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# Synthesis of graphene oxide from used electrode graphite with controlled oxidation process

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**Abstract.** Graphene oxide and reduced graphene oxide attract a lot of attention due to graphene provides some properties that suitable for wider application. Properties of graphene are unique since it can be tuned regarding to its controlled synthesis method and several treatments. This work, graphene oxide was synthesized from used graphite electrode by modified Hummer's method in which oxidation process controlled. Zinc was used to produce reduced graphene oxide. Graphene oxide and reduced graphene oxide were characterized by SEM, EDS, FT-IR, UV-vis, and XRD. Effective strategy was studied to produce graphene oxide and reduced graphene oxide by controlling its oxidation process. These results prove that chemical and structural properties of graphene oxide and reduced graphene oxide depend on oxidation duration. Furthermore, carbon/oxygen ratio was studied to evaluate effective oxidation process.

## 1. Introduction

Carbon got tremendous attention since last decade. Its nanostructure and carbon allotropes properties overcome other potential atoms. Among all various classes of carbon allotropes, graphene provides adorable properties for numerous applications. Those adorable properties of graphene showed in superior electronic, optical, mechanical and other properties. Graphene, is a two dimensional material made up of densely packed carbon atoms through sp2 hybridization [1].

Graphene based material have numerous applications such as light weight, flexible, thin, durable display screens and electrical circuits, super capacitor [2], transistor [3], transparent conducting electrodes for the replacement of ITO, conductive polymer composite [4], energy storage [5] and solar cells [6]. Lots of efforts have been intended to produce graphene in recent year by several ways. However, effective graphene's synthesis method still remains challenging task.

Various graphene oxide synthesis methods are learned for last decade to provide most effective way. Graphene provides remarkable properties since its properties can be tuned and modified for certain application. Chemical method is the prominent method of producing graphene based material in mass production [7]. However, conventional chemical methods were dangerous and toxic. Modified Hummer's method appears to be one of safe method and one of the oldest technique yet it is one of the most suitable methods to produce graphene oxide [8].

Graphene oxide (GO) comes out with advantages which are easily to produce. Furthermore, it consumes low cost and abilities to convert to graphene. The most common ways synthesizing graphene oxide is from bulk of graphite. Flake graphite is naturally occurring mineral that is purified by removing the heteroatomic contamination [8]. However, graphene exfoliation from used battery illustrates a possible way of recycling used batteries [9].

Graphene oxide was prepared by treating used electrode with $NaNO_3$, $H_2SO_4$, $H_2O_2$, and $KMnO_4$. However, effective oxidation duration of graphene oxide still remains unclear. Among all the protonic acid used to produce graphene from electrochemical exfoliation method, Sulfuric Acid is the most commonly used one because its interlayer spacing between graphite layers (0.335 nm) is quite comparable to $SO_4$ ion size (0.46 nm) in which facilitates easy intercalation of sulphate anion within the carbon layers in graphite [10,11]

## 2. Method
Chemicals used in this synthesis were Potassium Permanganate ($KMnO_4$), Sulfuric Acid ($H_2SO_4$), Sodium Nitrate ($NaNO_3$), Hydrogen Peroxide ($H_2O_2$) and used electrode graphite.

In order to synthesize graphite oxide, it was done by mixing 0.5 gr of Sodium Nitrate, 2.5 gr Potassium Permanganate, 0.5 gr used electrode and last but not least 23.3 mL of $H_2SO_4$ as oxidant. Dissolved and mix all those chemicals under 20°C, and stir for about 2 hours.

After being stirred about 2 hours, mixture's temperature should be lifted up to 35° C-40° C controlled by water bath. This oxidation process will be controlled by varying stirring time 3h, 5h, 7h and 14h. Texture of the mixture and the colour changed into brown paste starts from 3h of oxidation which indicated oxidation process was occurred.

Distilled water then came into the place in order to stop the reaction. 41.67 mL of distilled water pour into the beaker then followed by 3.3 mL of hydrogen peroxide ($H_2O_2$) to indicate the level of oxidation. When fully oxidation (high level of oxidation) occurs, the addition of $H_2O_2$ resulted in yellow colour and mixture stirred for 30 minutes to speed up reaction. 133.3 mL of distilled water added up into mixture and 5% of HCl was added into the mixture. Washed the sample with aqueous until the pH neutral and furnace the sample at 70°C until dried and brown black sample was obtained. 0.1 g of graphite oxide added up into 50 mL of distilled water and sonicated for 30 minutes. Then sample was done by centrifugation and after that dried samples using oven at 60°C.

