Scalable Production of Reduced Graphene Oxide (rGO) from Graphite Oxide (GO)

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KEYWORDS. Graphene, graphite oxide, reduced graphene oxide, Hummer's method

BRIEF. Reduction of graphene oxide as a cost-effective method of producing high quality carbon materials with tunable C/O ratios.

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ABSTRACT. Graphene, a two-dimensional carbon layer, has recently attracted significant research attention because of its impressive thermal, elastic, optical, electrical, and mechanical properties. Current methods of producing high-quality graphene, such as the chemical vapor deposition method (CVD), are expensive and complex. Developing an alternative path for the production of scalable graphene-related materials is the major focus in this study. Similar in structure to the pristine graphene, reduced graphene oxide (rGO) is derived from graphite powder. rGO is traditionally produced from graphite oxide (GO) using Hummer's method. Reducing graphene oxide is a cost-effective and scalable route for producing high quality carbon materials with tunable Carbon-to-Oxygen (C/O) ratios. This report introduces several methods to reduce graphene oxide, including two wet methods (reducing GO in solvent using a microwave or a hot plate) and a dry method (CVD using hydrogen as a reducing agent at elevated temperatures). Samples were characterized using Thermogravimetric Analysis (TGA) for the thermal stability studies, Fourier Transform Infrared Spectroscopy (FTIR) for the determination of functional groups, Carbon Hydrogen Nitrogen (CHN) elemental analysis for identification of C/O ratios, Scanning Electron Microscopy (SEM) for visualization of surface diagram and structure, and Ultraviolet-visible Spectroscopy (UV-VIS) for photo-activity. The results conclude that each method successfully reduced GO. However, thermal reduction with dimethylsulfoxide (DMSO) using the hot plate method achieved the most effective results regarding the conversion of GO to rGO.

INTRODUCTION.

Composed of sp^2-hybridized carbon atoms arranged in a hexagonal pattern, graphene has an abundance of desirable properties, including high thermal conductivity (5000 $W\ m^{-1}\ K^{-1}$), high charge carrier mobility (250000 $cm^2\ V^{-1}\ s^{-1}$), and high mechanical stiffness (1 TPa) [1]. Because of these properties, graphene is an ideal substance for applications such as gas sensors [1], super-capacitor electrodes [2], and many others [3-5]. In 2004, the first isolated single layer of graphene was characterized after mechanical exfoliation of graphene using Scotch tape [6]. However, this method was very time-consuming and did not produce a large amount of sample. Current procedures of producing graphene (also called reduced graphene oxide, rGO) are successful, but can be expensive (such as CVD [6]) and toxic (such as chemically reducing with hydrazine [7]).

The most common method for producing graphene consists of reducing graphene oxide from graphite powder [6]. This procedure begins with graphite powder as the carbon source [6]. Graphite oxide is formed when the powder reacts with a mixture of sodium nitrate, potassium permanganate, and sulfuric acid in a process known as Hummer's method [6]. This is typically followed by sonication to further exfoliate the GO layers and produce graphene oxide [6]. However, this derivative of graphene has many oxygen-containing functional groups, such as epoxides, carbonyls, hydroxyl groups, and carboxyl groups that disrupt the conjugated π system and prevent it from reaching its maximum strength and conductivity [1]. These oxygen-containing functional groups can be mostly eliminated by reducing the graphene oxide to form rGO [1], improving the material's strength and conductivity.

In this report, an effective technique for producing rGO is presented. We used a modified Hummer's method [6] and sonication to make graphene oxide from graphite powder. Then we converted the graphene oxide to rGO using three different reduction techniques. These methods included reducing the sample using CVD in a hydrogen atmosphere, thermally reducing in organic solvent in a microwave, and thermally reducing in organic solvent on a hot plate. By reducing graphene oxide, many oxygen functional groups can be removed, making rGO with high C/O ratios, improved thermal stability, improved photo-activity, and an exfoliated surface structure.

MATERIALS AND METHODS.

Graphite Oxide (GO) Preparation.

Graphite Oxide (GO) samples were prepared using a modified Hummer's method [6]. Sulfuric acid (40 ml, Purity certified ACS from Fisher Scientific) was added to a beaker in an ice bath. While spinning, 2 g of graphite powder (150 micro from Asbury Graphite Mills Inc.), 5 g of $NaNO_3$ (Purity certified ACS from ACROS), and 9 g of $KMnO_4$ (Purity certified ACS from Fisher Scientific) were added slowly and stirred for 30 minutes before placing into a water bath at 35 ^{o}C for 3 hours. The flask was removed from the water bath and 70 ml of de-ionized water was added. The reaction mixture was stirred for 30 minutes before finally using a buret to terminate the reaction with a mixture of 10 ml of H_2O_2 and 50 ml of DI water. The samples were washed to pH 0 with a centrifuge (Adams Analytical centrifuge from Clay Adams) and then dried in a furnace at 40 ^{o}C.

