

# Synthesis of Graphene Oxide Nanosheets via Modified Hummers' Method and Its Physicochemical Properties

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## Article history

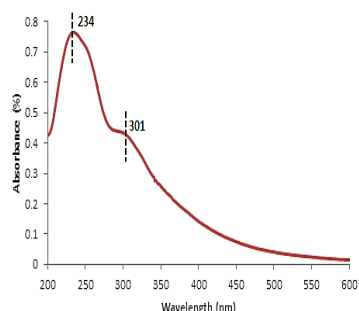
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## Graphical abstract



## Abstract

The efficient synthesis of exfoliated graphene oxide nanosheets (GO) via modified Hummers' method was successfully carried out. The physicochemical properties of GO were determined by Fourier transform infrared spectroscopy (FTIR), UV-visible spectrophotometry (UV-vis), x-ray diffraction analysis (XRD), Raman spectroscopy, and transmission electron microscopy (TEM). The graphite was fully oxidized by strong oxidizing agent caused the oxygen-containing functional groups such as C-O-C, C=O, and COOH were introduced into the graphite layers as analyzed by Raman and FTIR. XRD pattern of GO showed  $2\theta$  of  $12.0^\circ$  with interlayer spacing  $\sim 7.37\text{\AA}$  which describe non uniform crystal structure with the addition of oxygen containing functional groups. UV-vis spectrum of GO exhibit maximum absorption peak at  $\sim 234\text{ nm}$  corresponding to the aromatic C=C bond with  $\pi-\pi^*$  transition. The morphology of GO was observed to have flake-like shape and less transparent layers by TEM. The properties of synthesized GO suggest high potential in producing the high quality of graphene which is can be applied as the electrocatalyst support for direct methanol fuel cell application.

**Keywords:** Graphene oxide nanosheets; graphite; Hummers' method; chemical oxidation; characterization

## Abstrak

Sintesis kepingan-kepingan nano grafin oksida secara berkesan melalui kaedah Hummer yang telah diubahsuai telah berjaya dijalankan. Sifat-sifat fizikokimia grafin oksida telah ditentukan oleh spektroskopi infra merah transformasi Fourier (FTIR), analisis pembelauan x-ray (XRD), spektrofotometri UV-visible, spektroskopi Raman dan mikroskop transmisi electron (TEM). Grafit telah teroksida sepenuhnya oleh agen pengoksidaan yang kuat menyebabkan kumpulan-kumpulan berfungsi yang mengandungi oksigen seperti C-O-C, C=O and COOH telah diperkenalkan ke dalam lapisan-lapisan grafit seperti yang telah dianalisis oleh Raman dan FTIR. Corak XRD bagi GO menunjukkan  $2\theta = 12.0^\circ$  dengan jarak diantara lapisan menghampiri  $7.37\text{\AA}$  menjelaskan struktur kristal yang tidak sekata dengan penambahan kumpulan-kumpulan berfungsi yang mengandungi oksigen. Spektrum UV-vis bagi GO menunjukkan puncak maksimum penyerapan adalah menghampiri pada  $234\text{ nm}$  sepadan dengan ikatan C=C aromatik dengan peralihan  $\pi-\pi^*$ . Morfologi bagi GO telah di kenalpasti memiliki bentuk seperti kepingan dan kurang lapisan telus oleh TEM. Sifat-sifat GO yang telah disintesis mencadangkan potensi yang tinggi dalam menghasilkan grafin yang berkualiti tinggi dimana boleh digunakan sebagai sokongan kepada pemangkin untuk sel bahan api terus.

**Kata kunci:** kepingan-kepingan nano grafin oksida; grafit; kaedah Hummer; pengoksidaan kimia; pencirian

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## 1.0 INTRODUCTION

Graphene, a carbon allotropes of two-dimensional material arranged in a honeycomb lattice structure consisting of  $sp^2$  hybridized carbon atom, is the most attractive material in technological and scientific interest.<sup>1,2</sup> In recent years, it has

received a rising attention in research fields, and shown a great promise due to its unique characteristics such as good mechanical properties<sup>3</sup>, extraordinary electrical conductivity<sup>4</sup> and high thermal conductivity<sup>5</sup> with commonly utilized in the field of energy conversion device applications, such as fuel cell<sup>6</sup>, batteries<sup>7</sup> and solar cell<sup>8</sup>.

