

# Graphene Oxide from Bagasse/Magnetite Composite: Preparation and Characterization

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**Abstract.** The objective of this research is to synthesis and characterization of graphene oxide (GO)-nano Fe<sub>3</sub>O<sub>4</sub> composite from bagasse. The analysis graphite, GO, and Fe<sub>3</sub>O<sub>4</sub> using XRD result peak at position  $2\theta$  24.56°; 26.61° and 35.4°. GO-nano Fe<sub>3</sub>O<sub>4</sub> composite shows mixture peak of GO and Fe<sub>3</sub>O<sub>4</sub>. When GO was characterized by FTIR, it comes the distinctive vibration bands of -COOH, C = C, C-O, and -CH. While on the composite there are additional bands belonging to Fe-O and Fe-C. The ratio of D band and G band on composite is higher than that of GO, ie 1.45 and 0.79 when characterized used Raman spectroscopy. The morphology structure of the composite when analyzed using FE-SEM-EDX appears to have a large surface area filled with Fe particles on the surface with the largest composition of elements C, O, and Fe. Pore characteristics when determined using SAA belong to mesoporus with surface area total 35.911 m<sup>2</sup>/g and a specific surface area of 42.523 m<sup>2</sup>/g.

**Keyword :** Preparation, Characterization, Graphene Oxide, Magnetite, Composite

## 1. Introduction

Graphene is a single two-dimensional (2D) layer of carbon atoms, has attracted much attention in recent years [1]. It poses as a rising star in material fields due to its large surface area as well as remarkable mechanical, structural, electrical, and thermal properties [2,3]. Graphene oxide (GO) nanosheets are another promising nanomaterial owing to their interesting chemical and physical properties including optoelectronic, fluorescence, and ferromagnetic properties [4]. The solubility of graphene in water and rich of oxygen-containing functional groups on their surfaces make them very attractive for bioapplications [1]. In the other hand, magnetite (Fe<sub>3</sub>O<sub>4</sub>) has unique properties, including decent magnetic, catalytic, electric, biocompatibility and low toxicity properties so attracted considerable research interests in materials chemistry [5]. Hybridizing zero-dimensional nanoparticles with two-dimensional graphene oxide nanosheets has been regarded as one of the most promising way to improve the adsorptive and catalytic performance of nanomaterials [6].

The application of GO-magnetite has been widely used. It used for protein adsorption [1], dye removal [7], heavy metal removal [8, 9], drug delivery system [10, 11], and sensor [12, 13]. Generally, the GO-magnetite has been synthesis by Hummers method and co-precipitation process from commercial graphite [14]. Here, the purpose of this study was to enhance the economical feasibility of the waste, in particular bagasse to be the raw material of graphite. The synthesis of graphite from bagasse using simple pyrolysis.

To see the composite morphological structure, FE-SEM-EDX was used. XRD was used to see the composite crystalline structure, while SAA was used to observe the pore characteristics (volume, diameter and pore type) and the area of composite surface. Raman spectroscopy was used to see the bonding characteristics of carbon and FT-IR was used to observe the type of bonding presented in the



composite.

## 2. Experimental Method

Bagasse was washed with water to remove the water-soluble contaminants and oven-dried for a day. After ground and screened, it was placed and burnt in a furnace under atmospheric pressure for 3 h at 550 °C. because of the high content of silica, it was removed using HF. The graphite was then analyzed using the XRD and spectroscopic instruments and continued to made graphene oxide using Hummers method with various characterization to make sure the target material has successfully done [14].

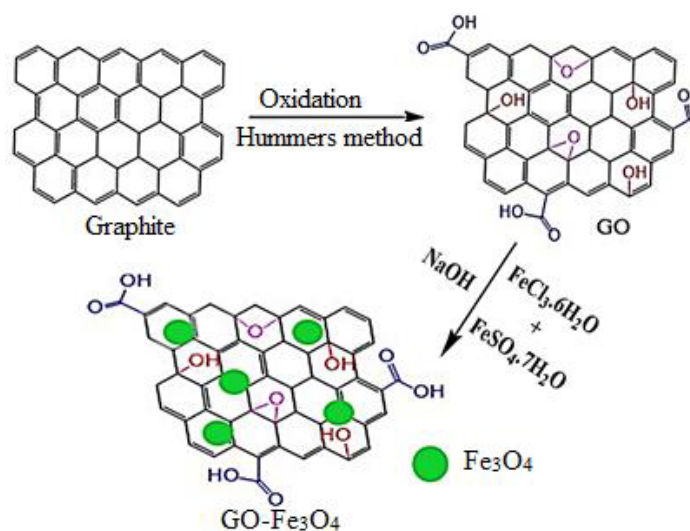
To make the GO/magnetite composite, A 100 mL solution was prepared containing 1.081 g of iron (III) chloride hexahydrate and 0.556 g of iron (II) sulfate heptahydrate dissolved in deionized water. The solution was added with 1 M sodium hydroxide until pH 4 with constant stirring for 30 min. 50 mL of 0.55 mg/mL sonicated GO from graphite which made from bagasse which has studied before [14] solution added in the suspension with constant stirring for 30 minutes. The mixture was added with 1 M sodium hydroxide until the pH 10 then allowed to aged for 30 minutes. The results of black precipitation are separated by magnetic separation using neodymium magnet and washed several times using deionized water and ethanol and heated to 60° C for 48 hours then. The synthesis of Fe<sub>3</sub>O<sub>4</sub> composite can be carried out by the same method without any addition of GO.

