

Preparation of reduced Graphene Oxide (rGO) assisted by microwave irradiation and hydrothermal for reduction methods

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Abstract. Graphite is a natural carbon source that can be used for graphene synthesis because of its abundant availability and relatively low cost. In this research, Graphene Oxide (GO) and reduced Graphene Oxide (rGO) have been prepared through modified Hummers method that uses microwave irradiation and hydrothermal process as reduction methods. This research can be divided into two main steps, i.e. preparation of GO and preparation of rGO. The preparation of GO was done using modified Hummers method that refers to graphite powder oxidation for five days. Then, preparation of rGO was done using two methods, i.e. microwave irradiation for 8 minutes at 1,000 watts and hydrothermal process for 10 hours at 200°C. The characterization of the samples was observed by Fourier-Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Ultraviolet-Visible Spectroscopy (UV-Vis). XRD pattern of GO sample shows a peak at $2\theta = 10.63^\circ$, rGO sample from hydrothermal process at $2\theta = 25.94^\circ$, and rGO sample from microwave irradiation method at $2\theta = 25.94^\circ$ with low intensity and at $2\theta = 10.63^\circ$ that indicates the presence of GO. IR spectroscopy data shows an absorption peak of aromatic C=C at $1,573\text{ cm}^{-1}$ that indicates rGO formation. SEM images of GO illustrates a structure of stacked flakes. While the morphology of rGO has a structure of stacked flakes that is more transparent than GO. According to UV-Vis spectroscopy, GO and rGO of samples show absorption peak at $\lambda_{\text{max}} = 225\text{ nm}$ and $\lambda_{\text{max}} = 274\text{ nm}$, respectively, which indicates $\pi \rightarrow \pi^*$ transition of aromatic C=C bond. Based on the results of this study, the preparation of rGO using modified Hummers that combined with hydrothermal reduction method is more effective than microwave irradiation reduction method.

1. Introduction

Technological advances trigger the discovery of new materials and modifications to previous existing materials to be applied in various fields. One of the most developed materials is graphene. Graphene is



a two-dimensional carbon material that has unique and extraordinary properties that has considerable potential in many applications. One of the most interesting characteristics of graphene is the very well-ordered and nearly perfect arrangement of carbon atoms [1]. Based on its unique nature, graphene has been widely modified and widely used for variety of different applications such as batteries, sensors, supercapacitors, solar panels, photocatalysts and adsorbents [1].

The most popular method used for graphene synthesis is chemical oxidation of graphite [1]. The advantages possessed by graphite, one of which is abundantly available and cheap, strongly support the use of graphite as the main ingredient in the production of large amounts of graphene. To achieve commercial value, the process of graphene oxide (GO) synthesis must be simple and cost-effective. There are many methods that can be used to produce GO by chemical oxidation, such as the Hummer method, Staudenmaier's method, and Brodie's method [2].

The Hummer method is the most widely used chemical oxidation method used to produce GO. However, the use of NaNO_3 in this method will produce NO_2 and N_2O_4 toxic gases released during the oxidation process. In the Hummer modification method [3] the use of NaNO_3 is removed to eliminate toxic gas released from the Hummer method. This modification has no effect on the dispersibility, chemical structure, thickness, and lateral dimensions of the resulting GO compared to GO generated from the Hummer method. Reduced graphene oxide (rGO) is the result of GO purification, by chemically reducing GO using hydrazine, NaBH_4 or alcohol with a certain method such as microwave irradiation or hydrothermal [4].

In this study, the synthesis of Graphene Oxide (GO) using the Hummer modification method [3] was followed by reduced Graphene Oxide (rGO) synthesis by hydrothermal method [4] and microwave irradiation [5]. Graphite is used as an ingredient for synthesizing GO.

2. Methodology

This research is divided into two stages, GO synthesis from graphite powder and hydrothermally-assisted rGO synthesis using autoclave and microwave irradiation using commercial microwave oven [5]. The materials used are sulfuric acid (H_2SO_4 95-98% wt., Merck), potassium permanganate (KMnO_4 97%, Merck), peroxide (H_2O_2 30% wt., Merck), hydrochloric acid (HCl 37% wt., Merck), ammonia solution (NH_3 25%, Merck), ethanol absolute, chloroform and demineralised (DM) water. Instruments used for characterization are X-Ray Diffraction (XRD), IR Spectroscopy, Scanning Electron Microscope (SEM) and UV-Visible Spectroscopy.