Preparation of Reduced Graphene Oxide (rGO).

Solutions of the GO powder were prepared at a concentration of 0.5 mg/ml in a variety of organic solvents, including dimethylformamide (DMF, anhydrous, 99.8% from Sigma-Aldrich), dimethylsulfoxide [1] (DMSO, 99.7% pure from ACROS Organics), ethylene glycol (EG, Laboratory Grade from Fisher Scientific), methanol (M, GC Resolv from Fisher Scientific), ethanol (E, anhydrous histological grade from Fisher Scientific), DI water (H_2O), and thiophene [8] (T, ≥ 99% from Aldrich Chemistry). The solutions prepared for the microwave treatment used 180 mg GO/360 ml solvent, whereas the solutions prepared for the oil bath treatment used 60 mg GO/120 ml solvent to accommodate the size of the microwave or oil bath containers. To change graphite oxide to graphene oxide, the solution was placed in a water bath and shaken in an ultrasonicator (Hielscher Ultrasound Technology) for 0.5 hours at 200W to distribute the powder in the solvent. An ice bath froze the solvent. Microwave samples M1a-M6a and M3b were not ultrasonicated first.

Method 1 – CVD. Three different methods for preparing reduced graphene oxide are discussed. First, CVD was used (Table 1). Approximately 200 mg of GO were placed in a ceramic bowl covered in aluminum foil and heated in a 95% argon 5% hydrogen atmosphere. The CVD samples did not use solvents or ultrasonication.

Method 2 – Microwave. In the second method, we thermally reduced graphene oxide using a microwave (Ethos Microwave Digestion System from Milestone). After ultrasonication, the sample solution was distributed into six microwave containers. These were placed in the microwave and set to the appropriate temperature (Table 1). All samples took 10 minutes to rise to desired temperature and were heated in the microwave for 1 hour at 500W.

Method 3 – Hot Plate. The third method consisted of heating the solution on a hot plate with an oil bath. The solutions were poured in a flask with a Teflon-coated magnet inside. The flask was surrounded by vegetable oil and a water-cooled condenser was used to cool the solution. The samples were stirred and heated, using insulation to keep the heat in. Once the solutions reached the desired temperature (Table 1), a timer was set for 1 hour. Sample H7c was heated for 24 hours with a solution mixture of 10 mg GO, 10 ml DI water, and 2 ml thiophene, as stated in previous work [8]. Samples with M, E, H_2O, and T could not be tested at 150 °C and 200 °C because their low boiling points caused the solution to spill out of the condenser causing a safety hazard. The amount of insulation and the heat level on the hot plate were adjusted periodically to keep the solution at the set temperature.

Table 1. Conditions for GO reduction using the CVD, microwave, and hot plate methods.

CVD			MICROWAVE			HOT PLATE		
Sample	Temperature (°C)	Time (hr)	Sample	Solvent	Temperature (°C)	Sample	Solvent	Temperature (°C)
C1a	150	1	M1a	DMF	150	H1a	DMF	150
C2a	200	1	M2a	DMSO	150	H2a	DMSO	150
C3a	250	1	M3a	EG	150	H3a	EG	150
C1b	150	4	M4a	M	150	H1b	DMF	200
			M5a	E	150	H2b	DMSO	200
			M6a	H_2O	150	H3b	EG	200
			M1b	DMF	200	H1c	DMF	153
			M2b	DMSO	200	H2c	DMSO	189
			M3b	EG	200	H3c	EG	197
			M4b	M	200	H4c	M	65
			M5b	E	200	H5c	E	79
			M6b	H_2O	200	H7c	T	80
			M3c	EG	197			
			M4c	M	65			
			M5c	E	79			
			M6c	H_2O	100			

Obtaining Solid rGO Sample.

After thermal treatment, the M, E, H_2O, and T samples were poured into petri dishes and heated in a furnace at 50 °C. These solvents have low boiling points, so the solvent could evaporate in the furnace. Because DMF, DMSO, and EG all have high boiling points, the samples were first washed with DI water and vacuum filtered (Maxima Dry from Fisher Scientific) so a solid sample could be obtained. Then, the solid, but wet, sample was scraped into a petri dish with a wooden tongue depressor and heated in a furnace at 30-40 °C. After the samples were dry, they were collected into vials and labeled.

