A simple preparation of graphene oxide with a modified Hummer's method

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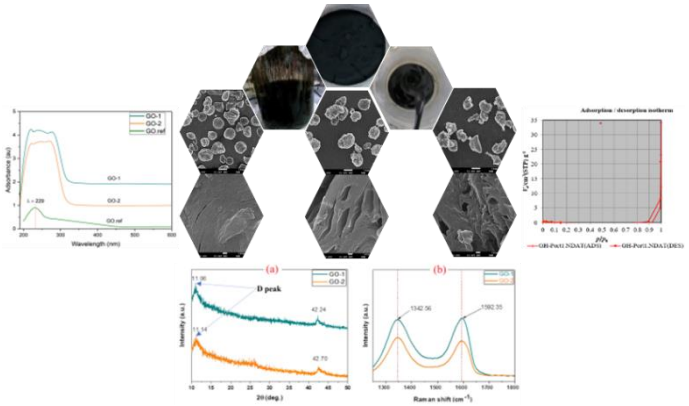
Abstract

Graphene oxide (GO) has gained a lot of interest in recent years as a key precursor and a derivative of graphene. The GO was retrieved from graphite flakes using a modified Hummer's approach that differed from the normal Hummer's method. GO-method 1 using sodium nitrate and GO-method 2 not using sodium nitrate ($NaNO_3$). Used approach is chemical exfoliation, where chemicals are used to intercalate between the graphene layers and expand the interlayer spacing. This expansion weakens the van der Waals forces, making it easier to separate the layers. GO-method 1 and GO-method 2 run on ultrasound and dry. Increasing the ultrasonic process of the procedure reduces the preparation time for graphene oxide compared to the original Hummer's method. The X-Ray Diffractometer result of GO-method 2 shows the diffraction peaks at 2θ at 11.06˚ and 42.24˚ which corresponds to graphene oxide. Raman spectroscopy and UV-visible spectrophotometry were used to investigate the molecular structure and optical properties of graphene oxide, respectively. Field Emission Scanning Electron Microscope of GO to perform elemental mapping on graphene samples and Brunauer Emmet Teller (BET) for surface area determination and pore size distribution results found that GO-method 1 and GO-method 2 corresponds to graphene oxide, which has a macroporous size, and the adsorption response is more respectively.



Keywords: Graphite; Graphene Oxide; Hummer's method

Introduction

Graphene oxide (GO) is an extensively investigated material with a range of potential applications, including use as a reinforcing agent in composite materials, catalyst, energy storage and conversion devices [1]. Graphene oxide (GO) is a chemically modified derivative of graphene, wherein oxygen-containing functional groups, including hydroxyl, epoxy, and carboxyl groups, have been introduced into its structure.

The modified Hummer's method is a widely used method for the preparation of GO. It involves the oxidation of graphite using a mixture of sulfuric acid, sodium nitrate, and potassium permanganate. Properties of graphene such as a large specific surface area of 2,630 $m^2\ g^{-1}$, good electrical conductivity up to 100 MS m^{-1}, translucency up to 97%, high thermal conductivity, 5,000 W $m^{-1}{\cdot}K^{-1}$ [1 – 4]. In this method, high-purity graphite flakes are ground to a fine powder and then mixed with a solution of sulfuric acid, sodium nitrate, and potassium permanganate. The mixture is allowed to react for a period of time to produce GO. The resulting GO solution is then washed and concentrated, and the final product can be used as a suspension or dried and ground to a powder for further use. Overall, the modified Hummer's method is a simple and efficient method for the preparation of GO, but it is important to carefully control the reaction conditions to obtain consistent and high-quality GO materials.

The primary objective is to improve the process for preparing GO with a focus on achieving thin layers, reduced multilayers, high crystallinity, and desirable morphologies.