Graphene Oxide was synthesized by oxidizing graphite powders based on the Hummer modification method [3]. Graphite powder sized 53 μm , 10 grams, was incorporated into 230 mL concentrated sulfuric acid solution in a beaker and then cooled in an ice bath. Then 30 grams of KMnO_4 and 300 mL of DM water were added into the mixture and then stirred for 2 hours at 35°C . Suspension was set for 5 days. Then 500 mL of DM water and 25 mL of H_2O_2 were added into the suspension. The suspension was filtered and washed using 1 L of 1:9 HCl solution, followed by washing the suspension using DM water until approached neutral pH. DM water, 15 mL, was added into the suspension and ultrasonicated for 30 minutes with a frequency of 40 kHz. Then the aqueous suspension was centrifuged at 4,000 rpm for 30 minutes. It was then dried in an oven for 20 hours at 70°C , and then characterized.

The rGO synthesis was assisted by microwave irradiation and hydrothermal process [4-5]. In the heating process of GO sample in a commercial microwave oven, 0.15 grams of GO sample was dissolved by 50 mL of DM water. The solution was sonicated for 1 hour and NH_3 was added until it reached pH 11. The sonicated solution was then heated in a commercial microwave oven for 8 minutes at 1000 watts. The solution was then filtered and washed with ethanol. The obtained residue was dried using an oven at 110°C for 6 hours. In the hydrothermal reduction process of GO, 1 gram of GO sample was added into 100 mL of ethanol and stirred for 30 min. The solution was transferred into an autoclave teflon and heated by an oven at 200°C for 10 hours. The solution was filtered and washed using DM water. The obtained residue was dried in an oven at 70°C for 6 hours. The solid was then dissolved in 100 mL of chloroform, sonicated for 30 minutes, and centrifuged at 4000 rpm for 5 minutes. The obtained rGO solid were then characterized.

3. Results and discussion

In this study, GO is synthesized using the Hummer modification method that has previously been done [2-3]. Hummer modification method is done by eliminating the use of NaNO_3 . It aims to avoid the formation of NO_2 and N_2O_4 toxic gases during the oxidation process. Based on the synthesis procedure that has been done, the difference between synthesized GO and rGO can be seen in figure 1. The synthesis process of rGO into graphene sheets is observed from the color change from brown to black as shown in figure 1. The synthesis results show differences in the supernatant color on sample GO and rGO. The color difference indicates the presence of oxidation process in the sample.



Figure 1. Synthesized sample (a) GO and (b) rGO.

The characterization using UV-Vis spectroscopy with a wavelength range of 200-800 nm is performed to identify the conjugated double bond of the aromatic system from the GO and rGO sample structures formed. The conjugated double bond is due to the transition of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ of the conjugate system in a molecule [4]. The GO UV-Vis spectrum shows an absorption band at 225 nm of λ_{max} from the absorption caused by the $\pi \rightarrow \pi^*$ transition in the aromatic $\text{C}=\text{C}$ bond. After GO is reduced to rGO, the absorption band at λ_{max} shifts to the right at 274 nm, the absorption band indicates the formation of rGO [4].