Characterization of the composite using ADX-2500 XRD was used to see the composite crystalline structure. To identify pore characteristics including volume, diameter and pore type, it used Nova 1200e with Quantachrome Instruments, Florida, United States of America SAA. Horiba Jobin Yvon, Japan Raman spectroscopy was an spesific instrument which used to see the bonding characteristics of carbon compound and FT-IR was used to observe the type of bonding presented in the composite. Lastly, to see morphological structure of composite, it used Hitachi SU8020 FE-SEM-EDX).

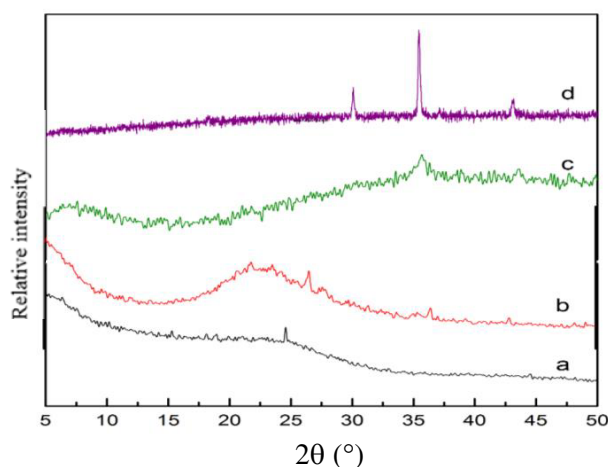
## 3. Result and Discussion

The GO-nano Fe<sub>3</sub>O<sub>4</sub> composite was synthesized by a stepwise reaction as shown in Figure 1, which was from raw material of pirolizes bagasse at 400° C to produce graphite and grounded until 140 mesh. The graphite was then synthesized into GO through the Hummers method which widely known for oxidation process and further converted into a GO-Fe<sub>3</sub>O<sub>4</sub> composite through a co-precipitation reaction between GO, iron (III) chloride hexahydrate, and iron (II) sulfate heptahydrate. XRD is an effective tool for identifying crystalline structures and material purity. The result of characterization using XRD can be seen in Figure 2. Based on the characterization results using XRD, graphite has a peak of 2θ = 24.5649 and 44.4891° with d-spacing of 3.6242 and 2.036 Å. This result indicated the same result as the active carbon compound [15]. The formation of GO compound derived from biomass was characterized by a peak of 2θ 26.6133; 36.5476; and 42.9257 with d-spacing of 3.3493; 2.46274; and 2.1053 Å [16]. The occurrence of peak changing indicates the occurrence of new compounds from graphite to GO has been formed.

The result of Fe<sub>3</sub>O<sub>4</sub> characterization compound shows peak at position 2θ 30.0768; 35.4042; 43.1260; and 37.1878° with d-spacing of 2.97124; 2.5341; 2.09765; and 2.4178 Å. Whereas after becoming a GO-Fe<sub>3</sub>O<sub>4</sub> composite peak at 2θ 26.8; 35.5761; 36.2987; and 43.126° with d-spacing of 3.34953; 2.5341; 2.47496; and 2.097 Å. In XRD results of the composite has the combination of 2 compounds, GO and Fe<sub>3</sub>O<sub>4</sub>. Peak of 2θ 26.86 and 36.2987° due to the peak owned by GO and it has increment of d-spacing at the peak of 36.2987°. While at peak 2θ 35.5761 and 43.126° was the peak of Fe<sub>3</sub>O<sub>4</sub> with increased of d-spacing because the composites may be due to the intercalation of functional groups. It was possible that there was no new reaction between GO and Fe<sub>3</sub>O<sub>4</sub> and only produced GO-Fe<sub>3</sub>O<sub>4</sub> composites.

