO_3 (red) and $KClO_3$(green); and the black discontinuous diffractogram corresponds to the pristine graphite in each case.

For the B samples oxidized with HNO_3, the peak at $2\Theta \approx 26{,}6^o$ clearly dislocates and divides itself into two peaks, the first of them appearing at $2\Theta \approx 25.6^o$ and the second one at $2\Theta \approx 26.5^o$. 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 $KClO_3$, the peak $2\Theta \approx 26.6^o$ just displaces to 25.8^o also indicating an increment of the basal distance and a possible intercalation.

For the A oxidized samples using HNO_3 as an oxidizing agent, in which the peak becomes wider or displaces from $2\Theta \approx 26.6^o$ to $2\Theta \approx 26.0^o$. When used $KClO_3$ as an oxidant, the peak $2\Theta \approx 26.6^o$ does not displace, it becomes only a little wider. Therefore, it seems that the Type A graphite exfoliated or intercalated better when HNO_3 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 $NaClO_3$. 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 H_2O_2, HNO_3 and $KClO_3$, 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 HNO_3 and $KClO_3$. The second order band D+D' ($\approx$ 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].

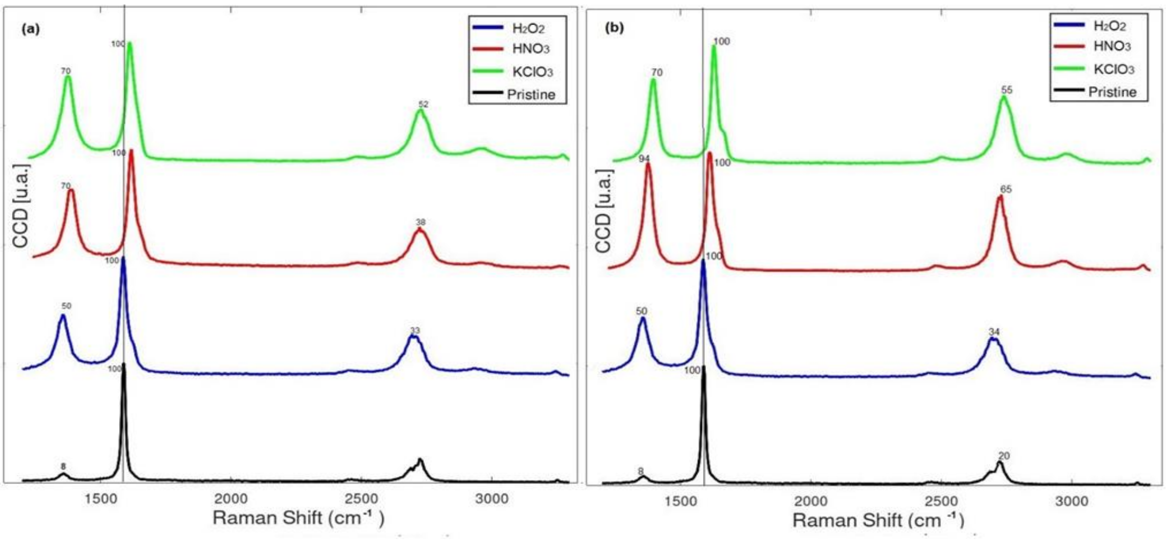

Figure 2: Raman spectra of the samples of (a) graphite A and (b) graphite B oxidized with H_2O_2, HNO_3 and $KClO_3$.

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 (H_2O_2, HNO_3 or $KClO_3$, 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 HNO_3 as oxidizer and it shows the degradation effect and the flake layers clearly separated due to the exfoliation or delamination process that occurred.

