Facile Synthesis of High Quality Graphene Oxide from Graphite Flakes Using Improved Hummer’s Technique

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Graphene is a promising candidate for making next-generation nanotechnology devices due to its outstanding properties in terms of physical, chemical, mechanical aspects. Based on the theoretical point of view, graphene is a two-dimensional (2D) crystal structure with sp² hybridized carbon atoms arrangement and has attracted extensive attention in a considerable number of applications such as solar energy, sensor and energy storage, naming a few. Herein, graphene oxide (GO) is synthesized from graphite flakes using the Improved Hummer’s method. The results demonstrated the comparison of synthesized GO samples based on stirred duration of 6 h and 72 h. The FTIR results proved that the 72 h GO sample was well-bonded with the C–O functional group, signifying the successful synthesis of GO under an extended stirred duration. The FESEM images showed that the synthesized GO was well-arranged in crystal lattice of graphene sheets whereas the EDX result showed that higher atomic% of Oxygen, O₂ was obtained with a longer stirred duration due to the high opportunity for oxygenated bonded to occur on the C–C functional group.

Keywords: Graphite, Graphene Oxide, Graphene, Improved Hummer’s Method.

1. INTRODUCTION
Graphene is a mono-layer carbon sheet which exhibits the unique high electron mobility (200 000 cm² v⁻¹ s⁻¹), high thermal stability (∼5000 Wm⁻¹ K⁻¹), and optimum mechanical properties (∼1.0 TPa).¹⁻³ Graphene also shows promising potential in several applications such as organic photovoltaic cells,⁴⁻⁵ field-effect transistors,⁶⁻⁷ and transparent electrodes⁸ due to its excellent and unique electrical properties.

Basically, the chemically oxidized GO consists of certain functional groups such as carbonyl, hydroxyl, and peroxyxyl in C–C bond.⁹ These functional groups determine that graphene layers will peel off layer by layer from graphite after weakening the Van der Waals bonding between C–C bonds of graphite.⁹

Recently, there are several methods reported for graphene synthesis such as chemical vapor deposition¹⁰ and mechanical exfoliation for cleavage.¹¹ However, these methods have some limitations such as limited surface area, time consuming to produce and require high production cost. To overcome these issues, we developed a simple and cost effective method to synthesize GO from graphite flakes by using chemical oxidation process.

In this study, GO was synthesized using the Improved Hummer’s method, which would generate high conductivity under 150 W xenon lamp. It was characterized using Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, and EDX Microanalysis.

2. EXPERIMENTAL DETAILS
2.1. Materials
Graphite flakes (code no 50870) were purchased from Fluka. Sulfuric acid (H₂SO₄, 0.5 M), phosphoric acid (H₃PO₄, 85%), potassium permanganate (KMnO₄, 97%), hydrogen peroxide (H₂O₂, 30%), and fuming hydrochloric acid (HCl, 37%) were purchased from Friendemann Schmidt.
2.2. Graphene Oxide (GO) Synthesis

The oxidation of graphite was synthesized by mixing $\text{H}_2\text{SO}_4$,$\text{H}_3\text{PO}_4$ (180:20 ml), graphite flakes (1.5 g), and $\text{KMnO}_4$ (9.0 g) using magnetic stirrer. The mixture was then stirred in ice-bath condition ($\leq 20^\circ\text{C}$) and the mixture was left stirring for 6 h and 72 h, respectively at a constant speed to investigate the changes in term of oxygenated molecules group and morphology of GO produced after the oxidation of graphite was completed. Next, at the end of the time mentioned earlier, the solution was poured into ice ($\sim 200$ ml) and then added with $\text{H}_2\text{O}_2$ to stop the oxidation process. The GO formed after the resultant mixture solution was centrifuged (7000 rpm) for three times with $\text{HCl}$ and the supernatant was decanted away. The process was repeatedly done with deionized water (DI water) until a pH of 4–5 was achieved. Finally, the product known as GO powder was formed after the washing process and the GO experienced exfoliation. The GO was dried at 90 $^\circ\text{C}$ in a vacuum oven overnight to form the black color of GO. Figure 1 shows the three major steps comprises of the morphological image of graphite, one intermediate products (graphite oxidation reaction) and the final product of GO.

In the initial stage, the graphite flakes (solid black lines) in multi-layers formation. Then it reacted with $\text{H}_2\text{SO}_4$, $\text{KMnO}_4$, and $\text{HNO}_3$. The wide light green lines represent $\text{H}_2\text{SO}_4/\text{HSO}_4^-$ intercalate during the oxidation process while the wide red lines represent a layer of mixture $\text{H}_2\text{SO}_4/\text{HSO}_4^-$ intercalant with the oxidizing agent. Lastly, the GO was fully formed by the oxidizing agent which contained the $\text{H}_2\text{SO}_4/\text{HSO}_4^-$ intercalant.

2.3. Characterization

For characterization purposes, the samples obtained were analyzed using the Fourier Transform Infrared Spectroscopy (FTIR) (Bruker-IFS 66/S) in order to compare the changes in functional groups of carboxyl group (–COOH), carbonyl group (–C=O), and epoxide group (–O–). Furthermore, the Raman spectra were obtained through the Renishaw inVia microscope, with a HeCd laser source for functional group and structural identification purposes. The morphology of the graphene materials were characterized by the field emission scanning electron microscopy (FESEM) instrument. The composition of the graphene materials were characterized by FESEM with energy-dispersive X-ray spectroscopy (EDX) microanalysis at 5.0 kV.