Materials and Methods

The modified Hummer's method is a widely used method for the preparation of graphene oxide (GO). This method involves the oxidation of graphite using a mixture of sulfuric acid, sodium nitrate, potassium permanganate and hydrogen peroxide. Here is a general outline of the modified Hummer's method for the preparation of GO-Method 1 denoted as GO-1 and GO-Method 2 denoted as GO-2:

1. Grind high-purity graphite flakes from Leadur, China size 325 mesh to a fine powder using a ball mill (Retsch PM400). Graphite powder, 15 g was in flask size 250 mL. The particle size of the powder sample was reduced by at least 20 mm by using 25 grinding balls at 350 rpm for 30 min. Then the sieve was shaken size of 90 microns and finally was obtained and 10 g of graphite powder were flask size 12 ml by using 5 grinding balls at 350 rpm for 30 min.

2. Mix the graphite powder with a sodium nitrate with a ratio of 1:1 (wt/wt) in a magnetic stirrer (Velp AREC) which all soak in an ice bath with a temperature not more than 5˚C and admix sulfuric acid 300 ml after that admix potassium permanganate and deionized water 200 ml in stirring 600 rpm in the agitator. Allow the mixture to react for a period of 30 min. Then add 120 ml of hydrogen peroxide to the stirrer and stir at 1100 rpm for 30 min.

3. The liquid graphite should be diluted with 400 ml of DI water before being centrifuged (SUPER DEAL PRO 800) at 4000 rpm for 30 min and to filter with papers (Whatman Grade 5) to remove any undissolved particles. After that ultrasonic vibration (GT Sonic) at 40 kHz for 30 min and add hydrochloric acid 100 mL in magnetic stirrer 1400 rpm for 30 min.

4. The rinsed with deionized water until the pH changed to 7, before being dried (Memmert, UNpa Paraffin Oven) 80˚C for 8 hr to achieve the final sample Graphene Oxide method 1 (GO-1).

5. Graphene Oxide, method 2 (GO-2) without sodium nitrate, and in the process is the same method as Method 1 as shown in Fig. 1 and analyze the crystallinity and structure (XRD, Shimadzu, LabX XRD-6100), identify the chemical composition (Raman, HORIBA, XploRA plus and UV-Vis Spectrophotometer, CCL-5800), surface and internal structure and elemental (FESEM & EDS, JEOL, JSM-7610F), and surface area and porosity (BET, MicrotracBEL, BELSORP-miniX).

