Effect of exfoliation method on graphite oxide. A comparison between exfoliation by ball milling and sonication in different media

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Abstract. Graphene oxide and reduced graphene have been exfoliated from graphite oxide synthesized by Hummer’s method. In order to establish a comparison, the exfoliation process was performed using two different methods, high energy ball milling and sonication. Each one was studied in two different media, organic solvent N-methyl 2 pyrrolidone and deionized water, obtaining four different products. The quality of the graphene and graphene oxides was studied using Raman spectroscopy. Structural characterization was performed using X-ray diffraction technique. The presence of oxygen-containing functional groups was determined by Fourier transform infrared spectra, while the morphology was investigated by scanning electron microscopy and energy-dispersive spectroscopy. The aim of this work is present a process to obtain graphene and graphene oxide of high quality at lower cost and better environmental conditions.

1. Introduction

Graphene (G) is an allotrope single layer of carbon atoms in the form of a 2D. Their structure consists of sp² carbon atoms arranged in a hexagonal network [1]. Graphene-based materials have excellent properties such as extremely high electron mobility, high thermal conductivity, tunable band gap, strength and elasticity. Moreover, graphene is a material with suitable magnetic and electronic properties [2]. Specifically, graphene oxide (GO) and reduced graphene oxides (rGO) show promising applicability in sensors, energy storage, optoelectronics, among others [3]. The main technique for graphene production from graphite are top-down. Top down includes solvent exfoliation or oxidation/ exfoliation/ reduction. This can be easily scaled at low cost [4]. One of the most common method to obtain graphite oxide (GrO) is oxidation chemical preparation by Hummer’s from graphite. This method is a promising route to achieve mass production [5,6]. GrO can be exfoliated by mechanical forces in water or can be dispersed in organic solvents by sonication. Liquid-phase exfoliation is a mass-scalable approach for the production of GO using less energy and reducing the re-combination of exfoliated sheets. This occurs by the formation of covalently linked 2D networks [7-9]. Otherwise, using exfoliation in organic solvents GO can be obtained using concentrations up to 0.01 mg/ml. This happens because the balance between the energy required to exfoliate graphene and solvent-graphene interaction [10]. Other process used in exfoliation is ball milling technique because it produces shear forces. This method is highly desired for achieving large size graphene flakes, using solvents as a media. Besides, provides crystals
of high quality and stable suspensions [11,12]. In the present work we present a comparative analysis of the exfoliation of graphite oxide by ball milling and sonication in two different media, organic solvent N-methyl 2 pyrrolidone NMP and deionized water. The effect of the different exfoliation conditions on the quality of the material, morphology and structural characteristics was studied.

2. Materials and methods

2.1. Synthesis
The graphite oxide GrH was prepared by Hummer’s method. 3 g of graphite powder (Alfa Aesar, 99%) 3 g of Potassium Nitrate KNO₃ (Sigma Aldrich 99%) and 60 ml of sulfuric acid H₂SO₄ (Acros 98%) were mixed and kept in an ice bath at temperature range from 0 to 5 Celsius degrees. The mixture was stirring during 2 h. 9 g of potassium permanganate KMnO₄ (Sigma Aldrich 97%) was added to the suspension keeping the reaction at temperature lower than 15 °C. The ice bath was removed, and the mixture was stirred for 3 days. Finally, the mixture was washed with deionized water DI and centrifuged several times. After filtration and drying under vacuum at room temperature, the graphite oxide (GrH) was obtained as a powder. For the exfoliation by ball milling process it was added 300 mg of GrH in 30 ml of NMP solvent at room temperature in planetary ball mill Retsch PM 100. It was operated at 300 revolutions per minute in a stainless-steel vessel of 50 mL volume during 6 hours obtaining the sample GrHD1. For the sample processed in deionized water media it was used the same characteristics in the process mentioning before but putting in the vessel 300 mg of GrH in 30 mL of DI water obtaining the sample GrHD2. The exfoliation in sonication was done in a Fisher Scientific FS20 ultrasonic cleaner mixing 300 mg of the GrH in 30 mL of NMP solvent for 8 hours. The same procedure was done but mixing 300 mg of GrH in 30 mL of DI water obtaining the samples GrHD3 and GrHD4 respectively. For purification the mixture was washed with DI water and centrifugation several times. After filtration and drying under vacuum at room temperature, the graphene oxide (GO) was obtained as a powder.

