Solvothermal Reduction of Graphite Oxide Using Alcohols

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In the present work, we use either ethanol or ethylene glycol as reducing agents through the solvothermal method for graphite oxide reduction. A sulfuric acid treatment before the reduction process was also applied to evaluate its influence on the epoxy group ring-opening reaction. Reduced graphene oxide (RGO) samples were obtained with morphology like crumpled sheets. X-ray diffraction analyses (XRD) showed that the RGO produced via ethylene glycol (EG) reduction followed by treatment with sulfuric acid (RGO**EG**H) presented the largest *d*-spacing (0.4114 nm). For reduction with ethanol (RGO**Et**), the *d*-spacing value was 0.3883 nm. Infrared spectroscopy (FTIR) results indicated that RGO**Et** exhibited very low-intensity bands related to oxygenated functional groups, suggesting a high reduction degree, while the sample reduced with EG contained oxygen group bands in the spectrum that disappeared when H_2SO_4 pretreatment was performed. Thermal gravimetric analyses (TGA) results showed that the samples present high stability and confirmed the reduction process. Moreover, the synthesized RGO sheets were comparable to those produced via more expensive and toxic methodologies.

Keywords: *graphite oxide reduction, ethanol, ethylene glycol, characterization, sulfuric acid treatment.*

1. Introduction

Graphene is a two-dimensional material with mechanical and electronic properties that have attracted interest in technological areas and fundamental study. It has been probably the most studied material in the last decade and possesses a wide variety of potential applications, such as electrocatalysts[1], nanocomposites[2], sensors[3], batteries[4], photocatalysts[5], supercapacitors[6], bulletproof vests[7], among many others.

This material has similar physical properties to those of carbon nanotubes, with the biggest difference being its specific surface area, which is considerably higher (2620 m^2/g-theoretical)[8]. The first obstacle in the process of obtaining graphene is surpassing the high van der Waals force that holds the structure of graphite and, therefore, the graphene sheets together. Hence, there are quite a handful of difficulties associated with the preparation of stable graphene sheets with interlayer spacing significantly greater than that of the original graphite[9]. In general, the methodology applied to graphene preparation is based on the Hummers and Offeman[10] (1958) experiment, which uses strong oxidants for the exfoliation of graphite and produces graphene oxide (GO), which subsequently undergoes a process of reduction and formation of graphene or reduced graphene oxide (RGO). Countless studies have proposed changes in the methodology

employed by Hummers and Offeman to improve graphene or RGO formation and its stability[11-14]. The number of stacked sheets defines the material as graphene or RGO since graphene is formed by only one sheet[15,16].

Traditionally, for the GO reduction, strong reducing agents are used, such as hydrazine[2] and sodium borohydride[2], which are dangerous and toxic reagents. The reducing agent usually determines the quality degree of RGO. Each one of these agents have their advantages and disadvantages related to the structure of the material and their desired application. For instance, hydrazine introduces C-N bonds in the sheets which can act as active sites, while sodium borohydride reduces the -OH group density[17,18]. Lately, efforts have been made to find environmentally friendly and cheap methods for reduction of GO. Different studies suggest the use of sugars[19,20], sulfuric acid[21,17], copper substrates[6], alcohols[22], solvent-assisted thermal treatment[23], electrodeposition[24], sodium carbonate[18], vitamin C[25,26].

Among them, the use of sulfuric acid[17] and alcohols[22] attract attention due to their simplicity and low cost. Kim and colaborators[17] proposed a reduction method using only sulfuric acid. According to the authors, it is a simple, cost-effective and environmentally benign method, leading to an efficient GO reduction with a comparable structure to that of RGO synthesized through traditional routes. Dreyer et al.[22] proposed the use of alcohols (methanol, ethanol, isopropanol and benzyl alcohol) under mild conditions (100 °C). It was verified that the process produced highly reduced GO using

benzyl alcohol as reductant, with *d*-spacing of 0.354 nm, which was very close to the value obtained using hydrazine (0.364 nm). However, the reaction takes place in five days.