Characterization Methods.

TGA. The thermogravimetric data were collected on a TA Instrument Hi-Res TGA 2950 thermogravimetric analyzer at a heating rate of 10 °C/min from room temperature to 800 °C in a 100 ml/min nitrogen atmosphere. While heating rGO, TGA measures the sample's weight loss and thermal stability.

FTIR. The FTIR infrared spectra were recorded from 4000 to 650cm^{-1} with a resolution of 2cm^{-1} and 4 averaged scans on a Perkin Elmer Spectrum One FTIR spectrometer with a UATR attachment using KBr pellets. FTIR determines the functional groups of GO and rGO.

C/O Ratios. Seventeen solid samples were examined with a LECO TruSpec CHN elemental analyzer that detects carbon, hydrogen, and nitrogen using a high temperature combustion method. C and H are detected by IR cells, and N is detected by thermal conductivity. After calculating the oxygen content from these values, the C/O ratios were identified. These ratios indicate the reduction completeness of rGO.

SEM. The SEM solid samples were prepared and tested using a JEOL JSM-5400LV scanning electron microscope. SEM images helped visualize the surface diagram and structure in GO and rGO.

UV-VIS. Ultraviolet-Visible (UV-VIS) diffuse reflectance spectra were obtained using a Varian Cary 100 UV-VIS spectrophotometer that was equipped with the DRA-CA-30 diffuse reflectance accessory. It uses light in the visible and adjacent ranges to detect photo-activity.

RESULTS.

TGA Characterization.

In the thermogravimetric analysis curves of GO, there were three major weight loss peaks (total weight loss of about 60%) at 72 °C, 206 °C, and 255 °C, respectively. The first weight loss was attributed to the loss of moisture (a weight loss of about 10%), and the second and third were attributed to the decomposition of GO (the sum of weight losses of about 50%).

The total weight of CVD-derived rGO decreased to 50%, compared to its GO precursor. Again, the first weight loss peak was attributed to moisture loss. The second peak at about 280 °C should be attributed to unreduced GO functional groups. The third peak above 650 °C accounted for a 10% weight loss. Using the same CVD method, increasing the reduction temperature to 250 °C seemed to greatly improve the reduction efficiency. The temperatures of major weight loss attributing to the decomposition of rGO increased to 475 °C and 640 °C. The total weight loss, including moisture loss, was about 40%.

The rGO produced from the microwave method seemed unstable compared to the rGO produced by the CVD method. The total weight loss was 60% at 150 °C and was not improved as the reduction temperature increased to 200 °C. The temperatures of the decomposition peaks were around 250 °C, 350 °C, and 650 °C. In the hot plate method, the rGO that was reduced at 150 °C was very similar to the material from the CVD method, regarding the staged decomposition peak temperatures and the total weight loss at 50%. However, this was not true when the hot plate method was conducted at 200 °C, when the major decomposition peak appeared at a much higher temperature of 537 °C (Figure 1). Generally, higher decomposition peaks correspond to the occurrence of more thermally-stable functional groups [6]. At such a high temperature, the rGO from the hot plate method at 200 °C was fully decomposed.

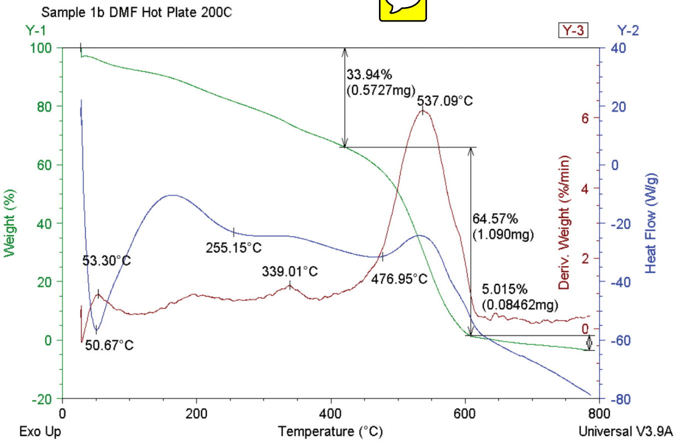

Figure 1. TGA curves of Sample H1b reduced at 200°C using the hot plate method with a major decomposition peak at 537°C. This high-temperature decomposition peak corresponds to the occurrence of more thermally-stable functional groups.

FTIR Characterization.