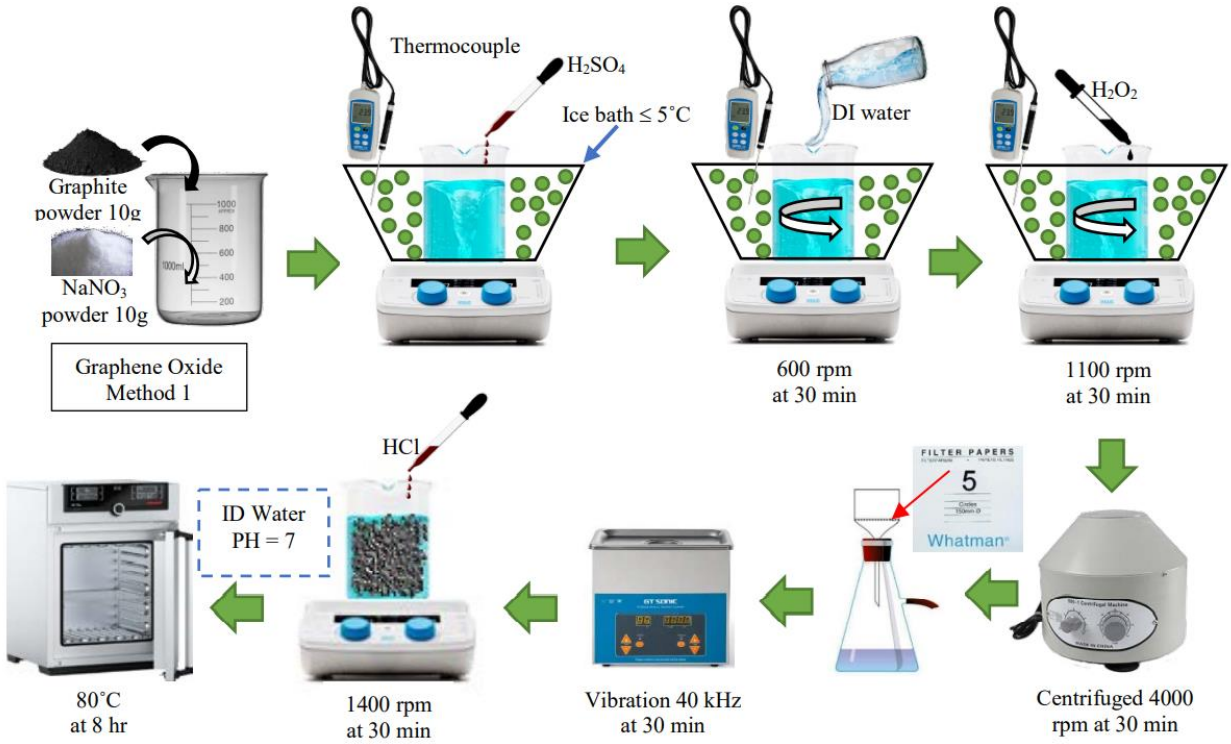


Fig. 1 The illustration of the steps of the preparations of GO-Method 1 and GO-Method 2.

Results and Discussions

The X-ray diffraction (XRD) of graphene oxide (GO) is typically characterized by a broad and weak peak at around 10˚ – 11˚ 2θ. This peak corresponds to the interlayer spacing of the graphene oxide layers and is usually referred to as the "D" peak. The D peak position and intensity can be used to estimate the degree of oxidation of the GO sample [14].

The XRD of GO-1 and GO-2 show other peaks corresponding to the crystalline regions of the graphene layers. These peaks are typically located at around 26˚ and 43˚ (Fig. 2(a)) and correspond to the (002) and (100) planes of the graphene crystal, respectively. This peak represents the plans spacing (d-spacing) between adjacent carbon atoms within the graphene lattice. The high intensity of this peak indicates the high crystallinity and the presence of a well-ordered hexagonal lattice in the graphene sample.

The XRD peak of GO-2 is wider than that of GO-1 as a result of smaller graphene flakes. The smaller the scale, the wider the base of the XRD peak and the peak appearing at approximately 11˚ is peak of graphite.

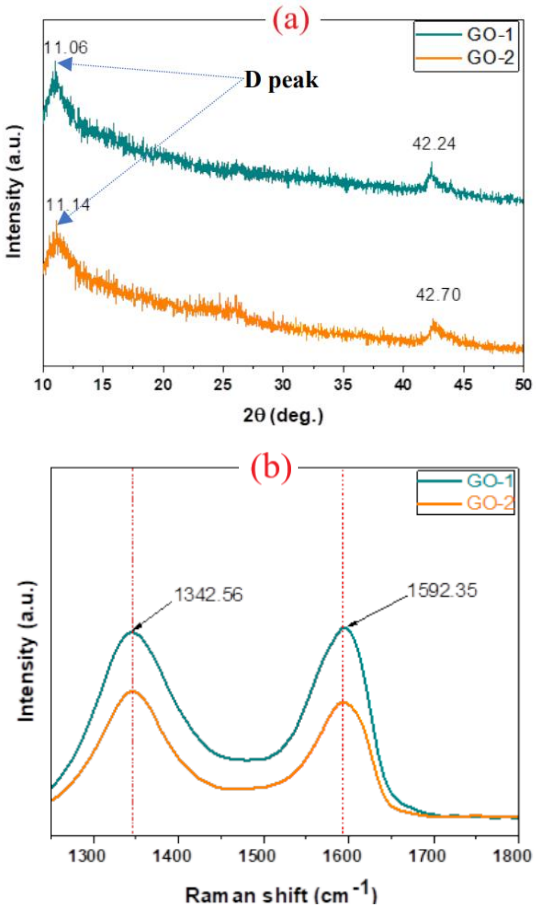


Fig. 2 X-ray diffraction (XRD) pattern and Ramann spectra of the samples, GO-1 and GO-2.