In the present study, we describe an RGO production method using a few distinct GO reduction routes by simple alcohols (ethanol and ethylene glycol). Also evaluating if the use of sulfuric acid can improve the epoxy group ring-opening reaction, which is one of the greatest challenges when the solvent or reducing agent can form strong hydrogen bonds, such as EG[23].

2. Experimental

Graphene oxide was prepared from natural graphite following a modified Hummers method (1958). First, graphite flake was treated with an HCl solution (5 wt%/v). The resulting suspension was filtrated and washed with distilled water repeatedly in order to remove impurities. Finally, it was dried at 100 °C for 12h. The treated graphite was mixed with H_2SO_4 (95 wt%/v) and $NaNO_3$, kept at around 0 °C and stirred. Then, $KMnO_4$ was slowly added to the mixture, and the temperature was maintained at 35 °C for 60 minutes. After this, distilled water was added slowly, and the temperature increased to 98 °C and maintained for 15 min. After that, heating was interrupted, and the suspension was cooled to 20 °C, following the addition of hydrogen peroxide (10 wt%/v). The suspension was stirred for 60 min, filtered and washed twice with hydrogen peroxide (10 wt%/v) and H_2SO_4 (5 wt%/v) solutions. In the end, samples were taken and washed with distilled water until pH = 6.

2.1. GO Reduction

A portion of GO sample was diluted in deionized water with a 10:8 proportion (wt/v) and sonicated for 30 min. Later, 5.55 mL of concentrated sulfuric acid (95 wt%/v) was added, and the suspension was filled to a volume of 100 mL and left under magnetic stirring during 24h at room temperature. The product was washed several times with distilled water until pH = 5.5. Then, the solid suspension was placed into an autoclave reactor (PTFE), where 25 mL of the alcohol was added (either ethanol or ethylene glycol). The reactor was heated in an oven at 140 °C for 19h. After the reaction had been finished, the obtained samples were centrifuged and washed with acetone several times. An additional

sonication was performed on the GO precursor used for the synthesis of two RGO samples. It was done before the whole methodology described above to evaluate the possibility of an additional exfoliation of the graphene sheets. These samples were labeled in Table 1 under the "Additional Sonication" column. Also, samples were synthesized without sulfuric acid treatment to evaluate its effectiveness. Sample naming was assigned respecting the following convention: RGO (reduced graphene oxide) + **EG/Et** (used alcohol) + H (for samples pretreated with sulfuric acid) + **_s** (for samples with an additional sonication).

2.2. Characterization

The RGO samples were characterized by scanning electron microscopy (SEM) using a JEOL JSM-6510LV (30kV), without metal coating. Infrared spectroscopy analyses (FTIR) used a Frontier model spectrometer (Perkin Elmer), 4 cm^{-1} resolution, and a DTGS detector. X-ray diffraction (XRD) patterns were obtained with a Rigaku D Max Ultima diffractometer using a graphite monochromator, Cu-Kα radiation (V = 40 kV, I = 40 mA); scans were taken in a 5° < 2θ < 40° range, with a step size of 0.05° and scanning time of 2s. The crystallite sizes (τ) values were calculated using Scherrer's equation[27]. Thermal gravimetric analyses (TGA) were performed in an SDT Q600 (TA Instruments) under N_2 atmosphere (50 mL/min) and a heating rate of 5 °C/min.

3. Results and Discussions

Figure 1 shows SEM images of GO used as a precursor, which appears to exhibit morphology similar to crumpled sheets with wrinkles and folds. This is expected and is attributed to the interaction of oxygen groups present in the oxide sheets.

The X-ray diffraction pattern of GO is shown together with the graphite used as a precursor (Figure 2). Graphite has a characteristic diffraction peak at around 2θ = 26.7° (*d* = 0.3375 nm, JCPDF) and the decrease of its intensity is used to evaluate the oxidation process[6,18,28,29]. This peak is still present in the synthesized GO although with a very low intensity, which indicates the presence of some residual graphite; however, its enlargement suggests changes in the structural organization when compared to graphite. Furthermore, the new peak at 2θ = 11.12° confirms changes in the lattice

Table 1. Reaction conditions of RGO synthesis.