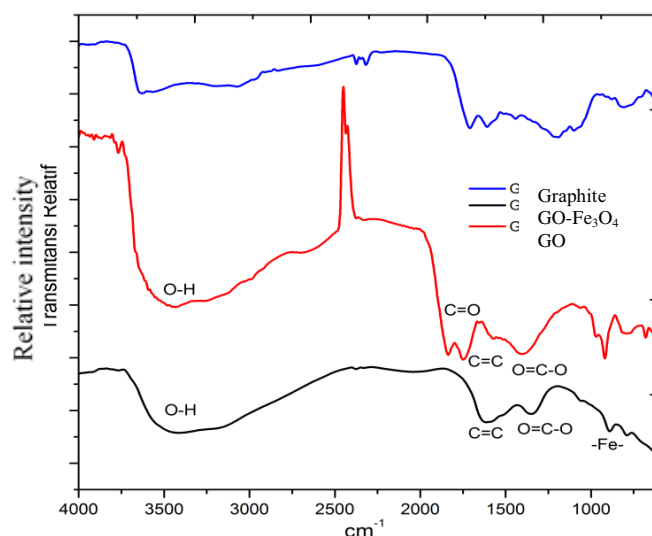


**Figure 1.** GO-Fe<sub>3</sub>O<sub>4</sub> synthesis scheme



**Figure 2.** XRD spectra of (a) graphite, (b) GO, (c) GO-Fe<sub>3</sub>O<sub>4</sub>, and (d) Fe<sub>3</sub>O<sub>4</sub>

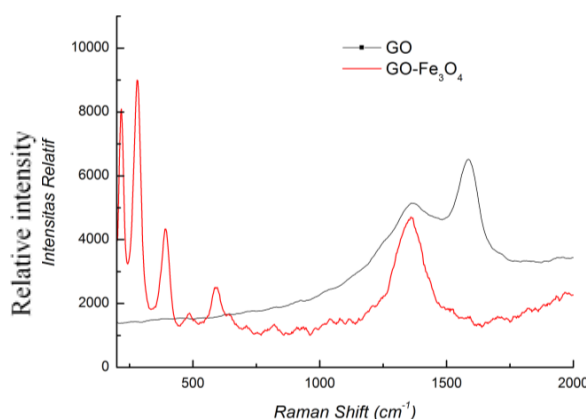
To determine the functional group of the composite structure, characterization was performed using FTIR. The result of composite characterization can be seen in Figure 3. There are some differences between graphite and GO characterization results using FTIR, graphite has two bands on the wavenumber of 3620 cm<sup>-1</sup> and 3182 cm<sup>-1</sup> which showed the presence of CH aromatic sp<sup>2</sup> which was supported by the emergence of another band that was at the wavelength of 1610 cm<sup>-1</sup> and 1434 cm<sup>-1</sup>. There is an epoxy group at wavelength of 1040 cm<sup>-1</sup>. There was a typical band of carboxylic acid groups of GO, ie the presence of a broad band on the 3406 cm<sup>-1</sup> indicating the presence of hydroxyl group (-OH) and the wavenumber of 1705 cm<sup>-1</sup> indicating the presence of the carbonyl group (C = O). In addition, there was an epoxy group (C-O) which appeared at wavenumber of 1215 cm<sup>-1</sup>. The presence of -OH, C = O, and C-O groups on GO when analyzed using FTIR, it can be said that GO has been formed.



**Figure 3.** FT-IR spectra of graphite, GO, and GO-Fe<sub>3</sub>O<sub>4</sub>

In the GO-nano Fe<sub>3</sub>O<sub>4</sub> composite, the band of hydroxyl group (-OH) which has wavenumber of 3417 cm<sup>-1</sup> did not change significantly but another new band was appeared as Fe-O/Fe-C bands at 570 cm<sup>-1</sup>. Compared to the bands of GO, especially in wavenumbers of 1700 cm<sup>-1</sup> and 736 cm<sup>-1</sup>, there was a changed of band intensity, it was due to the structure of carbonyl and C-H in benzene changes in that tend to binded with Fe<sub>3</sub>O<sub>4</sub>. Thus, it can be seen that there was a changes of the composite from sp<sup>2</sup> into sp<sup>3</sup> due to the entry of Fe<sub>3</sub>O<sub>4</sub> on the surface of GO. In the other words, the composite has been formed.