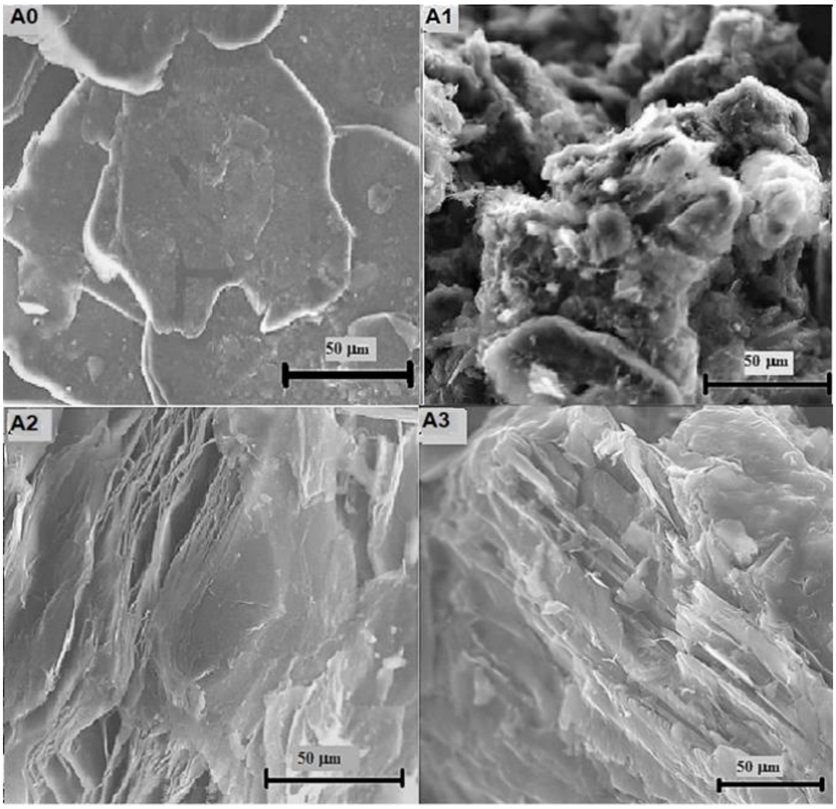

Figure 3: SEM micrographs of graphite type A samples: A0 (original), oxidized with H_2O_2 (A1), with HNO_3 (A2) and with $KClO_3$ (A3).

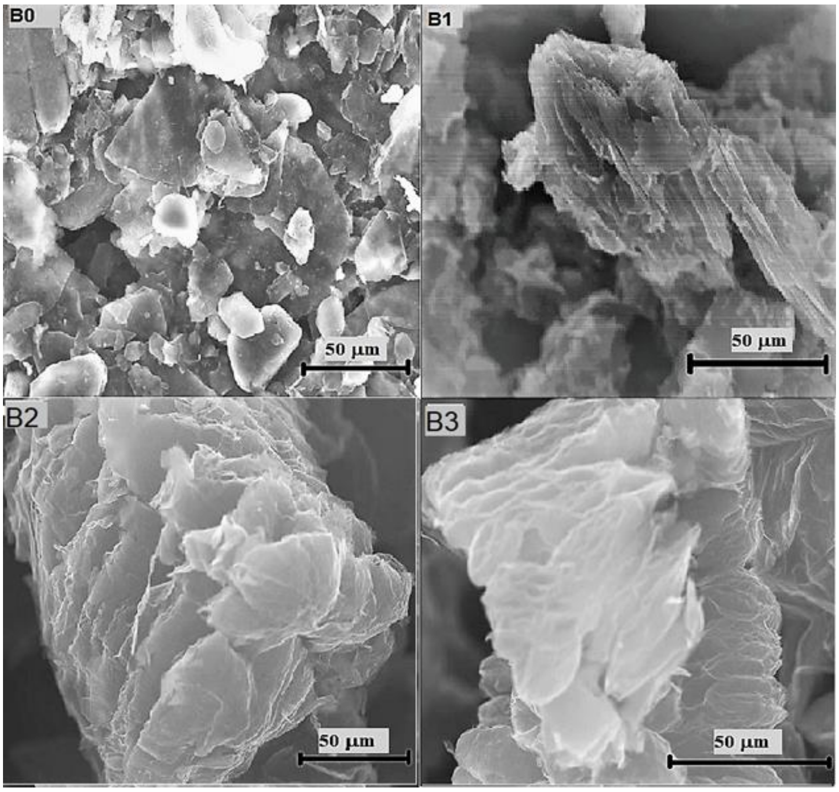

Figure 4: SEM micrographs of graphite type B samples: B0 (original), oxidized with H_2O_2 (B1), with HNO_3 (B2) and with $KClO_3$ (B3).

A similar result is found with the treatment of graphite A using $KClO_3$ 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 HNO_3 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 synthetization processes each one them characterized by the mixture used as oxidant agent H_2SO_4/H_2O_2, H_2SO_4/HNO_3 or $H_2SO_4/KClO_3$ but under the same experimental conditions: ultrasonication 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 ^oC 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 H_2SO_4/HNO_3 and $H_2SO_4/KClO_3$ 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 synthetization process with the oxidizer H_2SO_4/HNO_3 lead to better results (stronger delamination and exfoliation) for both graphite types.

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6. BIBLIOGRAPHY

[1] RÜDORFF, W., HOFMANN, U. "Über Graphitsalze", *Zeitschrift für anorganische und allgemeine Chemie*, v. 238, n. 1, p. 1-50, Jun. 1938.

[2] EBERT, L.B. "Intercalation compounds of graphite", *American Rev. Mater. Sci*., v. 6, pp. 181–211, 1976.