Sample	Reducing agent	Additional Sonication	Reaction Time	Reaction Temperature
RGOEGH	Ethylene Glycol and H_2SO_4	No		
RGOEGH_s	Ethylene Glycol and H_2SO_4	Yes		
RGOEtH	Ethanol and H_2SO_4	No		
RGOEtH_s	Ethanol and H_2SO_4	Yes	19h	140 °C
RGOEG	Ethylene Glycol	No		
RGOEt	Ethanol	No		

Figure 1. SEM images of GO (1,000x).

Figure 2. XRD patterns of graphite and GO.

Figure 3. SEM images of: A (2,200x) and B (9,000x) - RGO**EG**; C (1,000x) and D (1,500x) - RGO**Et**.

Figure 4. SEM images of RGO**EG**H (5,000x and 10,000x).

Figure 5. SEM images of RGO**EG**H_s (2,500x and 7,000x).

Figure 6. SEM images of: A (1,600x) and B (1,700x) - RGO**Et**H; C (2,500x) and D (7,000x) - RGO**Et**H_s.

structure after the oxidation process with an increase of the interlayer distance (d) in the GO[29,30]. Variations in the d values are directly related to the degree of oxidation of the graphite[31]. A value of 0.8043 nm was calculated as the d-spacing of GO, showing that a high degree of oxidation was achieved, which can be attributed to the introduction of oxygen-containing groups and intercalated water molecules in the lattice structure, increasing d-spacing[20].

After GO is reduced, changes in the morphology are observed, which were dependent on the reducing reagents combination as shown in Table 1. In general, SEM images suggest that the structure became more compact, and the sheets began to restack due to a decrease in the number of oxygen-containing groups present between them (Figures 3-5). Such stack does not appear intense for the samples reduced with ethylene glycol regardless of H_2SO_4 pretreatment, as shown in Figures 3A-B, 4 and 5.

The additional sonication performed in the GO precursor to prepare the RGO**EG**H_s sample (Figure 5) caused slight changes in the RGO morphology and, thus, some cracks were observed in the RGO sheets.

When using ethanol as a reducing agent, RGO presents morphology of thin, crumpled sheets (Figures 3C-D). Pretreatment with H_2SO_4 seems to cause stacking, resulting in slightly thicker sheets (Figures 6A-B). Additional sonication decreased the agglomeration of pretreated RGO reduced with ethanol, and the sample obtained showed a morphology similar to RGO**Et**, but with cracks and tears (Figures 6C-
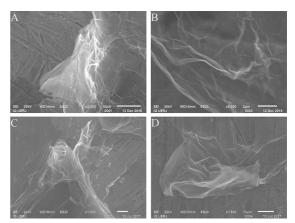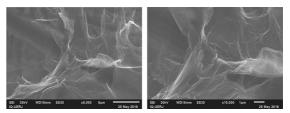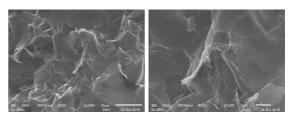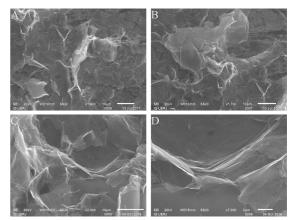
D). Therefore, these results suggest that the additional sonication is necessary when GO is pretreated with H_2SO_4 and then reduced with ethanol in the solvothermal method as presented here.

Figure 7 shows the structural analysis of the RGO samples and Table 2 summarizes the values obtained from the XRD patterns of the synthesized samples (Figure 7), GO and graphite (Figure 2).

When comparing the XRD patterns of the GO with the samples after reduction, it is observed that the characteristic GO peak at 2θ = 11.12° (d = 0.8043 nm) disappeared, and new broad peaks were formed with maximum values centered at around 2θ = 23 - 25° for all samples. This suggests the occurrence of the reduction pro cess[18]. The decreasing of *d*-spacing occurred due to the removal of oxygen groups during the reduction process. Also, the absence of the characteristic diffraction peak at 2θ = 11.12° indicates a complete reduction of GO.

For RGOEG and RGOEt samples, we see similar *d*-spacing and crystallite sizes (τ, Figure 7, Table 2), which suggests that the reduction process using either ethylene glycol or ethanol solely leads to the formation of RGO with a similar degree of disorder. The *d*-spacing values are also very similar to those obtained by Dreyer et al.[22], even though their GO reduction was incomplete using ethanol.