The FTIR spectra were generally used to specify actual functional groups on organic compounds. The peak at 1725 cm^{-1} is due to a C=O bond (carbonyl/carboxyl functional group). The peak at 1590 cm^{-1} suggests a C=C bond (aromatics functional group, skeletal vibrations from unoxidized graphitic domains). The peak at 1415 cm^{-1} can be assigned to a C-O bond (carboxyl functional group). The peak at 1220 cm^{-1} is due to C-OH (epoxy functional group). The peak at 1057 cm^{-1} suggests a C-O bond (alkoxy functional group) [6].

Based on the spectra of rGO from the CVD method, it seemed that higher temperatures and longer residence times improved the completeness of reduction. This was found by investigating variation trends of the peak heights of the individual functional groups as temperatures increased from 150 °C to 200 °C to 250 °C and as the residence time was increased from 1 hour to 4 hours under the same temperature.

Regarding the microwave method, the reduction performance was categorized into two groups which differed in effectiveness and completeness of reduction, depending on reducing solvents, temperatures, and residence times. Reducing solvents such as H_2O, ethanol and DMF in a temperature range of 100-200 °C seemed less efficient at reducing GO, after reviewing the variation of their peak intensities compared to those of the GO precursor. EG and methanol at 150-200 °C were effective reducing agents. More significant is the effectiveness of the GO reduction using DMSO at a lower temperature (150 °C), where almost all oxygen-containing functional groups of GO disappeared.

Similarly, for the GO reduction based on the hot plate method, two groups performed differently in effectiveness and completeness of reduction. Again, reducing solvents and temperatures played a major role in determining the completeness of the reduction. Methanol, ethanol, and thiophene under their vaporization temperatures could not reduce GO, and EG was also less effective in reduction of GO at temperatures as high as 200 °C. DMF and DMSO in a temperature range between 150°C and 200°C were effective (Figure 2). More significantly, effectiveness of the GO reduction using DMSO at 200°C was evidenced.

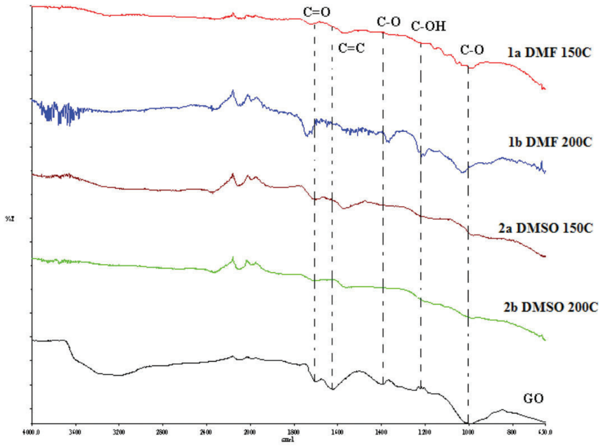

Figure 2. FTIR spectra of GO and the rGO samples produced from the hot plate method under the more effective conditions.

Determination of C/O Ratios.

The C/O ratios could be regarded as the indicator of reduction completeness of rGOs. Generally, the C/O ratios (the molar ratios of carbon and oxygen) of GO are lower than 1 and rGO ratios are greater than 1 [1]. As expected, the GO C/O ratio in this study was 0.693. Most all of the rGO C/O ratios were greater than 1. The C/O ratio of the sample with DMSO was the greatest in the microwave method at 2.173. Similarly, in the hot plate method, the application of DMSO almost completely reduced all oxygen functional groups, thus its high C/O ratio of 484.216 was expected. This agreed with the results of FTIR characterization under a similar condition. It should be noticed that thiophene was effective even when temperature dropped to its vaporization temperature, which was 80 °C, and the corresponding C/O ratio was 4.316.

SEM images.

The regular thickness of exfoliated layers of different methods was in a range of ten to many hundred nanometers. The carbon layers seemed to be successfully exfoliated to some extent in the stage from graphite to GO and were further exfoliated in the stage from GO to rGO using DMF based on the microwave method (Figure 3).

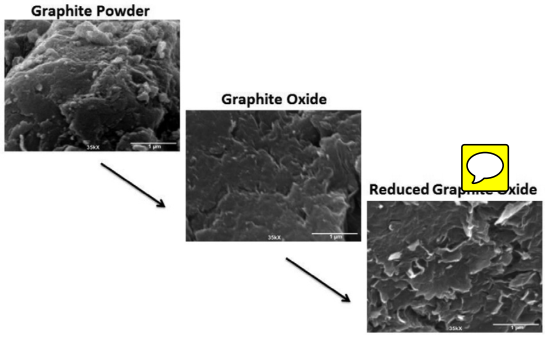

Figure 3. This SEM image shows a successful development of the graphite raw material to GO to rGO.