Currently, several methods have been explored to produce graphene, including micromechanical exfoliation or “Scotch-tape” method<sup>9</sup>, electric arc discharge<sup>10</sup>, chemical vapor deposition<sup>11</sup> and solvent stripping method<sup>12</sup>. However, these methods are less effective for large scale manufacturing and difficult to achieve high-quality industrial production since the yield of graphene produced was very low<sup>13</sup>. Therefore, the effective, simple and economic route to synthesis of graphene is necessary in order to obtain high quality and quantity of graphene. The chemical oxidation of graphite is the initial routes employed to synthesis graphene. This method is commonly known as Hummers’ method and involves the oxidation of graphite to form graphene oxide nanosheets (GO) by using strong oxidizing agent such as potassium permanganate and potassium perchlorate. Then, GO will be reduced to graphene using various reducing agents.

The hummers’ method provides several advantages such as the capability to produce a large quantity of products<sup>14</sup>, simple, easy to handle and cost effective. Therefore, this method is the most promising way to prepare bulk-scale of graphene materials. In order to turn graphene application into reality, the fabrication of GO as an intermediate product is important since it is the precursor and has a critical influence towards the quality of graphene. For this purpose, herein, a simple way to prepare the graphene oxide nanosheets via modified Hummers’ method under facile condition would be reported. The physicochemical properties and chemical structure of GO have been described properly.

## 2.0 EXPERIMENTAL

### 2.1 Materials

Purified graphite powder (Superior Graphite Co), 35% Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ ) (Riedel-de Haën), Sodium Nitrate ( $\text{NaNO}_3$ ) (Riedel-de Haën), 37% Hydrochloric acid ( $\text{HCl}$ ) (RCI Labscan), Potassium Permanganate ( $\text{KMnO}_4$ ) (COMAK), (95-97)% concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) (QRëC®). All the chemicals were analytical grade and used as received without further purification.

### 2.2 Synthesis of Graphene Oxide Nanosheets (GO)

GO was synthesized through the oxidation of purified graphite powder via modified Hummers’ method<sup>15</sup>. Three g of  $\text{NaNO}_3$  was dissolved in 140 mL of concentrated  $\text{H}_2\text{SO}_4$  in an ice bath. Next, 15 g of  $\text{KMnO}_4$  and 3 g of graphite powder were gradually added into this mixture. The temperature below  $20^\circ\text{C}$  was maintained with vigorous stirring using a mechanical stir bar for 2 hours. The temperature of this mixture was then increased and maintained up to  $35^\circ\text{C}$ . The mixture was continuously stirred for 12 hours at this temperature to form a brown paste. Deionized water (DI, 250 mL) was then poured into the mixture and stirred for  $\frac{1}{2}$  hour. Twenty mL of 35%  $\text{H}_2\text{O}_2$  and 800 mL of DI water were consequently added into the mixture. The mixture color was observed changing from brown to brilliant yellow. The mixture was filtered and washed using 1 M  $\text{HCl}$  and DI water until the pH of filtrate became neutral. Lastly, the mixture was dried in the oven at  $80^\circ\text{C}$ . The reaction pathway for the formation of GO is shown in Figure 1.

### 2.3 Characterizations

The FTIR spectra of GO was obtained using Nicolet 5700 FTIR in the wavelength range of  $500\text{--}4000\text{ cm}^{-1}$ . Ultraviolet-visible

(UV-vis) spectra were obtained using Shimadzu UV-visible spectrophotometer (UV-1601 PC) with the wavelength of 200–600 nm. X-ray diffraction (XRD) patterns were taken on a High Resolution X-ray diffractometer (Bruker D8 Advance) using  $\text{Cu-K}\alpha$  ( $\lambda = 1.54\text{\AA}$ ) radiation in  $2\theta$  range between  $10^\circ$  and  $40^\circ$ . The morphology and the microstructure of synthesized GO was characterized by transmission electron microscopy (TEM, FEI/Philips CM12) at acceleration voltage of 120 kV. The samples were prepared by dispersing the GO in ethanol ultrasonically for 10–15 minutes and subsequently dropping the suspension on a carbon-coated copper grid. Thermo-gravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/SDTA 851e thermal analyzer in a dynamic atmosphere of dinitrogen. The samples were heated in alumina crucible at the rate of  $10^\circ\text{C min}^{-1}$ . Raman spectra were recorded from  $800$  to  $2000\text{ cm}^{-1}$  on a Renishaw 1000 confocal Raman microprobe (Renishaw instruments) using a 514 nm argon ion laser.

