Development of rGO/Fe₃O₄ Composites as Glucose Biosensors

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Abstract

The rGO/Fe₃O₄ composite is one type of composites that can be used as a biosensor material, especially glucose sensors. The main ingredients of the composite synthesis are graphite and iron sand. The synthesis process of Fe₃O₄ was done using the coprecipitation method, while the graphite oxidation process was accomplished using the modified Hummer's method. The composites were formed using the ex-situ wet mixing method. The formed iron sand and graphite were characterized using FTIR and XRD, and it was found that Fe₃O₄ was formed from the appearance of the Fe-O bond, the oxidation process of graphite was seen from the appearance of the C=O bond, and the detection of Fe peaks corresponded to the cubic crystal plane. Likewise, the composites formed were also characterized using FTIR and XRD for identification of the rGO/Fe₃O₄ composite formation. It was proven from the presence of Fe-O and C-O bonds and the appearance of an amorphous peak of rGO in the XRD results. The performance of the rGO/Fe₃O₄ composites as the glucose biosensor was examined by varying the mass of Fe₃O₄ on the composite, using UV-Vis spectroscopy. The performance of the rGO/Fe₃O₄ composite biosensor in absorbing glucose reached optimum at a mass variation of 0.3 grams of Fe₃O₄, as demonstrated by by the lowest absorbance peak with an intensity of 0.0048 at a wavelength of 440 nm, corresponding to glucose entrappment of 7.1 mg/gram.

Keywords: rGO/Fe₃O₄; Biosencsor; Glucose

INTRODUCTION

Research on carbon-based materials is growing rapidly. One of the most researched allotropes of carbon is reduce Graphene Oxide (rGO). rGO has unique properties that can cover a wide range of applications, including supercapacitors, microwave absorbers, electrocatalytics and biosensors. The unique characteristics of rGO include high electrical conductivity, wide surface area and a good electrocatalyst. As such, rGO is a good material for mobilizing and absorbing ions. This property makes rGO the material of choice and is attractive to be used as a biosensor. The biosensor derived from rGO has been studied and applied for glucose, especially for people with Diabetes Mellitus (Qiu et al., 2012). Glucose Oxidase (GOx) shows high catalytic activity, but because it is in a non-conductive environment, it is difficult for ion transfer to occur (He et al., 2012). Therefore, to improve the performance of the glucose biosensor, a magnetic material that has good adsorption properties catalytic and electrical conductivity is needed.

Biosensors using composite materials have been studied by compositing graphene with Au (Chen et al., 2011). In addition, biosensors made from rGO/ZnO have been investigated (Palanisamy et al., 2014). Compositing carbon allotropes was proven to improve the performance of glucose biosensors in catalytic activity and ion transfer.

The rGO/Fe_3O_4 biosensor (B. Wang et al., 2018) demonstrated of fast electron transfer and good electro-catalytic activity because it had good electrochemical properties. The Fe_3O_4 used was in the form of nano particles of about 50 nm in size. Fe_3O_4 nano particles can be synthesized from abundant natural materials (iron sand). The Fe_3O_4 synthesis methods are largely available, which can be selected accordingly. Likewise rGO, can be made from natural ingredients that are often found in several regions in Indonesia (coconut shell). Composite of rGO and Fe_3O_4 is expected to improve the performance of glucose biosensors.

METHOD

The rGO/Fe_3O_4 composites were synthesized using the wet-mixing (ex-situ) method. Fe_3O_4 used was derived from natural iron sand synthesized by the coprecipitation method and rGO was obtained from graphite synthesized by the *Hummer's* method. The wet-mixing process used an alcohol solution, and stirred at high speed to speed up the reaction process between rGO and Fe_3O_4. The resulting composites were characterized using FTIR to determine the functional groups formed. In addition, the composite was also tested using XRD so that the microstructure formed could be identified. As a biosensor, the resulting composite was dissolved in glucose solution, by varying Fe_3O_4 compositions in the composite. Furthermore, the solution was tested using UV-Vis to determine the glucose absorption ability of the developed composites. Besides that, a CV test was also carried out to determine the electron transfer ability and chemical reactions during the absorption process of the rGO/Fe_3O_4 composites.