2.2. Characterization
The prepared samples were examined by Raman. It was used to study the structure and transformations occurred in the material, by mean of continuous wave (CW) argon ion (Ar +) laser (model 177G02, Spectra Physics) of 514.4 nm in wavelength was used as a source of monochromatic radiation placed horizontally. Backscattered Raman spectra were collected by a high-throughput holographic imaging spectrograph (model HoloSpec f/1.8i, Kaiser Optical Systems) with volume transmission gratings, a holographic notch filter, and thermoelectrically cooled charge-coupled device (CCD) detector (Andor Technology). It was used Fourier transform infrared (FTIR) JASCO FT/IR, 4100 type A to analyze the functionalities groups of the samples. The X-ray diffraction patterns (XRD) were obtained by Diffractometer Siemens 500D CuKa (n = 1.54060 °A) radiation with 28 in the range of 5 -50°. The structural characterization was studied with scanning electron microscope (SEM), JEOL 6330F, Peabody, microscope.

3. Results and discussion
The Raman spectra of graphite oxide (GrH), and the processed samples, GrHD1, GrHD2, GrHD3 y GrHD4 are shown in Figure 1. The main Raman bands characteristic in graphene materials are D at 1350 cm⁻¹, G at 1580 and 2D at 2700 cm⁻¹. Band D is associated with defects and disorders due to physical or chemical treatments that cause defects in graphite, such as oxidation processes. The G band is associated with active phonon modes with E₂g symmetry for graphite material. The 2D-band is attributed to the development of graphene structure and number of layers in graphene and their intensity corresponds with graphene structure. The ratio ID/IG increases with the amount of disorder [13-17]. Table 1 shows the position, intensity and ratio ID/IG.
Figure 1(a) shows that the GrHD2 and GrHD3 samples have a good oxidized structure with the highest ID / IG ratios (Table 1), however in Figure 1(b) it is observed that the GrHD3 sample has the lowest intensity in the band 2D (see Table 1) presenting structure of graphene oxide. In addition, the shape of its spectrum indicates that it is composed of several layers showing that there was exfoliation without losing oxidation. The shift of the G-band towards higher frequencies demonstrates the increase in the space between layers characteristic of graphene oxide. On the other hand, the intensity and shifted of the 2D band shows that the GrHD1 and GrHD4 samples have a structure close to the reduced graphene oxide, showing that in the processes followed for these samples, the degree of oxidation is lost.

![Graph](image)

**Figure 1.** Raman Spectra of GrHC, GrHD1, GrHD2, GrHD3, GrHD4 samples. a) D and G bands b) 2D band.

Figure 2 shows the FTIR spectra of the GrH and the processed samples to determine the presence of functional groups. With the exfoliation process it is expected that the intensities of the peaks corresponding to the oxygen-containing functional groups present in the GrHC sample will be maintained the main characteristic peaks that appear in graphite oxide at 3380 cm\(^{-1}\). This is associated to the presence of various functional groups, O-H stretching vibrational mode, C=O stretching vibration from carboxyl group which appears in 1715 cm\(^{-1}\), the peak at 1380 cm\(^{-1}\) that confirms hydroxide group while the oxygenated groups are in 1230 cm\(^{-1}\) and finally in 1015 cm\(^{-1}\) that is related to C-O-C stretching epoxy groups [18-20]. In Figure 2, the GrHD3 sample shows the most intense characteristic peaks of graphene oxide because the carboxyl, hydroxyl, epoxy and carbonyl groups were maintained. This is confirmed due to the oxygen molecules have a large occupation at the edges and the basal plane of GrHD3 showing the successful exfoliation of graphite oxide to obtain graphene oxide confirming what was observed in the Raman spectra. In the other samples, all the intensities of the peaks corresponding to the oxygen-containing functionalities of graphene oxide decreased and even some disappeared due to the removal oxygen, which shows that the corresponding exfoliation process used causes a degree of reduction in the processed samples.