The electrochemical properties of the samples were characterized using a potentiostat (Autolab PGSTAT101), and their current and voltage were measured accordingly. In order to evaluate the sample’s current–voltage ($I–V$) characteristics, the GO was coated onto a FTO glass using electro-deposition technique at 60 V for 15 mins. The electrolyte contained DI water and acetone nitrile. A 150 W xenon lamp (240–2000 nm Spectral Distribution) was used to produce a largely continuous and uniform spectrum for measurement purposes. The xenon lamp was switched on after all the electrodes were connected to the potentiostat. A linear sweep potential (LSP) was swept from $-0.3$ V to 0.3 V at a scan rate of 50 mV/s and the corresponding photocurrent was measured. The photocurrent applied was plotted versus the potential.

Figure 1. Schematic of GO synthesis from graphite flakes with corresponding images sample appearances at each stages.
3. RESULTS AND DISCUSSION
During the Improved Hummer’s method, the colour of the mixture changed from dark purple to dark brown as shown in Figure 2(a). Figure 2(a) revealed that the oxidizing agent (KMnO₄) was fully mixed with the solutions (H₂SO₄, H₃PO₄, and graphite). After being mixed, the colour of the mixture turned to bright yellow indicating that the high oxidation level of graphite was obtained as shown in Figure 2(b).

In this experiment, FTIR measurement was employed to analyze the bonding interaction in graphite and GO stirred duration samples, 6 h and 72 h respectively. Figure 3 shows that GO has a significant peak at 1081 cm⁻¹, which indicated that C–O bond with the presence of oxide functional group after the chemical oxidation process. At this peak, it is also shown that 72 h stirred duration sample exhibited a larger amount of C–O bond compared to the shorter stirred duration (6 h sample). In the same way, the C–C bond in the 72 h stirred duration attributed to the fact that they were strongly bonded with each other compared to the C–C bond in 6 h stirred duration. The C–C bond peak of GO normally occurred in the range of 1630 to 1650 cm⁻¹. In addition to that, the C–C bond in raw graphite was much weaker compared to both GO. Furthermore, the water contents in both GO and graphite were represented by O–H stretch of H₂O molecules by a broad peak at 2885 to 3715 cm⁻¹.\(^\text{i2}\)

![Figure 2. Color changes of (a) H₂SO₄, H₃PO₄, and Graphite to H₂SO₄, H₃PO₄, graphite, and KMnO₄ and (b) Mixture of (a) with H₂O₂.](image)

Raman scattering is a useful tool to characterize the symmetry of carbon molecules and its GO bonds. Raman spectrum of GO significantly changed between 6 h stirred duration and 72 h duration (Fig. 4). In the GO material, there were two fundamental vibrations and one minor band in the range of 500–3000 cm⁻¹. The D vibration band indicated that the breathing mode of \(k\)-point photons of \(A_1g\) symmetry of 6 h stirred of GO and 72 h stirred of GO were recorded at 1356.92 and 1353.85 cm⁻¹, respectively. While the G vibration band for 6 h stirred of GO and 72 h stirred of GO at 1607.77 and 1601.82 cm⁻¹, respectively represented the first-order scattering of \(E_{2g}\) phonons by its \(sp^2\) carbon. Besides, the 2D vibration band is an essential band to differentiate the layer of graphene. Based on Lorentzian peak for 2D band, the monolayer graphene sheets recorded at 2679 cm⁻¹ and the higher wavenumber were considered as multi-layer graphene sheets. For 2D vibration band, the 2D bands of 72 h stirred GO was observed at 2722.09 and 2962.03 cm⁻¹ was higher than the 2D band of 6 h stirred

![Figure 4. Raman spectra of GO, (a) 6 h stirred duration and (b) 72 h stirred duration.](image)
Facile Synthesis of High Quality Graphene Oxide from Graphite Flakes Using Improved Hummer’s Technique

Low et al.

4. CONCLUSION

In summary, the formation of GO from graphite flakes consisted of three major steps and one intermediate stage was successfully demonstrated. Furthermore, Carbon, C containing 65.80 atomic% of GO was obtained by using the Improved Hummer’s method. Large amount of oxygen molecules were generated due to the enhancement of mass transfer rate during the chemical oxidation process. The high photocurrent of 6.71 mA was mainly attributed to the high photo-induced electron–hole pair between consecutive carbon basal planes.

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References and Notes


Figure 6. I–V Characteristic curves of, (a) graphite, (b) GO 6 h stirred duration, (c) GO 72 h stirred duration.

shorter reaction time. This was mainly attributed to the fact that the oxidation reaction had reached its climax where all the GO had been fully oxidized due to higher opportunity to bond with the C–C functional group.

An electrical performance test was carried out based on the graphite and GO and the photoelectrode results are shown in Figure 6. Based on the current–voltage curves, the GO after 72 h stirred duration sample achieved slightly higher current at 0.3 V compared to 6 h stirred duration sample, 6.71 mA and 6.58 mA respectively. This phenomena indicated that higher photo-induced electron/hole pair were generated in longer stirred duration sample in between the consecutive carbon basal planes. Furthermore, the graphite obtained the lowest value at 0.3 V with 2.34 mA which is attributed to the lack of oxygenated bonds to accelerate the photocurrent reaction.

Table 1. EDX results of graphite, GO 6 h stirred, and GO 72 h stirring duration.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Stir duration (hours)</th>
<th>Carbon, C (atomic%)</th>
<th>Oxygen, O (atomic%)</th>
<th>Total (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>0</td>
<td>97.10</td>
<td>2.90</td>
<td>100.00</td>
</tr>
<tr>
<td>GO</td>
<td>6</td>
<td>69.20</td>
<td>30.80</td>
<td>100.00</td>
</tr>
<tr>
<td>GO</td>
<td>72</td>
<td>65.80</td>
<td>34.20</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Figure 5. FESEM Images of GO, (a) 6 h stirred duration and (b) 72 h stirred duration.

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