Evaluation of Graphene Oxidation Methods

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Graphene oxide is one of the most important graphene derivates. Due to its unique chemical properties, this compound is largely used as starting point for functionalized products. Functional groups present in graphene oxide surface have large influence in the following steps of these reactions. Here, we make the evaluation of three different routes to obtain graphene oxide, and which functional groups are present in each product. Based on results, it was possible to conclude that different routes may favor the formation of specific functional groups.

Introduction

Since isolated for the first time in 2004 [1], graphene has demonstrated many excellent mechanical, electrical and chemical properties and held promise for a variety of applications [2]. In the family of graphene-based materials, graphene oxide (GO), a single layer (also, few layers or multiple layers) of graphite oxide is intensively studied due to its importance in graphene production by reduction [3-5] and easy functionalization into interest compounds [5-6]. The atomic structure of GO is essential for understanding its fundamental properties and realization of future technological applications. Solid-state ^{13}C and ^{1}H nuclear magnetic resonance revealed evidences of epoxy, hydroxyl, carboxylic, and a small amount of other groups in GOs [2]. Among these groups, the latter is probably the most commonly used as functionalization site, although epoxy and hydroxyl may be preferred for particular cases [5]. Due to this selectivity, it is important to obtain GO with desired characteristics. In this paper we analyzed GO obtained by the conventional Hummers' method and compared with those produced by two modified methods. Energy dispersive, infrared and Raman spectra were evaluated and electron scanning microscopy was used to detect visual aspects of each sample.

Materials and Methods

Materials

Commercial graphite (Nacional de Grafite Ltda, Brazil) was used. All reactants used were analytical grade.

Methods

Grafene Production. Two methods, describe in literature were used: The Hummers' method [7] – GO1 - and the adaptation made from Marcano et al. [8] – GO2. Additionally, a method based on Cote et al. [9] was used – GO3.

GO1. Approximately 69 mL of concentrated H_2SO_4 were added to a 3g mixture of graphite and 1,5g $NaNO_3$. It was cooled in an ice bath and received $KMnO_4$, after that it was heated for 30 min, cooled in an ice bath and finally received 138 mL H_2O DI (18 MΩ.cm). It reacted for 15 min at 98ºC and cooled once again. 420 mL H_2O and 3 mL 30% H_2O_2 were added. Product was washed and filtered with H_2O, HCl and C_2H_5O.

GO2. About 360 mL H_2SO_4 and 40 mL H_3PO_4 were added to 3 g graphite and 18 g $KMnO_4$. Reaction was heated to 50 ºC and stirred for 12h. Due to high viscosity, mixture needed auxiliary manual stirring. Reaction was cooled in ice bath and received 3 mL H_2O_2 30%. Product was filtered and washed as mentioned before. The product of this reaction presented lighter brown color than the others, with golden dots.

GO3. Close to 0,5 g NaNO3 were added to 23 mL concentrated H_2SO_4. Keeping the mixture in ice bath 0,5 g graphite were added, with magnetic stirring. 3 g of $KMnO_4$ were added, and reaction occurred for 1 h at 27-38 ºC. After this, 40 mL H_2O were added and mixture was heated to 95 ºC. During cooling process, 100 mL H2O and 3 mL H_2O_2 were added. Product was filtered and washed with water. This solution presented darkest color than the others.

Graphene Evaluation. All three samples were analyzed by infrared spectroscopy (Spectrum 100 - Perkin Elmer Precisely), Raman spectroscopy (T6400 – Jobin Yvon and Ntegra Spectra - NT MDT) and energy dispersive spectroscopy (model CM 120 – Phillips). Additionally, some pH measures were taken from samples to evaluate the presence of acidic groups.