Reduced graphene oxide was prepared by green reductant. 0.2 gr of graphene oxide dissolved in 200 mL of distilled water, sonicated mixture for 2 hours. 9.5 mL of HCl 37% and 1 gr of zinc powder added up into solution and sonicated until mixture become transparent. 5 mL of HCl 37%was added up to solution and washed by ethanol and aqueous to remove metal ions from the solution. Then the result was dried at 60°C for several times until it dried.

## 3. Results and Discussion
Graphite oxide provides phenomenon where colour and texture changed. A mixture of sulfuric acid and used electrode graphite added by potassium permanganate and sodium nitrate resulted dark green colour. It stirred for 2 hours under 20°C to keep mixture away from explosion. Texture and colour changed after oxidation occur with slight exothermic it changed into brown paste sample. After adding distilled water into the mixture, no purple colour shown which indicated $KMnO_4$ reacted or not fully reacted. Hydrogen peroxide added into the mixture to show the level of oxidation. $H_2O_2$ would consume the residue of oxidant agent besides showing the level of oxidation. The obtained graphite oxide was dispersed in $H_2O$ upon the mechanical stirring, this might be through the introduction of functional groups which are responsible for hydrophilic nature of graphite oxide [12].

To obtain graphene oxide powder without metal ions, the mixture filtrated and washed by HCl to remove the rest of metal ions. Graphite oxide powder resulted in brown paste. Reduced graphene oxide by zinc as reductant was observed by visual observation. Colour of resulted sample changed, black colour of rGO can be assigned to the partial restoration of the π-network between the sheets due to removal of oxygen functional groups resulted in electronic conjugation with in reduced sheets [13].

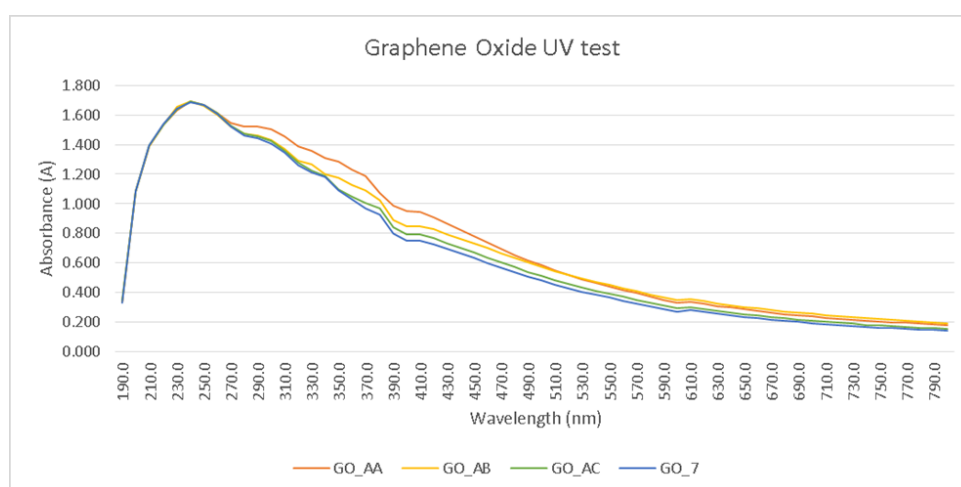**Table 1** Synthesis Parameter and designations of prepared sample

| Chemical used | GO AA | GO AB | GO AC | GO D |
|---|---|---|---|---|
| Used Electrode [gr] | 0.5 | 0.5 | 0.5 | 1 |
| KMnO4 [gr] | 2.5 | 2.5 | 2.5 | 5.0 |
| $NaNO_3$ [gr] | 0.5 | 0.5 | 0.5 | 1 |
| $H_2SO_4$ [mL] | 23.3 | 23.3 | 23.3 | 46.6 |
| $H_2O_2$ [mL] | 3.3 | 3.3 | 3.3 | 6.6 |
| Stirring Duration [h] | 3 | 5 | 7 | 14 |