Treatment with H_2SO_4 caused an increase in the interlayer spacing when EG was used as reducing agent, resulting in the highest d-spacing of 0.4114 nm and a slightly smaller crystallite size of 0.696 nm (Table 2). According to Kim and coworkers[17], the reduction of using solely sulfuric acid and performed in a two-step reaction is an efficient way to obtain reduced GO with the same structural characteristics as RGO produced using hazardous reducing agents such as $NaBH_4$. In the present study, the value of 0.3900 nm for interplanar distance obtained using solvothermal treatment with only EG are comparable to the

value of 0.38 nm achieved by Kim et al.[17]. Pretreatment with H_2SO_4 improved the reduction process and resulted in a material with larger interlayer spacing (0.4114 nm).

Regarding the sample RGOEtH, which used ethanol in the solvothermal step of GO reduction after sulfuric acid treatment, the *d*-spacing value (0.3678 nm) is lower than the same measurement for RGOEt (0.3883 nm), and there is a significant increase in the crystallite size (1.134 nm vs. 0.665 nm). Thus, in this case, treatment with H_2SO_4 was not effective.

The additional sonication, for RGOEGH_s sample, lowers *d*-spacing (0.3810 nm) when compared with the RGOEGH sample (0.4114 nm). It means that, although crystallite size and restacking degree remain approximately the same (Table 2), the RGO sheets are closer in the RGOEGH_s sample.

The XRD pattern of RGOEtH_s (Figure 7) suggests an increase of the degree of disorder when compared to the RGOEtH due to its broader peak. Also, the former shows a lower degree of stacking than the latter, as indicated by its crystallite size value of 0.626 nm (Table 2) and higher *d*-spacing. It could mean that, when H_2SO_4 is used followed by ethanol solvothermal treatment, it is necessary to perform an additional sonication to achieve satisfactory results.
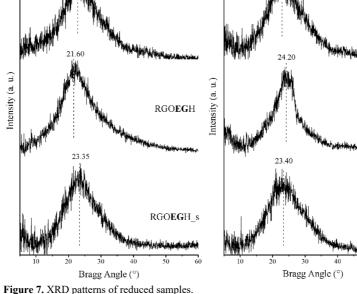
The synthesized samples were evaluated by infrared spectroscopy, which allows us to assess both the graphite oxidation and GO reduction process and, mainly, if sulfuric acid favors the epoxy group ring-opening reaction in the methodology proposed here.

The infrared spectrum of the GO sample confirmed the introduction of oxygen containing groups in the graphite structure (Figure 8). GO shows absorption peaks at ~1720,

Figure 7. XRD patterns of reduced samples.

Table 2. Microstructures determined by XRD results.

Sample	2θ (º)	d(nm)	τ*(nm)	No. of restacked layers
Graphite	26.65	0.3345	27.99	-
GO	11.12	0.8043	13.36	-
RGOEG	22.80	0.3900	0.755	2
RGOEt	22.90	0.3883	0.665	2
RGOEGH	21.60	0.4114	0.696	2
RGOEtH	24.20	0.3678	1.134	3
RGOEGH_s	23.35	0.3810	0.691	2
RGOEtH_s	23.40	0.3802	0.626	2

*crystallite size by Scherrer's equation.

~1625, ~1380 and ~1067 cm^{-1}, corresponding to C=O (carboxylic and ketone), C=C, C-O (carboxylic) and C-O (epoxy) functional groups, respectively[18,23,27,32-37].