Results

Infrared Spectroscopy

When evaluating the infrared spectra obtained for the samples GO1 (Fig. 1.a), GO2 (Fig. 1.b) and GO3 (Fig. 1.c) bands between 2500 and 3600 cm^{-1} are observable in GO1 and GO3 spectra. These bands indicate the presence of O-H (3200 to 3600 cm^{-1}) and O-H linked to C=O (2500 to 3200 cm^{-1}) bonds of carboxylic acid structures. Bands perceptible close to 3030 cm^{-1} indicate C-H bonds in aromatic rings and the bands close to 1710 and 1760 cm^{-1}, present in all samples, also indicates C=O from carboxylic acids. Finally, bands between 1200 and 1300 cm^{-1} are indicative of C-O bonds from the same functional group. So GO2 seems to have less carboxylic acid than the others.
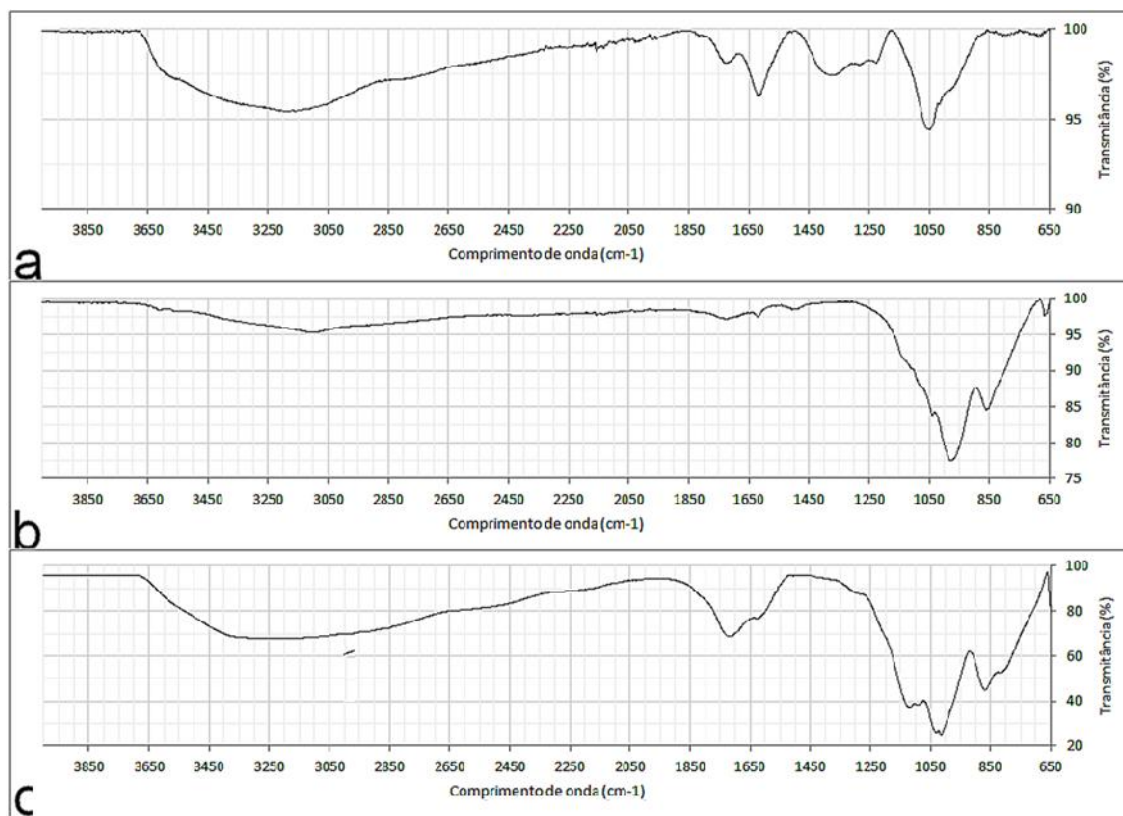
Figure 1. Infrared spectra for a) GO1, b) GO2 and c) GO3