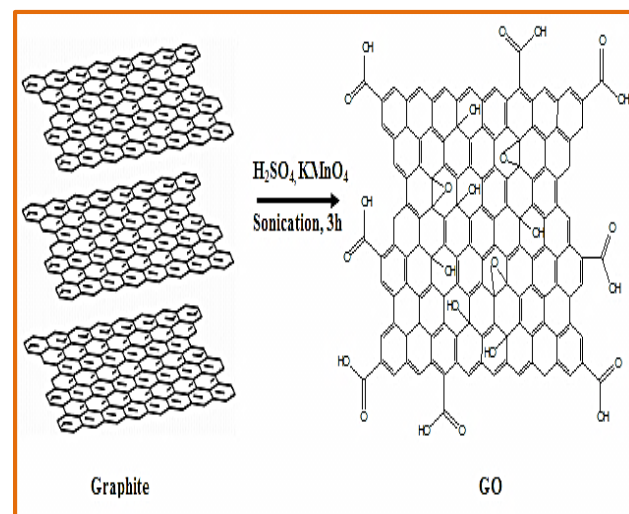
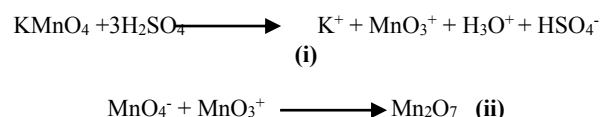


Figure 1 The illustration synthesis of GO from graphite

## 3.0 RESULTS AND DISCUSSION

The Hummers method is frequently used as a universal method for the formation of GO from the precursor which is the graphite. This method provided more efficient for oxidation of graphite and less hazardous. The preparation of GO can be achieved by mixing the graphite with concentrated sulfuric acid in the presence of oxidizing agent. Potassium permanganate is commonly used as an oxidizing agent in preparing of GO. The reaction between sulfuric acid and potassium permanganate has produced permanganyl ion as shown in chemical equation (i). Then, this ion will further react with manganate (VII) ion to form dark red oil as shown in (ii). This oil is referring to diamanganese heptoxide ( $\text{Mn}_2\text{O}_7$ ) which is more active species than permanganate.  $\text{Mn}_2\text{O}_7$  is able to oxidize unsaturated aliphatic double bonds over aromatic double bonds selectively which may have important implications for the reaction pathway occurred during the oxidation process and also the graphite structure<sup>16</sup>.



### 3.1 Structural Analysis

XRD was used to investigate the interlayer changes and the crystalline properties of the GO. Figure 2 shows the XRD pattern for GO. A strong diffraction peak near  $12.0^\circ$  which corresponded to the (002) basal plane with d-spacing  $\sim 7.37\text{\AA}$  was observed for the GO. The large interlayer spacing of GO was due to the existence of oxygenated functional group on GO during the harsh oxidation treatment of graphite powder and also the intercalation of water molecules<sup>2</sup>. This result was initially proved the formation of GO.