UV-VIS Spectra.

All GO samples were more active in the UV spectrum (200 nm to 400 nm) than in the visible light range (400 nm to 650 nm). The absorption peak appears at about 250 nm to 270 nm in the UV spectrum. Generally good quality GO should possess the $\pi-\pi^*$ transition of aromatic C–C single bonds [6], which is attributed to the absorption peak at 232 nm.

DISCUSSION.

The GO thermogravimetric analysis curves revealed the thermal instability of GO because of its many functional groups. When GO was reduced to rGO based on the three aforementioned methods, the thermal stability of the prepared rGOs significantly improved, indicating successful reductions using all three methods. However, the completeness of reduction varied and was dependent on the applied reduction method. Overall, none of the reduction methods could thoroughly convert the GO into straightforward graphene. There were diversified functional groups found on all rGOs. However, the thermal analysis technique could clearly visualize thermal stabilities of different functional groups on GO and rGOs, and simultaneously point out the progress and reduction of different functional groups.

The FTIR results of GO indicated that the significant difference of FTIR peaks among GO and the raw material (graphite) is the C=C bond at 1590 cm^{-1}. Both the exfoliation of graphite to GO and oxidation of graphite by links with C-O, C=O and C-OH were successful. This is clear evidence of a fairly complete oxidation.

Regarding C/O ratios, higher temperatures always improved the completeness of reduction process. For example, the C/O ratios of rGOs increased from 0.847 to 1.120 to 1.746 as the operational temperatures of the CVD method increased from 150 °C to 200 °C to 250 °C, respectively. Based on the CVD results, the increase of residence time from 1 hour to 4 hours also increased C/O ratios from 0.847 to 1.448, respectively. In both the microwave method and the hot plate method, the application of DMSO as the reducing solvent reduced the graphene oxide the most compared to the other solvents. It seemed the hot plate method is more effective than the microwave method using same reducing solvents, even under lower temperature conditions.

By comparing the SEM images of the EG and DMF samples, DMF seemed to be a better reducing solvent for exfoliation of carbon layers, which was an indicator of the conversion from GO to rGOs. It appears that the hot plate sample was better exfoliated compared to the microwave sample under the same temperature and solvent conditions in both the DMF and EG samples.

Prepared GOs showed strong light absorption in wide light spectrum from UV to visible light and should be photo-active. The microwave reduction method seemed to not greatly change the UV-VIS spectra of prepared rGOs because the reduction was less complete. The hot plate method showed improved reduction completion of rGOs, but was limited. The CVD reduction method significantly improved the completeness. This was concluded because the absorptions of the CVD-derived rGOs did not differ in either the UV range or the VIS range of light.

CONCLUSION.

Both the wet methods using selected organic solvents and the dry method using hydrogen are effective for the reduction of graphite-derived graphene oxide (conversion from GO to rGO). Between the wet solvent methods, the hot plate method seems more effective than the microwave method when the same temperatures and residence times are maintained. The hot plate method using DMSO is reported to achieve the best results regarding the complete conversion of GO to rGO. All test results are confirmed by multiple evidences from TGA tests, sample characterizations of FTIR spectra, C/O ratio determination, SEM images, and UV-VIS spectra. The goal of scalable production of reduced graphene oxide is confirmatively achievable based on the outcomes of this project.

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SUPPORTING INFORMATION.

Figure S1. The TGA curves of graphite oxide show 60% weight loss.

Figure S2. FTIR spectra of GO and rGO derived from the CVD method show that higher temperatures and longer residence times improved the completeness of reduction.

Table S1. The C/O ratios of GO and rGOs indicate that the use of DMSO in the hot plate method was the most effective reduction technique.

Figure S3. The UV-VIS spectra of samples from the CVD reduction method did not differ in either the UV or VIS range of light.

Table S2. A summary of the results is organized by reduction technique and characterization method.

REFERENCES.

1. Compton, O, Jain, B *et al.*, ACS Nano 2011, 4380–4391.
2. Akhavan, O, Ghaderi, E *et al.*, Journal of Materials Chemistry 2012.
3. Oostinga, J, Heersche, H *et al.,* Nat. Mater 2008, 151–157.
4. Wang, F, Zhang, Y *et al.,* Science 2008, 206–209.
5. Bolotin, K, Sikes, K *et al.,* Solid State Commun 2008, 351–355.
6. Lin, Y, Cao, Y *et al.,* JATC 2013.
7. Yu, W, Xie, H *et al.* Nanoscale Res Lett 2011, 6:47.
8. Some, S, Kim, Y *et al.,* Scientific Reports 3, 1929.

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