The reduction process changed the spectra profile considerably, with a decrease in the characteristics bands intensity of the oxygen containing groups present in the GO structure. The stretching mode C=C of skeletal graphene (1625 cm^{-1}) was shifted to 1636 cm^{-1} and also had its intensity decreased in RGO**EG**, which might be due to the intercalated water released from the structure during the reduction process since this band has a contribution to the -OH bending mode[32]. This sample still exhibits oxygen-related bands due to the C-O stretch of carboxylic (1380 cm^{-1})[33] and epoxy groups (1040 cm^{-1})[23]. Therefore, although EG could reduce the graphene oxide sample, producing RGO sheets with low stacking (Table 2), the reduction degree was low, and oxygen containing groups were still present in the RGO**EG** sample, mainly in epoxy groups. However, treatment with sulfuric acid (RGO**EGH**) was enough to open these functional groups and improve EG's performance. The spectrum of RGO**Et** sample presents very low-intensity bands related to oxygenated functional groups, indicating a high degree of reduction. However, it appears that introducing the pretreatment with sulfuric acid and applying an additional sonication was not as effective as using ethanol solely.

According to Lin et al.[23], the GO reduction rate is dependent on the interaction between GO and the solvent (reducing agent). Hydrogen bonds stabilize the epoxy groups present on the surface of the GO, which causes difficulties in their ring-opening reactions in a solvent-assisted thermal reduction. Since ethylene glycol can form up to two hydrogen bonds, the authors suggest that it would not be an effective solvent for the reducing process of GO. This was the case in the present results using ethylene glycol, but its performance was improved using an H$_2$SO$_4$ pretreatment as shown by infrared spectroscopy results. This indicates that sulfuric acid pretreatment can be used to improve EG's performance as a reducing agent.
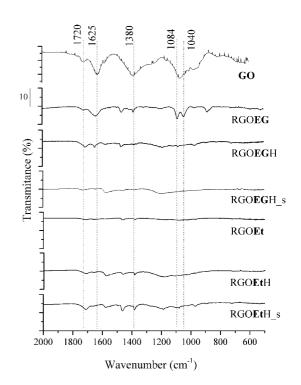

Figure 8. Infrared spectra of GO and of all reduced samples.
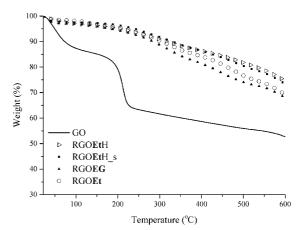

Figure 9. TGA curves of GO and RGOEG, RGOEt, RGOEtH and RGOEtH_s samples.

As the reduction process increases the thermal stability of the material, TGA analyses were performed and are shown in Figure 9 for GO and the samples reduced with ethanol, which presented better overall results than EG. The curve of GO exhibits a characteristic profile of mass loss with three stages at about 100 °C, 230 °C and 575 °C[14,17,18,23,38]. At 100 °C there was a mass loss of around 18%, which is attributed to the release of water trapped between GO sheets, and at 230 °C there is 36% of mass loss due to the decomposition of labile oxygen functional groups. At about

575 °C began to occur the decomposition of remaining oxygen groups and the burning of ring carbon[18]. The curves for the RGO samples exhibited a decrease of the mass loss, and all samples lost around 7% at 230 °C; while at 575 °C the mass loss was 15% for RGO**Et** and RGO**EG** and around 7% for RGO**Et**H and RGO**Et**H_s. These results show the high thermal stability of the samples obtained and confirm that the methodology used produces RGO with a reduction degree comparable to that reported in the literature[17,38].

4. Conclusions

In the present study, different methodologies to obtain RGO sheets using no-aggressive reagents via solvothermal method were revisited and evaluated. RGO sheets with a high degree of reduction and low sheet restacking were obtained using either ethylene glycol or ethanol.

For EG, the implementation of sulfuric acid pretreatment improved the reduction process, opening epoxy group rings and forming sheets with low morphological defects, large *d*-spacing, and low restacking degree. When using ethanol, H_2SO_4 treatment is not necessary and, in fact, it decreases ethanol's performance as a reducing agent; of note, if such treatment is performed, an additional sonication before it is necessary to obtain RGO sheets with similar morphological and microstructural characteristics as RGO**EG**H. However, this will cause cracks and tears in the RGO sheets.

Summarizing, GO can be reduced using either ethanol or ethylene glycol via a solvothermal route, using additional pretreatment dependent on the alcohol, leading to RGO sheets with a low degree of stacking, high thermal stability and desired morphology.

Therefore, the proposed methodologies are simple, low-cost, non-toxic and produce RGO sheets with characteristics that allow for its application in different areas of study.

5. Acknowledgements

6. References

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