Raman spectroscopy is a powerful technique that can be used to analyze the structural and chemical properties of GO-1 and GO-2. Raman spectroscopy works by measuring the inelastic scattering of light by a material, which results in a characteristic Raman spectrum. The Raman spectrum of GO is characterized by several peaks that can be used to determine the degree of oxidation and the structural properties of the material.

The G band is the dominant peak in the Raman spectrum of graphene. It is associated with the in-plane vibrational mode of sp^2-bonded carbon atoms arranged in the hexagonal lattice of graphene. The G band typically appears at around 1580 cm^{-1}. It is a signature of the graphitic structure and indicates the presence of high-quality graphene. The D band is a characteristic feature in the Raman spectra of graphene that is related to defects, disorder, and structural imperfections in the lattice. The D band peak typically appears at around 1350 cm^{-1}. Its presence indicates the existence of sp^3-hybridized carbon atoms in the lattice due to the presence of defects, edges, or disorder in the graphene structure. A strong D band signal suggests a lower quality or defective graphene sample [15, 16].

The main peak in the Raman spectrum of GO-1 and GO-2 (Fig. 2(b)) is the G peak, which is located at 1,592.35 cm^{-1}. The position and intensity of the G peak can be used to estimate the degree of oxidation of the GO sample. As the degree of oxidation increases, the G peak shifts to lower wavenumbers and its intensity decreases. Another important peak in the Raman spectrum of GO-1 and GO-2 is the D peak, which is located at 1,342.56 cm^{-1}. The D peak is associated with the disorder in the graphene lattice and its intensity is related to the degree of disorder in the GO sample. As the degree of oxidation increases, the D peak intensity increases.

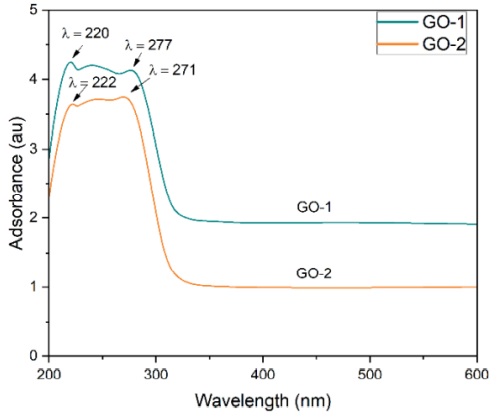


Fig. 3 The radiation absorption GO-1 and GO-2.

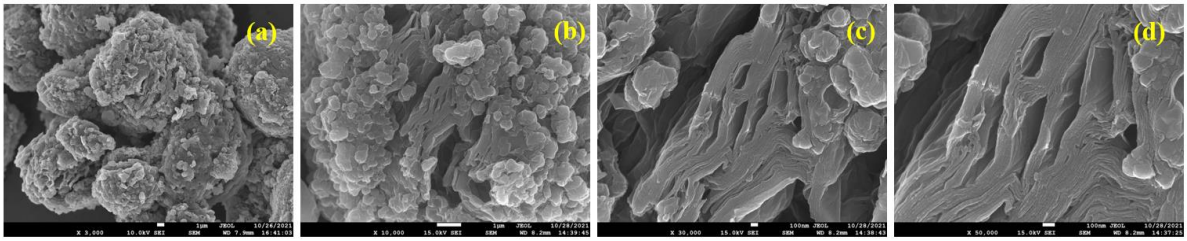


Fig. 4 The FESEM image of GO-1 at (a) 3k, (b) 10k, (c) 30k and (d) 50k).

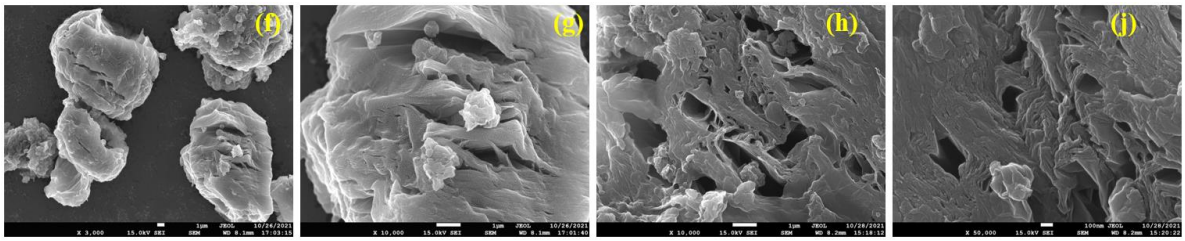


Fig. 5 The FESEM image of GO-2 at (f) 3k, (g) 10k, (h)30k and (j) 50k.