**Table 1.** Position D, G and 2D bands, intensity and ratio ID/IG.

| Sample ID | D Peak [cm\(^{-1}\)] | G Peak [cm\(^{-1}\)] | 2D Peak [cm\(^{-1}\)] | I\(_D\) | I\(_G\) | I\(_D\)/I\(_G\) |
|-----------|----------------------|----------------------|----------------------|-------|-------|-------------|
| GrH       | 1350.1779            | 1581.1025            | -                    | 505.1340 | 391.3040 | 1.2901      |
| GrHD1     | 1339.5780            | 1592.0727            | 2704.6764            | 146.5890 | 174.4040 | 0.8405      |
| GrHD2     | 1342.0443            | 1587.7561            | 2713.3937            | 276.4110 | 228.5740 | 1.2093      |
| GrHD3     | 1343.6737            | 1584.7627            | 2761.1307            | 461.5320 | 423.7940 | 1.0890      |
| GrHD4     | 1344.8047            | 1585.2884            | 2728.1736            | 555.7470 | 554.7230 | 1.0018      |
The XRD spectra measured in a range of 2θ from 5° to 50° is shown in Figure 3. The XRD pattern allows to determine the crystalline phase of the distance of the intermediate layer in graphitic materials such as graphite oxide, graphene oxide and reduced graphene oxide because the distance between two layers is an important parameter to evaluate the structural information of the graphene materials. Figure 3 shows the XRD spectra for the samples of GrHC, GrHD1, GrHD3 and in the inset is observed for the graphite. The diffraction peak for the graphite powder was 2θ = 26.4° with a corresponding inter-layer distance of 0.34 nm confirming the presence of a well-organized layer structure along the orientation.
which is according to the literature [5,19,20,21,22]. For the graphite oxide GrHC the 2θ peak is in 9.95° corresponding with a interlayer distance of 0.89 nm indicating the presence of functional groups. After exfoliation by sonication the sample GrHD3 of graphite oxide shows the diffraction peak is at around 2θ=10.88° corresponding to a layer-to-layer distance of 0.81 nm which is close to interlayer distance in the graphite oxide remain the oxide structure. In addition, the diffraction peak appeared at around 2θ=42.3° in XRD pattern, indicates that graphene oxide exhibits turbostratic band of disordered carbon materials [18,19]. The XRD pattern for the GrHD1 sample also shows the presence of the 2θ peak at 25.8°, which indicates that there was a partial reduction process due to the permanence of the peak at 2θ=10.9° as noted, the peak is shapeless due to an amorphous carbon comprising many defects, folding structures, impurities, sp1, sp2 and sp3 hybridization structures [23].

Figure 4. XRD Spectra a) GrHC, b) GrHD3, c)GrHD1, samples.

SEM pattern in Figure 4 allowed to verify the morphologies of the samples. The micrographs obtained from SEM gave an image of the surface of the material with an increase of 5000x. The SEM micrograph of GrHC revealed in Figure 4 (a) shows a morphology of wrinkled flakes forming layers which indicates that the graphite layers are oxidized. From this, it is possible to distinguish the edges of the individual sheets in GrHC which indicates that it has a layered structure of multiple sheets. In the SEM images is evident that the graphene oxide sheets are suspended and an increase in thickness was observed due to the introduction of the functional groups [24]. Figure 4 (b) corresponds to sample GrHD3 and shows that the films are stacked but it is possible to observe the layers while maintaining the structure of oxidized material this is due to the addition of functional groups that are combined mainly at the edges of the material forming the graphene oxide. Figure 4 (c) shows the micrograph GrHD1, where the surface shows fine wrinkled sheets that accumulate to form material of disordered structure. Figure 4 (c) shows the GrHD4 micrograph, where the surface shows fine wrinkled sheets that accumulate to form disordered structure material like thin sheets added at random with well-defined edges and folded surfaces. This type of wrinkled structure is typical of the reduced graphene oxide morphology, which confirms that graphene oxide reduction occurred in this process. The results of EDS for the GrHC GrHD3 and GrHD1 samples show Carbon C ratios of 62.72% - O Oxygen 16.18% for GrHC, C 69.18% - OR 27.01% for GrHD3 and finally of C 88, 23% - OR 10.42% and the remaining values correspond to other compounds, confirming that the GrHD3 sample retains its oxidized structure and the GrHD1 sample presents a reduction process.

4. Conclusion
The results of the characterization methods used showed similar and consistent information. According to the four methods used to exfoliate graphite oxide, the best result in obtaining graphene oxide is the one that uses sonication in NMP media GrHD3. However, Raman showed that the GrHD4 sample prosed by sonication in DI water media also shows a structure like graphene oxide. On the other hand, the samples processed by ball milling (GrHD1 y GrHD2) showed a degree of reduction where the sample processed in NMP media GrHD1 presented a structure like the reduced graphene oxide. These results are confirmed with the spectra held in FTIR, XRD and the SEM patterns. The characteristics bands D,
G and 2D of the Raman spectrum indicate that the sample obtained by exfoliation using sonication in NMP has a multilayer oxidized structure while the sample obtained by the ball milling process in NMP media has a reduced graphene oxide structure, although with few layers have major defects in their structure, which is confirmed with the XRD pattern. Therefore, the processes presented here both for obtaining graphene oxide and for obtaining reduced graphene oxide can potentially be applied for the production of graphene nano-sheets.