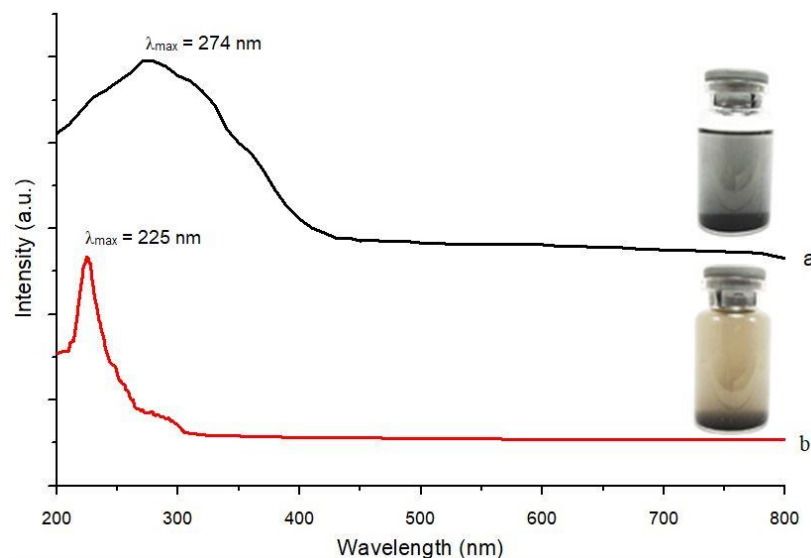


Figure 2. UV-Vis characterizations of (a) GO and (b) rGO.

Figure 2 shows the maximum absorbance value for the GO sample is smaller than the rGO. This is because in the GO sample, the aromatic $\text{C}=\text{C}$ bonds are affected by the bond of $-\text{O}-$ group [4], so the absorbance value is smaller. Then after the sample is synthesized into rGO, the oxide groups disappear causing the absorption band to shift to the right at 274 nm. This happens because the effect of $\text{C}-\text{O}$ bond

dissapears so that the C=C bond will increase [4], and the sp² bond will also increase. In the rGO sample the presence of C=C is more, causing its electrical properties to increase [4].

The characterization using IR spectroscopy is to identify the functional groups and bonding vibrations present in the sample during the synthesis process. The IR spectrum of the graphite shown in figure 3, shows the presence of oxygen bonds such as O–H, C=O, and C–O. The result of the graphite IR spectrum shows the 3,411 cm⁻¹ wave number identified as the O–H bond, but the absorption bands produced on the graphite are very weak. So it can be said that the graphite only has carbon bonds. The oxygen bond may be derived from KBr used when making pellets. KBr has a water-soluble and hygroscopic nature. The result of spectral analysis of IR sample of GO and rGO of synthesis was identified in table 1.

Table 1. IR analysis result of GO and rGO [7].

Bonds	GO	rGO (Microwave irradiation)	rGO (Hydrothermal process)
OH, dan H ₂ O	+	+	-
C=O	+	-	-
C=C	+	+	+
C-O	+	+	-

The O–H functional group in synthesized GO seems to appear at wave numbers of 3,388 cm⁻¹ [6-7]. This indicates the presence of water molecules and hydroxyl functional groups in the GO sample. The widening of absorption bands generated in the GO sample indicates that the oxidation process of graphite to GO is running well. Vibration at the 1,720 cm⁻¹ wave number is the C=O bond associated with the carboxyl group located on the edge of the GO layer. In addition, there are also ketone and quinone function groups [7-8]. Furthermore, the vibrations in wave numbers 1,224 cm⁻¹ and 1,061 cm⁻¹ correspond to the presence of C–OH and C–O bonds. The presence of the C–OH bond at wave number 1,224 cm⁻¹ signifies the success of graphite oxidation process to GO.