In addition to XRD and FT-IR, Raman spectroscopy instrument was used as an important tool for characterizing carbon crystal structures. In this study, Raman spectroscopy was used to investigate significant structural changes occurring between GO and GO-nano Fe<sub>3</sub>O<sub>4</sub>. Based on Figure 4, it shows peaks at 1361.77 cm<sup>-1</sup> and 1587.31 cm<sup>-1</sup> for D band and G band, respectively. While on the Fe<sub>3</sub>O<sub>4</sub> spectra there were several peaks appeared up to 600 cm<sup>-1</sup> which are the typical spectra of Fe<sub>3</sub>O<sub>4</sub>. The Raman spectra of the composite was actually a combination of Fe<sub>3</sub>O<sub>4</sub> and pure GO which implied that Fe<sub>3</sub>O<sub>4</sub> and GO were formed originally, no reaction occurred between them during the hydrothermal synthesis process.

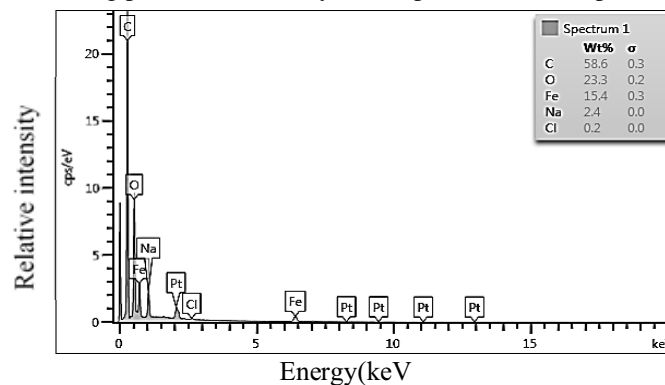


**Figure 4.** Raman spectra GO and GO-nano Fe<sub>3</sub>O<sub>4</sub>

The intensity ratio of D band and G band ( $I_D/I_G$ ) is very susceptible to structural changes of carbon matrix which can be affected by several factors such as doping, defect, substrate, and so on. D band relates to imperfections of carbon structures which reflected the structural defects and associated with part of the sp<sup>3</sup> carbon atom obtained due to graphite amorphization during the oxidation process while the G band is derived from vibrations in the sp<sup>2</sup> carbon atomic plane. There was an  $I_D/I_G$  ratio increase

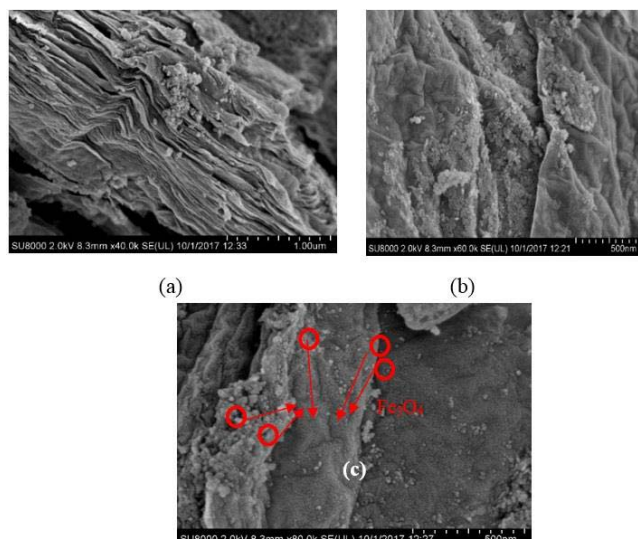
on the GO before and after being GO-nano  $\text{Fe}_3\text{O}_4$  composite of 0.79 to 1.45. Previous research has also produced similar changes [17]. It was caused by the n-type effect on the GO that made the  $\text{sp}^2$  carbon change to  $\text{sp}^3$  so that the intensity ratio of D band and G band increased. In other words, there has been a change of crystal structure from pure GO to GO-nano  $\text{Fe}_3\text{O}_4$  composite.

To determine the composite composition, EDX instruments was used as shown in Figure 5. The highest content of the GO-nano  $\text{Fe}_3\text{O}_4$  composite was carbon with the level of 58.6% as the basic ingredient of GO. The oxygen content of 23.3% was the constituent of GO and  $\text{Fe}_3\text{O}_4$ . While the amount of iron content was 15.4% which it was distributed on the surface of GO. There were other elements of composite composition, it were Na and Cl. It was suspected that Na was derived from the composite synthesis process used as a pH control through the co-precipitation process, whereas Cl was derived from the composite washing process after the synthesis process was complete.