[3] ENOKI, T., MIYAJIMA, S., SANO, M., *et al.* "Hydrogen-Alkali-Metal-Graphite Ternary Intercalation Compounds", *Journal of Materials Research*, v. 5, n. 2, pp. 435–466, 1990.

[4] OH, W.C., BAE, N.K., CHOI, Y.J., *et al.* "Structural stability and electron energy state of the H2SO4-graphite deintercalation compounds", *Carbon*, v. 33, n. 3, pp. 323–327, 1995.

[5] LERF, A., HE, H., FORSTER, M., *et al.* "Structure of graphite oxide revisited", *Journal of Physical Chemistry B*, v. 102, n. 23, pp. 4477–4482, 1998.

[6] MATSUMOTO, R., OKABE, Y. "Electrical conductivity and air stability of FeCl3, CuCl2, MoCl5, and SbCl5 graphite intercalation compounds prepared from flexible graphite sheets", *Synthetic Metals*, v. 212, pp. 62–68, Feb. 2016.

[7] ASGHAR, H.M.A., HUSSAIN, S.N., SATTAR, H., *et al.* "Environmentally friendly preparation of exfoliated graphite", *Journal of Industrial and Engineering Chemistry*, v. 20, n. 4, pp. 1936–1941, Jul. 2014.

[8] ASGHAR, H.M.A., HUSSAIN, S.N., SATTAR, H., *et al.* "Potential Graphite Materials for the Synthesis of GICs", *Chemical Engineering Communications*, v. 202, pp. 508–512, 2015.

[9] PARIZE, D.D.D.S, SANTOS, W.F., PEZZIN, S.H. "Nanocompósitos de matriz epoxídica com reforços produzidos a partir do grafite natural". *Revista Matéria*, v. 18, n. 2, pp. 1260–1272, 2013.

[10] LIMA, A.M., FARIA, G.S, NARDECCHIA, S., *et al.* "Produção e caracterização de filmes finos transparentes e condutores de óxido de grafeno reduzido", *RevistaMatéria*, v. 22, supl. 1, e-11908, 2017.

[11] FARIA, G. S., LIMA, A.M., BRANDÃO, L.P., *et al.* "Produção e caracterização de óxido de grafeno e óxido de grafeno reduzido com diferentes tempos de oxidação" *RevistaMatéri*a, v. 22, supl. 1, 2017.

[12] HACK, R., CORREIA, C.H.G., ZANON, R.A.D.S., *et al.* "Characterization of graphene nanosheets obtained by a modified hummer's method", *Revista Matéria*, v. 23, n. 1, e-11988, 2018.

[13] YAKOVLEV, A.V., FINAENOV, A.I., ZABUD'KOV, S.L., *et al.* "Thermally expanded graphite: Synthesis, properties, and prospects for use", *Russian Journal of Applied Chemistry*, v. 79, n. 11, pp. 1741–1751, 2006.

[14] SALVATORE, M., CAROTENUTO, G., DE NICOLA, S., *et al.* "Synthesis and Characterization of Highly Intercalated Graphite Bisulfate", *Nanoscale Research Letters*, v. 12, 167, 2017.

[15] MIR, A., SHUKLA, A. "Electrochemical exfoliation of graphite to stage-III graphite bisulfate flakes in low concentration sulfuric acid solution: A novel synthesis route to completely trilayer graphene suspension" *Applied Surface Science*, v. 443, pp. 157–166, 2018.

[16] DONG, L., CHEN, Z., ZHAO, X., *et al.* "A non-dispersion strategy for large-scale production of ultra-high concentration graphene slurries in water", *Nat. Commun*., v. 9, 76, 2018.

[17] BEPETE, G., ANGLARET, E., ORTOLANI, L., *et al.* "Surfactant-free single-layer graphene in water", *Nat. Chem*., v. 9, pp.347–352, 2017.

[18] GEIM, A.K., NOVOSELOV, K.S. "The rise of graphene", *Nature Materials*, v. 6, n. 3, pp. 183–191, 2007.

[19] LERF, A. "Storylines in intercalation chemistry', *Dalton Transactions*, pp. 1–33, 2014.

[20] TANCREDI, P., LONDOÑO, O.M, ROJAS, P.C.R., *et al.* "Step-by-step synthesis of iron-oxide nanoparticles attached to graphene oxide: A study on the composite properties and architecture", *Materials Research Bulletin*, v. 107, pp. 255–263, 2018.

[21] GRECO, A., TIMO, A., MAFFEZZOLI, A. "Development and characterization of amorphous thermoplastic matrix graphene nanocomposites", *Materials*, v. 5, n. 10, pp. 1972–1985, 2012.

[22] WOJTONISZAK, M., MIJOWSKA, E. "Controlled oxidation of graphite to graphene oxide with novel oxidants in a bulk scale", *Journal of Nanoparticle Research*, v. 14, n. 11, 2012.