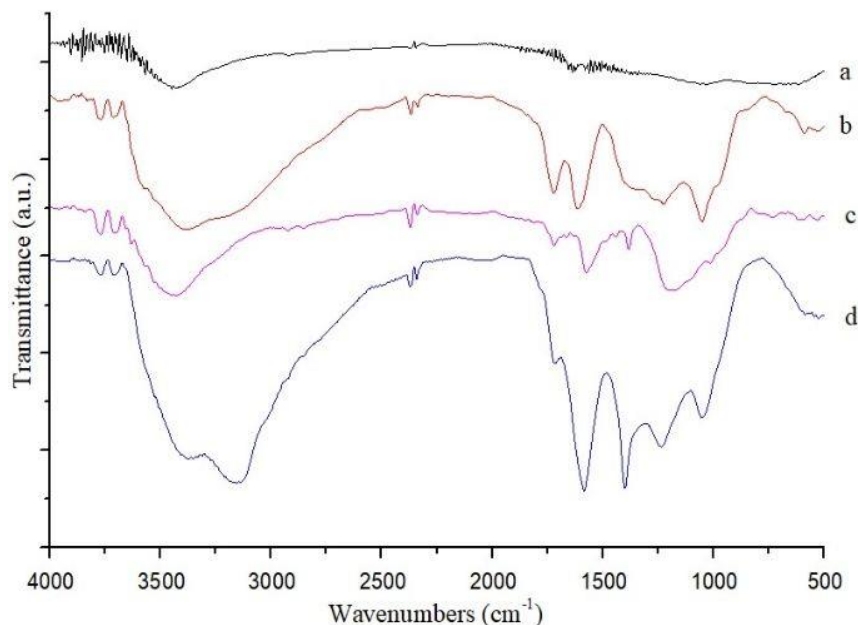


Figure 3. IR spectra of (a) graphite, (b) GO, (c) rGO (hydrothermal) and (d) rGO (microwave).

In the reduction process of GO to rGO, the thing to note is the loss of functional groups containing oxygen after oxidation process. The OH group present in GO will be reduced. This results in a loss of absorption peak at wave number $3,400\text{ cm}^{-1}$ which is the absorption peak of stretching vibration of the OH group [9]. In figure 3, the result of the rGO samples through the hydrothermal process, absorption peak at $3,429\text{ cm}^{-1}$ wave number weakens compared to GO, indicating that the hydroxyl group in rGO has been successfully reduced. Vibration at the $1,720\text{ cm}^{-1}$ wave number indicates the presence of a ketone bond present in the rGO layer. Vibration at this wave number has decreased peak compared to GO. Vibration at the $1,573\text{ cm}^{-1}$ wave number indicates the peak of the aromatic C=C bond. The aromatic C=C bond indicates the formation of rGO [7-8]. Vibration of the C–O bond at wave number of $1,014\text{ cm}^{-1}$ has a very small absorption peak, indicating functional groups such as alcohols, esters, and carbohydrates have been reduced from GO to rGO [8].

The spectrum result of the rGO sample through the microwave heating process shows that the reduction process has not gone well. It can be seen that the vibration at the $3,373\text{ cm}^{-1}$ wave numbers indicating the O–H group [8] has not disappeared completely. So the product resulting from the synthesis process by microwave method is still mixed with lot of impurities. However, the vibration of the wave number $1,718\text{ cm}^{-1}$ (C=O) [7] shows a peak weakening indicating that the functional group has been reduced.

GO and rGO test using XRD is done with a range of 2θ angle between $5\text{--}60^\circ$ and wavelength of 1.54 \AA . The XRD characterization is performed to determine whether the sample is graphite, GO or rGO. Based on previous research [10], graphite has a peak at 2θ angle of 26.58° , GO has a peak at 2θ between $10\text{--}12^\circ$ and rGO has a peak at 2θ between $24\text{--}28^\circ$ [9].