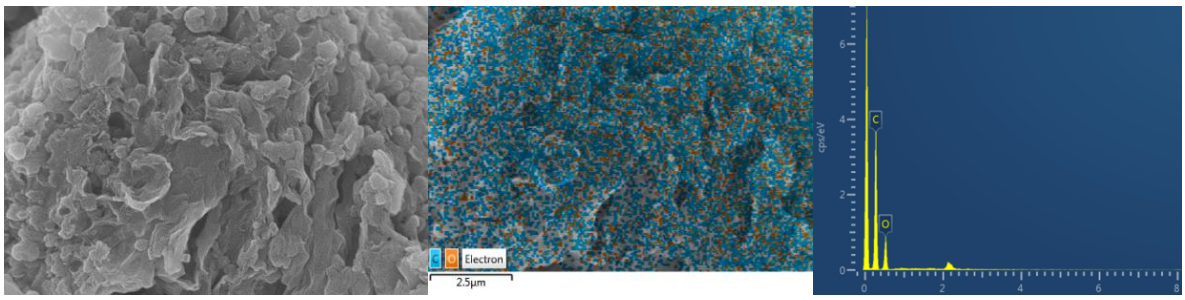


Fig. 6 The identify elements carbon:oxygen (C:O) in a GO-1.

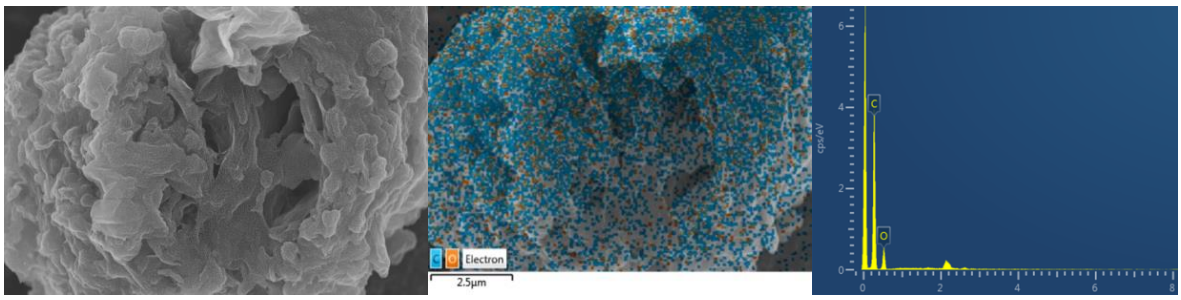


Fig. 7 The identify elements carbon:oxygen (C:O) in a GO-2.

Fig. 3 shows the UV-vis is absorption spectra of GO-1 and GO-2. GO-1 exhibits two absorption peaks at 220 and 276 nm, while GO-2 exhibits two absorption peaks at 222 and 271 nm. The slightly higher absorption peak at 220 nm and the broader absorption peak at 276 nm in GO-1 suggest that the CO bond overlaps more in GO-1 than in GO-2.

The microscopic photographs and elemental elements (FESEM) were shown prominently at a magnification of 3 k, 10 k, 30 k and 50 k (Fig. 4 and 5). Fig.4 (a) show fissures of GO-1 granules, which were more elongated and laminar than GO-2. To examine the elements denoting GO-1. Oxygen (O) was found to be more abundant than GO-2 (Table 1). Due to the porosity resulting from stronger oxidizing reactions, the formation of the element was formed. Oxygen (O) and Carbon (C) are different at the sub isotherm, GO-1 has a specific surface area of 193.31 $m^2 g^{-1}$,