Table 1 showed the designations of the prepared sample. GO AA, AB, AC, and D were experimental parameter to synthesis graphene oxide and reduced graphene oxide. Those parameters were synthesized from used electrode graphite with the 1:2 of used electrode graphite and $KMnO_4$, 1:1 with sodium nitrate. Same amount of reaction temperature was used but the reaction time was varied as shown in table 1.
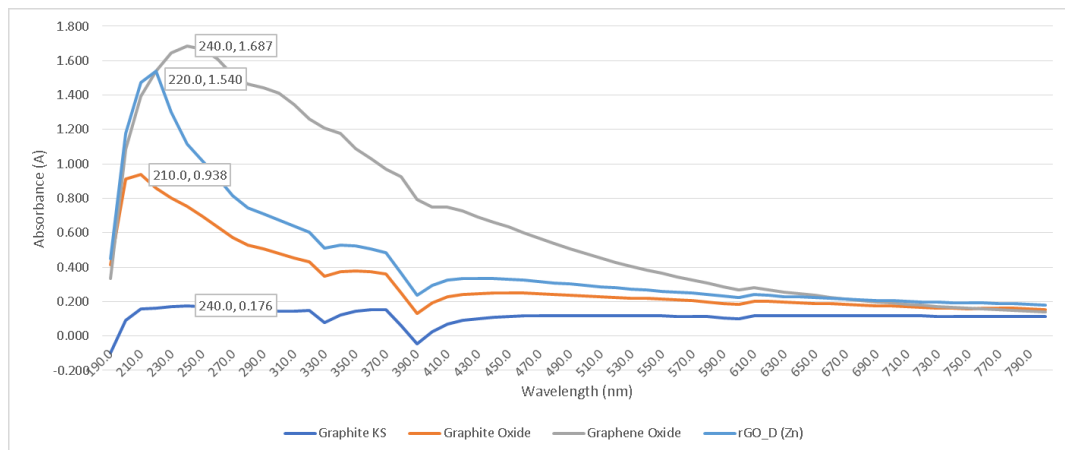
The amount of oxidant, reaction temperature, and reaction time were the main things to determine resulted graphene oxide and reduced graphene oxide. The effect of the parameter on oxidation level of graphite oxide was studied by visual observation. Yellow colour indicates the reaction fully happened while a bit of green colour means the reaction is not fully occurred. For further analysis, the degree of oxidation can be found and studied by using UV-Visible spectra. The effect of reaction duration of oxidant potassium permanganate, the equal concentration of graphite powder of GO AA, AB, and AC are collected. Resulted graphite oxide were grounded and dispersed into same amount of distilled water.

Dispersed graphene oxide of sample was characterized by UV Vis and the spectra for each sample were recorded as shown in figure 1. While each sample characterized, the sample of 14 hours reaction time also observed to compare with less than 10 hours reaction time. The adsorption peak was at 240 nm for all graphite oxide samples with different intensity level. The peaks are related to C and C bonding which similar to reported value in theoretical literature [23-24].

Enough time is required for higher degree of oxidation as observed by UV-Vis spectra. It could be over oxidation whenever the reaction time overcame the limits, and 14 hours is the limits for oxidation reaction time.
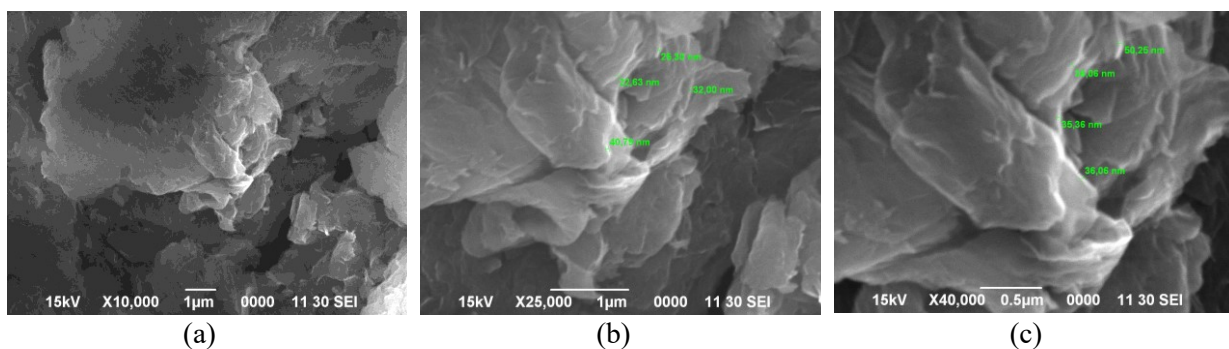


**Figure 1.** UV-Visible spectra recorded in distilled water at different reaction time

While the adsorption peak same for each sample at 240 nm, the intensity level different. GO AA provides 1.694, GO AB provides 1.692, GO AC provide 1.691 and GO D provide 1.687. The successful of reduced graphene oxide was also observed by UV Vis spectroscopy as shown in figure 2. GO D which resulted better than other sample in visual observation will be reduced by zinc as reductant. After reduction by zinc, the peak of reduced graphene oxide shifted to 220 nm which indicates decreased electron concentration after reduction.