[23] CASTRO NETO, A.H., GUINEA, F., PERES, N.M.R., *et al.* "The electronic properties of graphene", *Reviews of Modern Physics*, v. 81, n. 1, p. 109–162, 2009.

[24] WANG, H.S., TIAN, S.Y., YANG, S.W., *et al.* "Anode coverage for enhanced electrochemical oxidation: A green and efficient strategy towards water-dispersible graphene", *Green Chemistry*, v. 20, pp. 1306–1315, 2018.

[25] LIN, S., DONG, L., ZHANG, J., *et al.* "Room-Temperature Intercalation and ∼1000-Fold Chemical Expansion for Scalable Preparation of High-Quality Graphene", *Chemistry of Materials*, v. 28, n. 7, pp. 2138–2146, 2016.

[26] ROSHAN, M. J., JEEVIKA, A., BHATTACHARYYA, A., *et al.* "One-pot fabrication and characterization of graphene/PMMA composite flexible films", Materials Research Bulletin, v. 105, pp. 133–141, 2018.

[27] ZHANG, Y., XU, Y., ZHU, J., et al. "Electrochemically exfoliated high-yield graphene in ambient temperature molten salts and its application for flexible solid-state supercapacitors", *Carbon*, v. 127, pp. 392-403, Feb. 2018.

[28] PENG, L., XU, Z., LIU, Z., *et al.* "An iron-based green approach to 1-h production of single layer graphene oxide", *Nature Communications*, v. 6, pp. 1–9, 2015.

[29] MOGERA, U., DHANYA, R., PUJAR, R., *et al.* "Highly Decoupled Graphene Multilayers: Turbostraticity at its Best, *Journal of Physical Chemistry Letters*, v. 6, n. 21, pp. 4437–4443, 2015.

[30] MAHDY, S.M., GEWFIEL, E., ALI, A.A., "Production and characterization of three-dimensional graphite nanoplatelets", *Journal of Materials Science*, v. 52, n. 10, pp. 5928–5937, 2017.

[31] CANAL-RODRÍGUEZ, M., ARENILLAS, A., REY-RAAP, N., *et al.* "Graphene-doped carbon xerogel combining high electrical conductivity and surface area for optimized aqueous supercapacitors", *Carbon*, v. 118, pp. 291–298, 2017.

[32] LIN, J.H., "The Anionic Surfactant/Ionic Liquids Intercalated Reduced Graphene Oxide for High-performance Supercapacitors", *Nanoscale Research Letters*, v. 13, n. 215, pp. 9, 2018.

[33] EDWARDS, R.S., COLEMAN, K.S. "Graphene synthesis: Relationship to applications", *Nanoscale*, v. 5, n. 1, pp. 38–51, 2013.

[34] WEI, Z., VILLAMENA, F.A., WEAVERS, L.K. "Kinetics and Mechanism of Ultrasonic Activation of Persulfate: An in Situ EPR Spin Trapping Study", *Environmental Science and Technology*, v. 51, n. 6, pp. 3410–3417, 2017.

[35] ZHENG, X., HAN, X., ZHAO, X., *et al.* "Construction of Ni-Co-Mn layered double hydroxide nanoflakes assembled hollow nanocages from bimetallic imidazolate frameworks for supercapacitors". Materials Research Bulletin, v. 106, pp. 243–249, 2018.

[36] AMADE, R., MUYSHEGYAN-AVETISYAN, A., GONZÁLEZ, J. M., *et al.* "Super-capacitive performance of manganese dioxide/graphene nano-walls electrodes deposited on stainless steel current collectors", Materials, v. 12, n. 3, pp. 483-496, Feb. 2019.

[37] ABD-ELHAMID, A. I.; ALY, H. F.; SOLIMAN, H. A.M.; EL-SHANSHORY, A. A. “Graphene oxide: Follow the oxidation mechanism and its application in water treatment”, *Journal of Molecular Liquids*, v. 265, pp. 226–237, 2018.

[38] SILVA, D.L., CAMPOS, J.L.E., FERNANDES, T.F.D., *et al.* " Raman spectroscopy analysis of number of layers in mass-produced graphene flakes", Carbon, v. 161, pp. 181–189, 2020.

[39] WU, J-B, LIN, M-L., CONG, X., *et al.* "Raman spectroscopy of graphene-based materials and its applications in related devices", Chemical Society Reviews, v. 47, n. 5, pp. 1822–1873, 2018.

[40] PUREWAL, J. "Hydrogen Adsorption by Alkali Metal Graphite Intercalation Compounds", Thesis (Ph.D.), California Institute of Technology, USA, 2010.

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