Raman spectroscopy

Raman spectra were very similar for all three samples. All of them presented broadened peaks expected for graphene, see Figure 2 as an example. Analyzing this sample it is possible to note the similarities with those found in literature [5,10]. Two peaks among 1300 cm^{-1} and 1600 cm^{-1} are the main characteristics of these compounds.
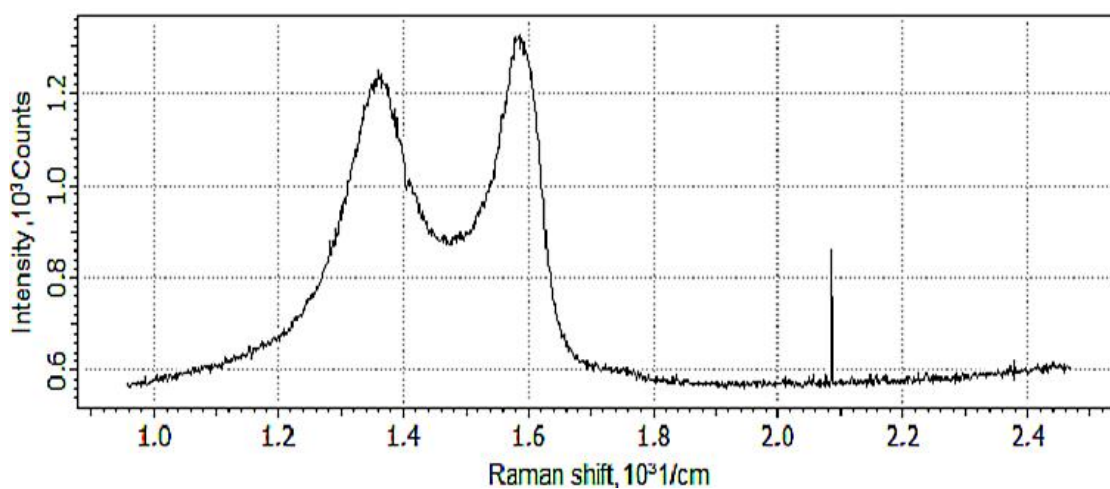

Figure 2. Raman spectrum for a GO sample

Energy dispersive spectroscopy

Energy dispersive spectra (EDS) were made from samples GO1 and GO3, once GO2 does not present good amount of carboxylic acid, the most interesting compound (Tab. I). GO3 presents higher O/C rate. This proportion reflects the presence of carboxylic, alcohol and epoxy groups, but may also indicate presence of water linked to GO.

TABLE I. EDS numeric results

Sample	GO1	GO3	GO1	GO3
Element	% mass		% atom	
C	58.44	29.91	65.19	36.25
O	41.56	70.09	34.81	73.75

PH

PH analyses were conducted considering that carboxylic acid would be the main responsible for variability in H^+ concentration. Solutions containing 0,01g/mL of each graphene oxide were prepared for analyses. GO1 sample has a pH of 2.7, while GO3 of 2,1. This is a good indicative that the latter has higher incidence of carboxylic acid groups, and consequently more active sites for reactions demanding these groups.

Conclusions

After careful analysis of the results achieved by the three routes described here, it is possible to conclude that the method adapted from Cote et al. [9] is a good alternative to produce carboxylic-acid-rich graphene oxide, able to be used as starting point for the most of functionalization reactions. On the other hand, graphene oxide samples based on Marcano et al [8] method are epoxy-rich, being useful for some particular applications.

Acknowledgments

References

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Gregorieva and A. A. Firsov, *Science*, **306**, 666 (2004).
2. L. Liu, L. Wang, J. Gao, J. Zhao, X. Gao and Z. Chen, *Carbon*, **50**, 1690 (2012).
3. M. J. McAllister, J.-L. Li, D. H. Adamson, H. C. Schniepp, A, A. Abdala, J. Liu, M. Herrera-Alonso, D. L. Milius, R. Car, R. K. Prud'homme and I. A. Aksay, *Chem. Mater.*, 19, 4396 (2007).
4. S. Park and R. S. Ruoff, *Nat. Nanotechnol.*, **4**, 217 (2009).
5. D. R. Dreyer and S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.*, **39**, 228 (2010).
6. S. K. Bhunia and N. R. Jana, *ACS Appl. Mater. & interfaces*, **3**, 3335 (2011).
7. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, **80**, 1339 (1958).
8. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L.

    B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, **4**, 4806 (2010).
9. L. J. Cote, F. Kim, J. Huang, *J. Am. Chem. Soc.*, **131**, 1043 (2009).
10. Y. Guo, X. Sun, Y. Liu, W. Wang, H. Qiu, J. Gao, *Carbon*, **50**, 2513 (2012).