**Figure 2.** GO to rGO comparison UV Vis spectra of GO D

Three different SEM magnification of graphene oxide sample was collected. GO AC was used for Scanning Electron Microscopy (SEM) analysis. Based on SEM image, it was indicated the typical surface of graphene oxide. At the edge of morphological characterization, it is a little bit thick rather than in the middle as shown in figure 3. It is due to oxygen functional groups contained in resulted sample. As reaction time increase to enough time, amount of oxygen functional groups will be decreased. SEM image would be supported by Energy Dispersive X-Ray Spectroscopy (EDS) data analysis to investigate its composition. It is proven that surface of graphene oxide consists mostly by carbon and oxygen.
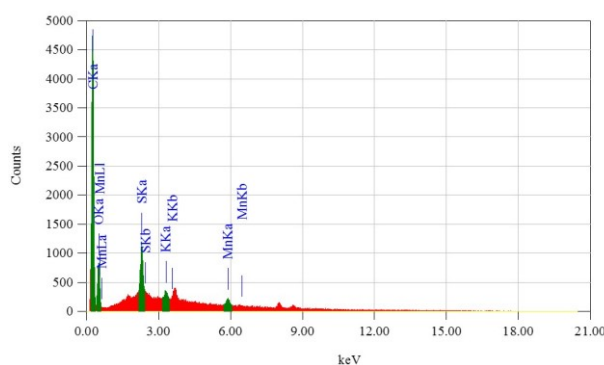


**Figure 3** SEM analysis of graphite oxide sample GO AC (a) 10K magnification. (b) 25K magnification. (c) 40K magnification.

Furthermore, the purities of GO AC were observed by EDS analysis. Material contains such carbon, oxygen, sulphur, potassium and manganese were detected. The detailed energy and mass atom stated in figure 4. Element composition of graphene oxide was obtained by Energy Dispersive Spectroscopy (EDS) analysis. Graphene oxide was made up of 69.09 wt% C, 23.94 wt% O, 4.09 wt% S, 0.73 wt% K, 2.15 wt% Mn. In terms atomic weight, it was composed of 77.38 at% C, 20.13 at% O as main composition of graphene oxide.

According to EDS analysis, maximum peak of C element occurred at approximately 0.277 keV. Furthermore, O element peak were obtained at 0.525 keV and 2.307 keV as Sulphur element's peak. Mn and K element peak also obtained as 5.894 keV and 3.312 keV. Graphene oxide should only contain carbon and oxygen for its composition. Meanwhile, we found such as sulphur, potassium and manganese. This defect is due to synthesize process while oxidation happened. Excess sulphur from sulphuric acid, potassium and manganese from potassium permanganate are shown in the table 2.

Sulphuric acid and potassium permanganate as oxidant agent were left on the mixture due to stirring duration at $40^\circ$ C. It is due to time limitation for oxidation process and full oxidation was not happened. For better oxidation process, stirring duration should be increase more than 12 h. Another factor that affects the impurities is raw material. Due to electrode was used for this experiment rather than pure graphite, we can assume that electrode is not pure carbon. It contains impurity inside it so will effect in last analysis on result. Thus, electrode itself may contain sulphur even before oxidation process.
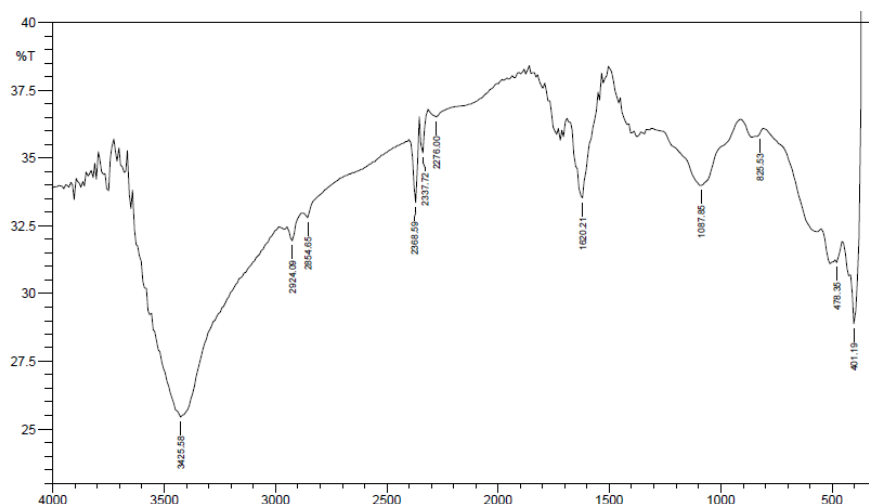