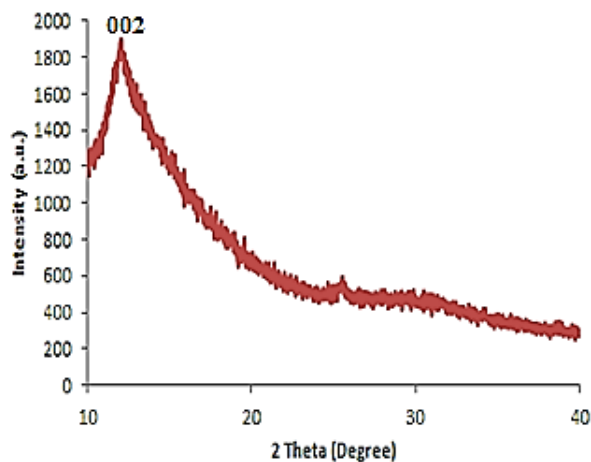


Figure 2 The XRD spectrum for GO

FTIR analysis was done to determine the structure and functional groups exist in GO. Figure 3 shows the FTIR spectrum for GO. The spectrum for GO shows a broad peak at  $3271\text{ cm}^{-1}$  corresponding to the O-H stretching of water molecules absorbed onto the GO. This oxygen-containing functional group provide GO with good dispersibility in water<sup>17</sup>. Therefore, it can be concluded that the GO is highly hydrophilic material. A sharp peak at  $1739\text{ cm}^{-1}$  was attributed to the C=O stretching vibration of carboxylic acid exist at the edges of GO<sup>18</sup>. The presence of absorption peak at  $1616\text{ cm}^{-1}$  can be attributed to the aromatic C=C stretching vibration. The absorption peaks at  $1149\text{ cm}^{-1}$  and  $1047\text{ cm}^{-1}$  were corresponds to epoxy C-O stretching vibration and alkoxy C-O stretching vibration, respectively<sup>2</sup>. The presence of oxygen-containing functional group reveals that the graphite has been successfully oxidized into GO. The surface morphology and structure of the synthesized GO was investigated by TEM analysis as shown in Figure 4. The morphology of multilayer GOs revealed rough surface, flake-like shape, not crumpled and corrugated together with non-uniform of particle size. Furthermore, GO image was observed to have less transparent layer resulting that the GO is not stable under high energy electron beam. This observation provided the evidence that the oxygen-containing functional groups were introduced onto the surface of GO.

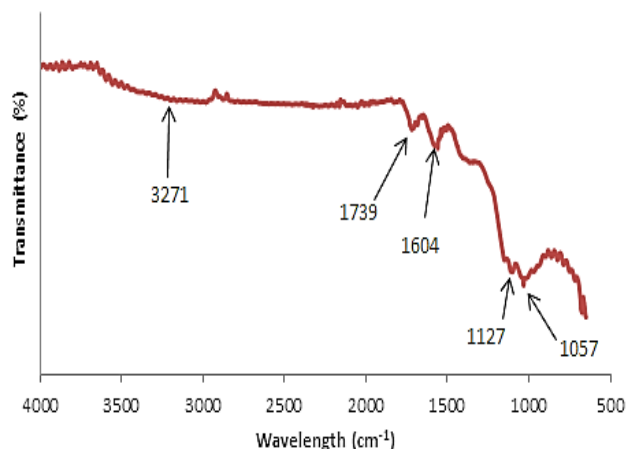


Figure 3 FTIR spectrum for GO

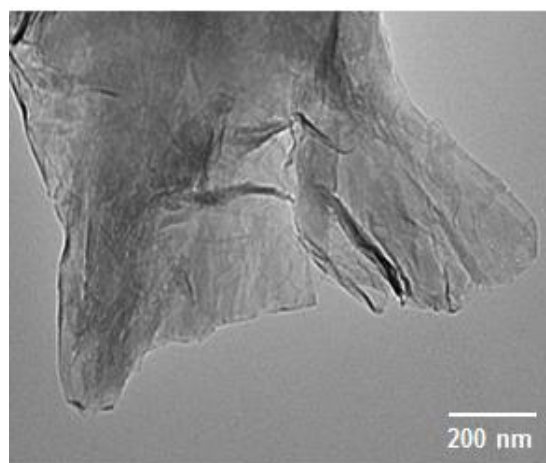


Figure 4 TEM image of GO

Figure 5 shows the UV-vis spectrum of GO. It is observed that GO shows a strong absorption peak at  $\sim 234\text{ nm}$ , corresponding to the conjugated aromatic double bonds (C=C) attributable to  $\pi-\pi^*$  transition. Another peak at  $\sim 301\text{ nm}$ , which was a shoulder band, corresponded to the carbonyl bonds (C=O) with  $n-\pi^*$  transition. This result provided a good agreement with the FTIR result.