**Figure 5.** EDX of GO- $\text{Fe}_3\text{O}_4$  composite

To observe the material morphology, characterization has been performed using FE-SEM. From the observation using FE-SEM, it can be seen that there was a thin sheet layer of GO-nano  $\text{Fe}_3\text{O}_4$  composite [18] as shown in Figure 6 (a) with irregular shape, some wrinkles on the surface, and has a large surface area. From Figure 6 (a), (b), and (c) it can be seen that the surface of GO has a large surface area and successfully coated of nano  $\text{Fe}_3\text{O}_4$  particles with average size of 6.67 to 26.67 nm evenly so that the GO- $\text{Fe}_3\text{O}_4$  composite has been formed.



**Figure 6.** FE-SEM of GO-nano  $\text{Fe}_3\text{O}_4$  with magnification of 40,000x (a), 60,000x (b), dan 80,000x (c)

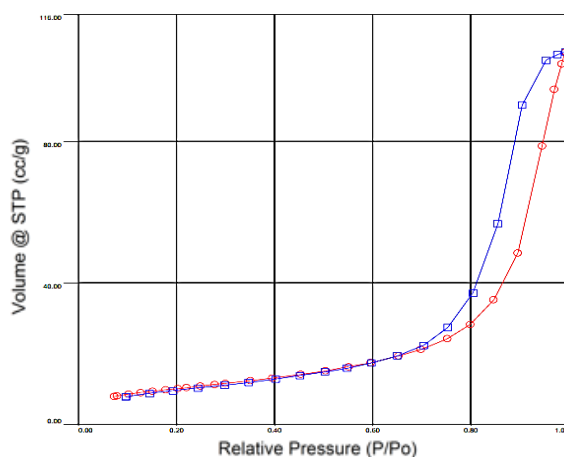
SAA ( $\text{N}_2$  adsorption desorption) characterization was used to investigate the composite texture characteristics of the result including surface area, pore distribution, pore volume, pore diameter, and

pore adsorption pattern using Brunauer-Emmett-Teller (BET) theory. The nitrogen isotherm of Figure 7 produces a type IV form with H3 hysteresis loops in the relative pressure range 0.3-0.98. These results indicated that the GO-nano Fe<sub>3</sub>O<sub>4</sub> composite was characterized by a mesoporous structure. In BET theory, the following equations was used:

$$\frac{1}{v \left[ \left( \frac{p_o}{p} \right) - 1 \right]} = \frac{c - 1}{v_m c} \left( \frac{p}{p_o} \right) + \frac{1}{v_m c}$$

which  $\frac{p_o}{p}$  is *relative pressure*,  $v$  means adsorbed gas volume, and  $v_m$  is the amount of adsorbed monolayer gas.

from that equation, it can be used to make the plot of BET with x axis was  $\frac{p_o}{p}$  and y axis was  $1/W \left( \frac{p_o}{p} \right)$  in the range of  $0.05 \leq \frac{p_o}{p} \leq 0.35$  so that the linear equation was  $y = ax + b$ . From the result of analysis with BET theory it was got linear equation  $y = 96.275x + 0.7449$  with  $R^2 = 0.9999$ . From the equation we can know the value of BET constant of 130.246 so the total surface area could be calculated of 35.911 m<sup>2</sup>/g and the spesific surface area of 42.523 m<sup>2</sup>/g.



**Figure 7.** Adsorption Pattern of GO-Fe<sub>3</sub>O<sub>4</sub> Composite

To see the characterization of pores, it can be done by using Quantochrome Instruments software with Horvath-Kawazoe (HK); Barrett, Joyner, and Halenda (BJH); and Dollimore and Heal (DH) methods. From the calculation results with HK method obtained micropore volume of 0.015 cc/g. While the result using DH method obtained the surface area of 34.738 m<sup>2</sup>/g, pore volume of 0.157 cc/g, and pore diameter of 12.135 nm. The results did not differ significantly when compared to the BJH method which produced a surface area of 34.302 m<sup>2</sup>/g; pore volume of 0.161 cc/g; and pore diameter of 12.135 nm. From these results, the GO-nano Fe<sub>3</sub>O<sub>4</sub> composite which has confirmed with previous instruments including crystallinity, bond type, and composition has a mesoporous material with the diameter size of ~ 12 nm.

#### 4. Conclusion

We have successfully demonstrated synthesis of GO-Fe<sub>3</sub>O<sub>4</sub> with raw material of bagasse and characterize using XRD, FTIR, Raman spectroscopy, SAA and FE-SEM-EDX.

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