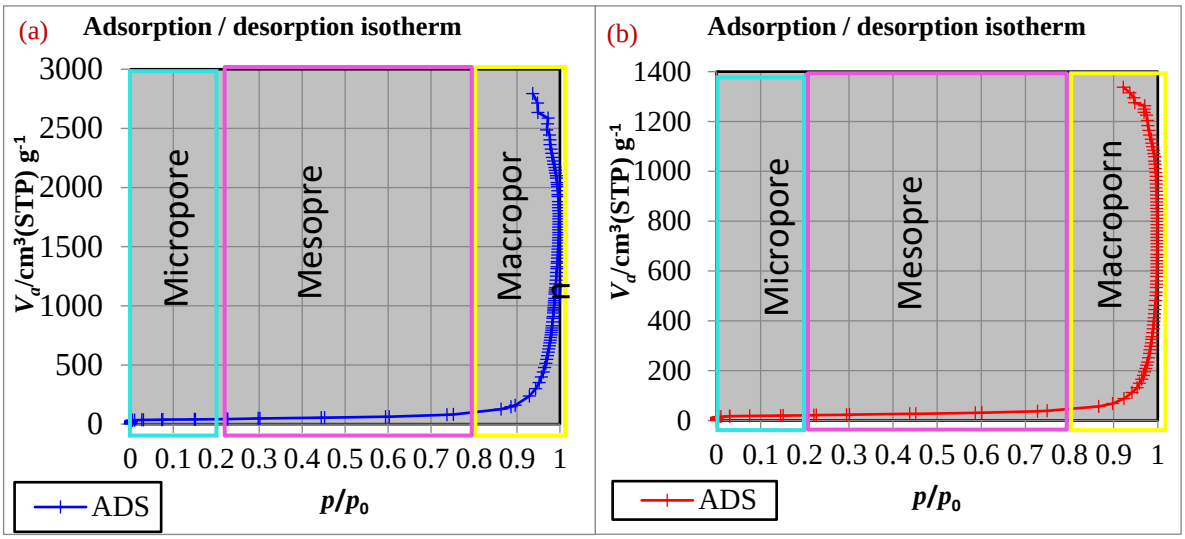


Fig. 8 The surface area measurement and porosity (a) GO-1 and (b) GO-2.

a pore volume of 36.45 cm^3 (STP) g^{-1}, while and GO-2 has a specific surface area and at 73.04 m^2 g^{-1}, the pore volume is 16.781 cm^3 (STP) g^{-1}.

The result of surface area and porosity (BET). Looking at the sub isotherm, GO-1 has a specific surface area of 193.31 m^2 g^{-1}, a pore volume of 36.45 cm^3 (STP) g^{-1}, while and GO-2 has a specific surface area and at 73.04 m^2 g^{-1}, the pore volume is 16.781 cm^3 (STP) g^{-1}.

Conclusion

1. The modified Hummer's method can be used to prepare graphene oxide (GO) from graphite flakes.

2. Chemical exfoliation is used in the process, where chemicals are used to intercalate between the graphene layers and expand the interlayer spacing, making it easier to separate the layers.

3. GO-method 1 and GO-method 2 were used, with the former using sodium nitrate and the latter not using it.

4. Increasing the ultrasonic process of the procedure reduces the preparation time for graphene oxide compared to the original Hummer's method.

5. XRD analysis of GO-1 and GO-2 showed peak angles at 11° and 42°, respectively, which corresponds to graphene oxide.

6. Raman spectroscopy analysis showed that GO-1 has greater structural anomalies due to its superior gravimetric characteristics, indicating the formation of hybrid orbital domains before the formation of C-O bonds.

7. The G band is the atomic arrangement, while maintaining the coherence of the C=C bond that is not different from that of graphite.

8. UV-vis absorption shows the overlap of the C-O bonds of GO-1, resulting in a red shift absorbance at a peak wavelength of 220 nm.

9. Field Emission Scanning Electron Microscope of GO to perform elemental mapping on graphene samples and Brunauer Emmet Teller (BET) for surface area determination and pore size distribution results found that GO-method 1 and GO-method 2 corresponds to graphene oxide, which has a macroporous size, and the adsorption response is more respectively.

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