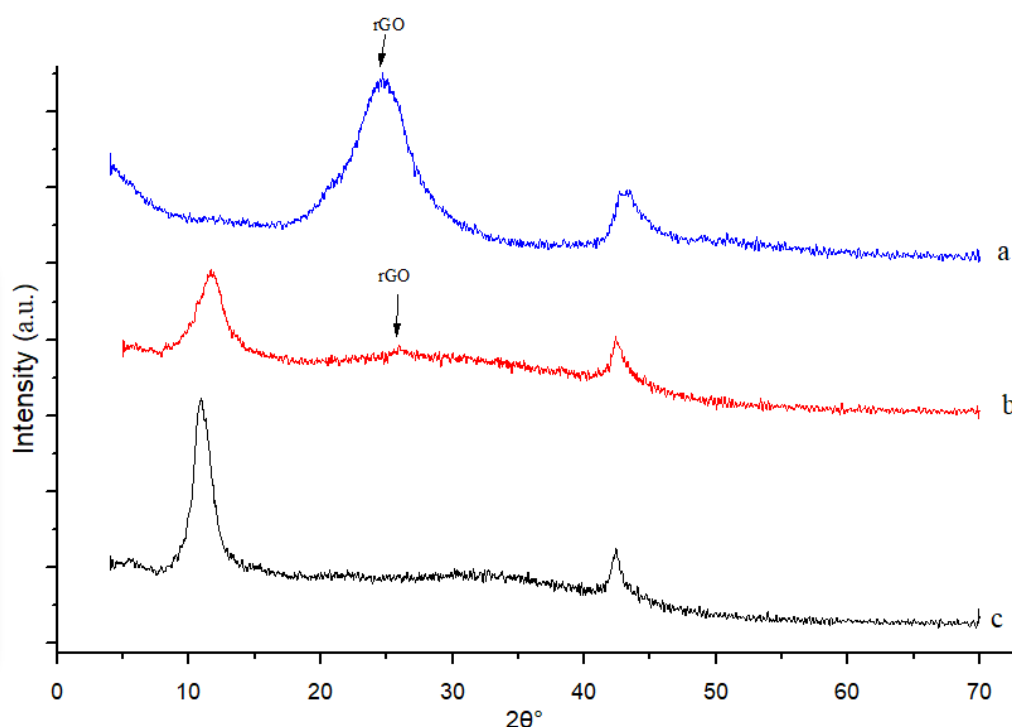


Figure 4. XRD diffractograms of (a) rGO (hydrothermal), (b) rGO (microwave) and (c) GO.

In figure 4 it can be seen that graphite has turned into GO and rGO. The graphite material has the highest band at $2\theta = 26.58^\circ$ with d-spacing of 3.35 \AA [6-7]. If the oxidized graphite is entirely GO then the peak will disappear and a new peak appears at $2\theta = 10.63^\circ$ which has d-spacing = 8.31 \AA . With GO d-spacing wider than graphite, it can indicate the presence of oxygen functional groups within the GO identified at the peak. The functional groups not only widen the distance between layers but create a hydrophilic

atomic layer [6-7]. This shows that the synthesis of GO has been successfully done with the Hummer modification method.

In the synthesis of rGO with the help of microwave, it can be seen in figure 4 that there is a new peak at the angle of $2\theta = 25.95^\circ$ with d-spacing = 3.43 Å. Smaller d-spacing than previous GO shows that GO has been reduced to rGO. However, the intensity gained from the XRD characterization for rGO using the microwave is quite small, in addition the GO peak has not completely disappeared, so that this result is still a mix of GO and rGO. The process of reduction using microwave has not been running well so that the product obtained is not pure rGO.



Figure 5. Thin layer of rGO sheet in water.

In the rGO of a 10-hour hydrothermal process with at 200°C , there is a new peak at the angle of $2\theta = 25.94^\circ$ with d-spacing = 3.43 Å. The loss of the GO peak in the $10\text{-}12^\circ$ angle range indicates the process of graphene reduction goes well. The XRD results show that the synthesis of GO and rGO has been successful. So graphite has been transformed into graphene sheets. The form of graphene sheet in water can be seen in figure 5.

The morphology of the GO and rGO sample at the $\times 10,000$ magnification is shown in figure 6. In figure (6a) can be observed the morphological form of GO. The GO is still a fairly solid flake shape and not yet fully peeled into thin sheets. Along with the ongoing synthesis process, the reduction, sonication, and hydrothermal processes are performed to obtain rGO as the final product that has thin transparent flake structure due to the exfoliation of the thick layers of graphite during the synthesis process, which became one of the parameters of the successful synthesis process of rGO [4]. When observed with SEM, in figure (6b) we can see that the rGO sample from microwave heating experiences peeling, where the sample looks more transparent compared to GO.

Differences in surface morphology also occur in rGO sample from hydrothermal process. Figure (6c) shows that rGO has a more transparent surface morphology than GO, identifying thin sheets. As previously explained, the hydrothermal process has turned GO into rGO well. So the shape itself is better than rGO from microwave heating. The shorter the spacing between the layers, the clearer the graphene will look, because graphene has a pretty good transparent characteristic [4]. If the distance between layers increases, then a transparent object will look blurry and look thick.