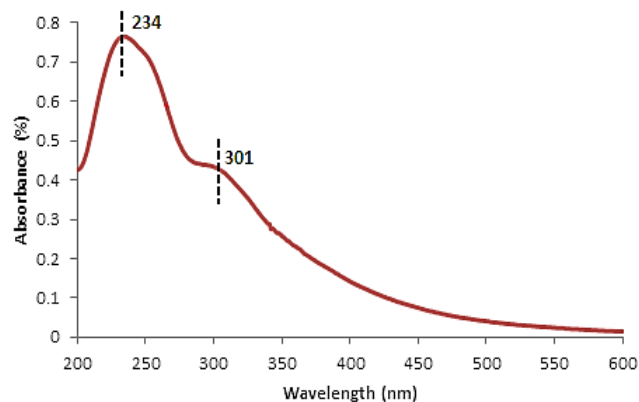


Figure 5 UV-vis spectrum spectrum for GO

Raman spectroscopy is non-destructive technique used to identify the structural and electronic properties of carbon materials. The Raman spectrum of GO is shown in Figure 6. The existence of D band and G band in the spectra of GO is attributed to the breathing mode of  $\kappa$  point photons of  $A_{1g}$  symmetry and the first order scattering of the  $E_{2g}$  phonons of  $sp^2$  hybrid carbon atoms respectively<sup>19, 20, 21</sup>. These two main features, D and G band are related to the defects of  $sp^2$  carbon lattice and disordered conformations<sup>22</sup>. The G band of GO is located at  $1600\text{ cm}^{-1}$  while the D band of GO appear at around  $1353\text{ cm}^{-1}$ . The measurement of the relative disorder present in the graphitic structure such as defects, edges and ripples can be detected through the ratio between the intensities of D and G bands ( $I_D/I_G$ ). The intensity ratio of D band and G band ( $I_D/I_G$ ) of GO was 0.90.

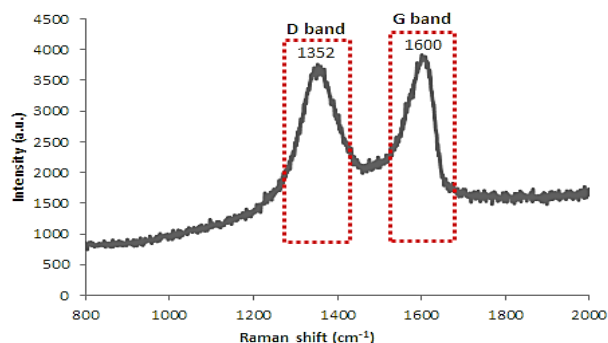


Figure 6 Raman spectrum for GO

### 3.2 Thermal Analysis

The thermal stability of GO was tested by TGA. The typical TGA curve of GO was shown in Figure 7. The TGA curve of GO exhibits three significant stages for mass loss of GO upon the increase in temperature. For the first stage, it is observed that there was a mass loss of about 6 wt% at the temperature of  $100^\circ\text{C}$ , which is due to the loss of remaining oxygen containing functional groups. While the second stage at around  $200^\circ\text{C}$ , it displayed about 33 wt% mass loss which is related to the pyrolysis of the labile oxygen-containing functional groups as well as the burning of ring carbon. Lastly, the mass loss occurred at around  $450^\circ\text{C}$  was about 52 wt% due to the combustion of carbon skeleton. These analysis results indicated that GO possess good thermal stability and stable in normal state.

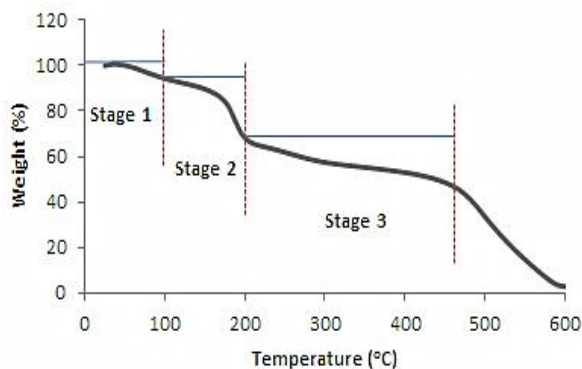


Figure 7 TGA diagram of GO

### 4.0 CONCLUSION

In this paper, we report the synthesis of scalable large-area GO via modified Hummers' method. The successful preparation of GO was analyzed by XRD and FTIR in which the presence of oxygen containing functional group in GO was further determined. This analysis results will provide a reference for further study the characteristics of graphene. GO has frequently used as the precursor for the production of graphene which is later can be utilized as electrocatalyst support in our future works for direct methanol fuel cell.

### Acknowledgement

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