**Figure 4.** EDS analysis of GO AC
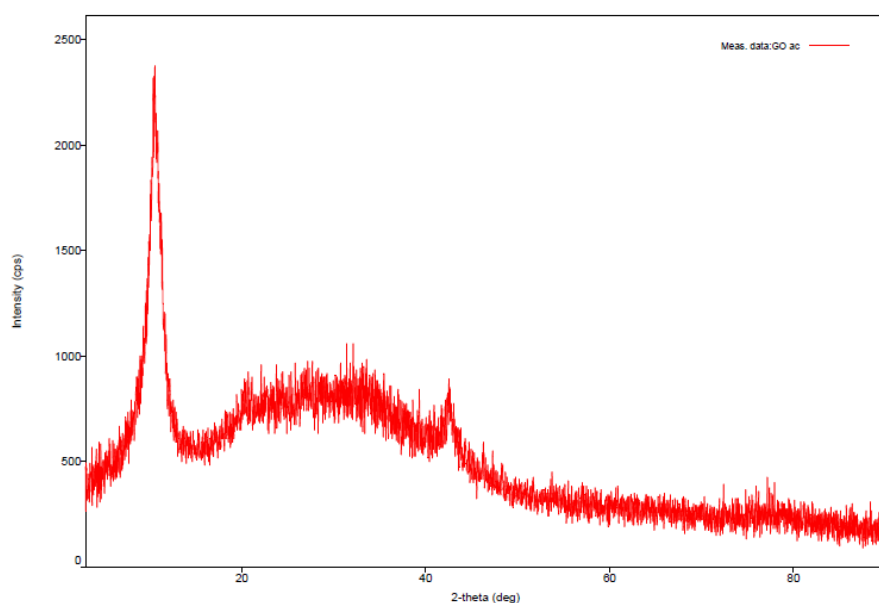
**Table 2** Material composition

| Element | keV | Mass % | Error % | Atom % |
|---|---|---|---|---|
| C | 0.277 | 69.09 | 0.27 | 77.38 |
| O | 0.525 | 23.94 | 1.49 | 20.13 |
| S | 2.307 | 4.09 | 0.27 | 1.72 |
| K | 3.312 | 0.73 | 0.43 | 0.25 |
| Mn | 5.894 | 2.15 | 1.14 | 0.53 |
| Total | | 100.00 | | 100.00 |

The presence of oxygen functional group that detected in SEM analysis, was observed by FT-IR characterization. GO D spectrum was recorded and a broad peak between 3500 cm$^{-1}$ to 2900 cm$^{-1}$ indicates the presence of O-H carboxyl or oxygen functional groups as shown in figure 5. The peaks between 2924 cm$^{-1}$ and 2854 cm$^{-1}$ occurred due to asymmetric and symmetric CH$_2$ stretching of GO respectively while the peak around 1620 cm$^{-1}$ is attributed to C=C stretches [14]. 1087 cm$^{-1}$ corresponds to C-O stretching vibration of C-O-C [12].

**Figure 5.** FTIR spectra of graphene oxide GO D

X-ray diffraction pattern of graphene oxide was collected from GO AC sample as shown in figure 6. The diffraction peak of the sample at around $2\theta=9$ till 12 degree corresponding to a layer to layer distance of 0.88 nm more or less which is close to the literature [15]. The patterns showed a larger interlayer spacing of graphene oxide due to oxygen functional groups between the layers [16], and exhibits turbostatic disorder [17]. The peak at 26 was not detected which confirm that the used electrode graphite is successfully oxidized after treatment of the oxidation and exfoliation resulted the formation of oxygen-containing functional groups of the graphene oxide.



**Figure 6.** X-ray diffraction analysis of graphite oxide from GO AC sample

Reduction of graphene oxide is mainly to remove oxygen functional groups. The interlayer distance of reduced graphene oxide (rGO) by zinc should be decreased due to removal of oxygen functional groups which resulted in restacking of rGO sheets. Further analysis should be characterized rGO by zinc to compare graphene oxide and rGO.

**4. Conclusion**

In this study of graphene oxide and reduced graphene oxide were successfully synthesized. The synthesis was done by convenient method. Graphene oxide obtained by oxidation treatment with potassium permanganate and reduced graphene oxide by zinc as green reductant. Both results characterized by UV vis, FT-IR, SEM and EDS, XRD.

This work showed that synthesizing graphene oxide and reduced graphene oxide could possible from used electrode and resulted a good result for numerous applications. Reaction duration observed showed that enough time is better to obtained higher oxidation level when using certain reaction temperature which is 40 C. 12 hours to 14 hours still remains the best reaction duration, but used electrode could be an alternative way to produce graphene oxide and reduced graphene oxide.

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