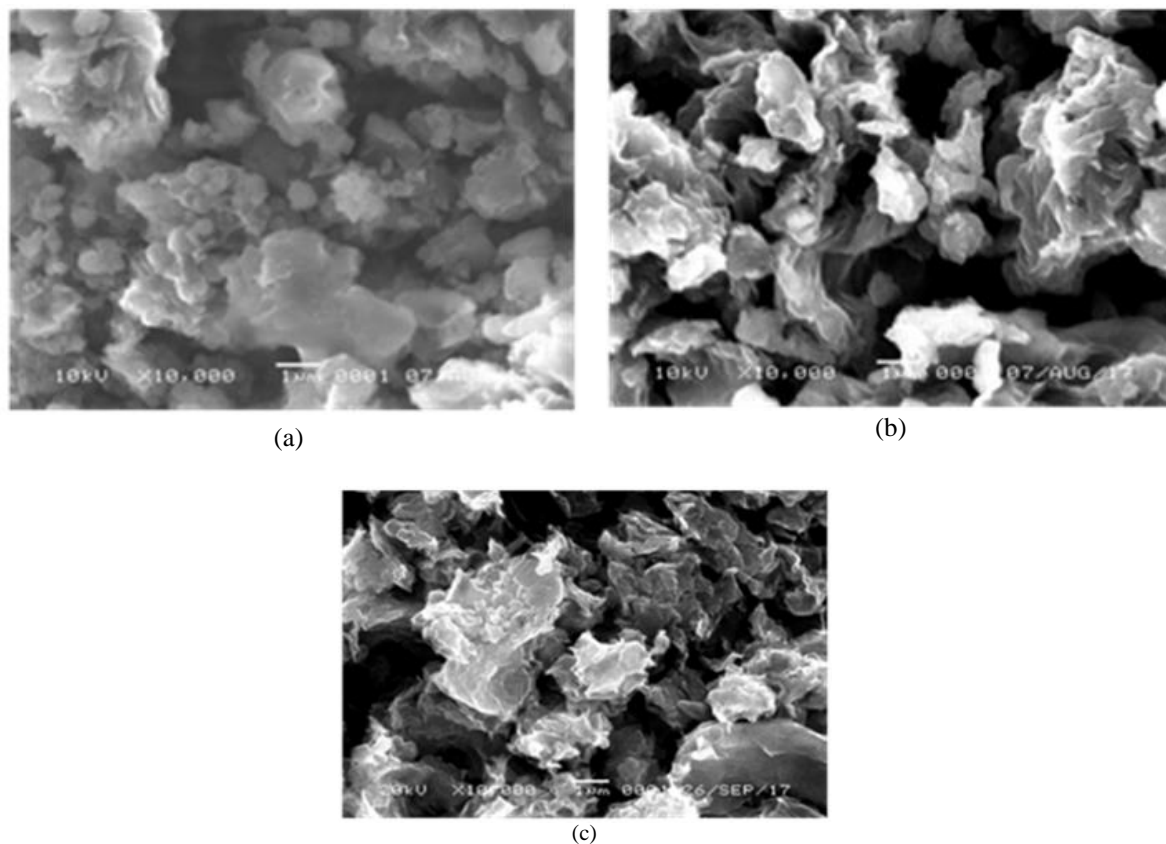


Figure 6. SEM images of GO and rGO ($\times 10,000$); (a). GO, (b). rGO (microwave), (c). rGO (hydrothermal).

4. Conclusion

GO and rGO are successfully synthesized from graphite. GO synthesis is performed using the Hummer modification method. rGO synthesis is done by optimizing two methods of heating, which are heating by using commercial oven microwave and hydrothermal method. XRD diffractogram shows the sample of GO has a peak at 2θ about 10.63° and the sample of rGO has a peak about 25.95° . The result of IR spectroscopy of rGO sample from microwave heating still shows the functional group of O–H and C–O bonds, in addition to aromatic C=C bond. However, the O–H and C–O functional groups are not found in rGO sample from hydrothermal process. The presence of an aromatic C=C bond indicates the formation of rGO. In this study, synthesis of rGO through hydrothermal heating is more effective than microwave heating.

Acknowledgments

This research was supported by Pusat Penelitian dan Penerbitan, Lembaga Penelitian dan Pengabdian Kepada Masyarakat (LP2M) UIN Sunan Gunung Djati Bandung.

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