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References
[1] Zhu H, Xu S, Xie D and Fang Y 2017 Graphene Fabrication, Characterizations, Properties and Applications (London: Academic Press)
[2] Zhong Y, Zhen Z and Zhu H 2017 Graphene: Fundamental research and potential applications FlatChem 4 20
[3] Muzyka R, Kwoka M, Smędkowski L, Diez N, Gryglewic G 2017 Oxidation of graphite by different modified Hummers methods New Carbon Materials 32(1) 15-20
[4] Sierra U, Álvarez P, Blanco C, Granda M, Santamaria R and Menéndez R 2015 New alternatives to graphite for producing graphene materials Carbon 93 812
[5] Stobinski L, Lesiak B, Malolepszy A, Mierzwka B, Zemek, J and Bieloshapka I 2014 Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods Journal of Electron Spectroscopy and Related Phenomena 195 145
[6] Dreyer D R, Park S, Bielawski C W and Ruoff R 2010 The chemistry of graphene oxide Chemical Society Reviews 39(1) 228
[7] Cai M, Thorpe D, Adamson D H and Schniepp H C 2012 Methods of graphite exfoliation Journal of Materials Chemistry 22(48) 24992
[8] Yang H, Hernandez Y, Schlierf A, Felten A, Eckmann A, Johal S and Palermo V 2013 A simple method for graphene production based on exfoliation of graphite in water using 1-pyrenesulfonic acid sodium salt Carbon 53 357
[9] Ciesielski A and Samori P 2014 Graphene via sonication assisted liquid-phase exfoliation Chemical Society Reviews 43 381
[10] Hernandez Y, Nicolosi V, Lotya M, Blighe F M, Sun Z, De S and Boland JJ 2008 High-yield production of graphene by liquid-phase exfoliation of graphite Nature Nanotechnology 3 563
[11] Yi M and Shen Z 2015 A review on mechanical exfoliation for the scalable production of graphene Journal of Materials Chemistry 3 11700
[12] Leon V, Quintana M, Herrero M A, Fierro J L, de la Hoz A, Prato M and Vazquez E 2011 Few-layer graphenes from ball-milling of graphite with melamine Chemical Communications 47 10936
[13] Kaniyoor A and Ramaprabhu S 2012 A Raman spectroscopic investigation of graphite oxide derived graphene AIP Advances 2 032183
[14] Ferrari A C 2007 Raman spectroscopy of graphene and graphite: disorder, electron–phonon coupling, doping and nonadiabatic effects Solid State Communications 143 47-57
[15] Calderon-Ayala G, Cortez-Valadez M, Mani-Gonzalez P G, Hurtado, R B, Contreras-Rascon J I, Carrillo-Torres R C and Flore-Acosta M 2017 Green synthesis of reduced graphene oxide using ball milling Carbon Letters 21 93
[16] Bokobza L, Bruneel J L and Couzi M 2015 Raman spectra of carbon-based materials (from graphite to carbon black) and of some silicone composites Journal of Carbon Research 1(1) 77
[17] Perumbilavil S, Sankar P, Priya Rose T and Philip R 2015 White light Z-scan measurements of ultrafast optical nonlinearity in reduced graphene oxide nanosheets in the 400–700 nm region Applied Physics Letters 107 051104
[18] Hidayah N M S, Liu W W, Lai C W, Noriman N Z, Khe C S, Hashim U and Lee H C 2017 Comparison on graphite, graphene oxide and reduced graphene oxide: Synthesis and characterization In AIP Conference Proceedings 1892 150002
[19] Emiru T F and Ayele D W 2017 Controlled synthesis, characterization and reduction of graphene oxide: a convenient method for large scale production *Egyptian Journal of Basic and Applied Sciences* **4** 74

[20] Kartick B and Srivastava S K 2013 Green synthesis of graphene *Journal of Nanoscience and Nanotechnology* **13** 4320

[21] Chen W, Yan L and Bangal P R 2010 Preparation of graphene by the rapid and mild thermal reduction of graphene oxide induced by microwaves *Carbon* **48** 1146

[22] Khan M, Al-Marri A H, Khan M, Shaik M R, Mohri N, Adil S F and Tahir M N 2015 Green approach for the effective reduction of graphene oxide using Salvadora persica L. root (Miswak) extract *Nanoscale Research Letters* **10** 281

[23] Shalaby A, Nihtianova D, Markov P, Staneva A D, Iordanova R S and Dimitriev Y B 2015 Structural analysis of reduced graphene oxide by transmission electron microscopy *Bulgarian Chemical Communications* **47** 291

[24] Alam S N, Sharma N and Kumar L 2017 Synthesis of graphene oxide (GO) by modified hummers method and its thermal reduction to obtain reduced graphene oxide (rGO) *Graphene* **6** 1