RESULTS AND DISCUSSION

The synthesized rGO/Fe_3O_4 composites were in the form of powder. The synthesized Fe_3O_4, GO and rGO powders are shown in Figure 1. The results of the rGO synthesis and the rGO/Fe_3O_4 composites were characterized using FTIR as shiwn in Figure 2. It can be seen that rGO was has been formed with the loss of the OH group in GO which forms a C = C group at a wavelength of 1645 nm^{-1}, or a C = O group at a wavelength of 1715 nm^{-1} (Hidayat et al., 2019). The FTIR results of rGO/Fe_3O_4 composites can be seen from the emergence of new Fe-O and C-O bonds at 434 nm^{-1} and 1948 nm^{-1} wavelengths. In rGO and Fe_3O_4 there was a reduction in functional groups that contain oxygenm due to a redox reaction during the synthesis process, as detailed elsewhere (B. Wang et al., 2018).
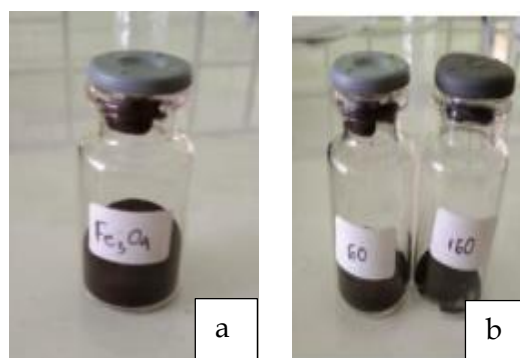
Figure 1. Fe_3O_4 powder (a), GO and rGO powder (b)

The rGO/Fe_3O_4 composite also showed the dominant peak of Fe_3O_4 because rGO is an amorphous material. The XRD results in Figure 3 cannot explain in detail the formation of the rGO/Fe_3O_4 composite, but with the appearance of the background at an angle of 2θ below 27 indicates the presence of rGO in the composite. (Munasir & Kusumawati, 2019; S. Wang et al., 2008). XRD characterization results showd that Fe_3O_4 peaks remained dominant in the rGO/Fe_3O_4 composite. The peak of Fe_3O_4 is at 2θ and corresponds to the cubic crystal plane, while rGO is amorphous so it was detected as a low intensity peak, as in the Table 1.
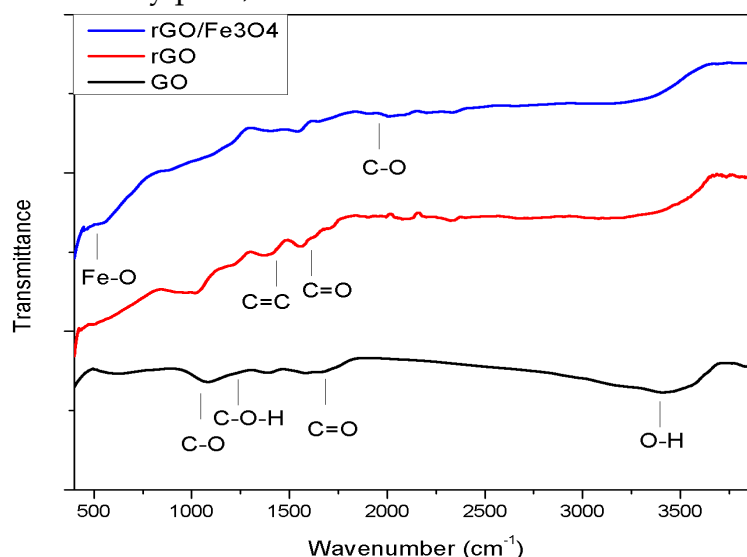

Figure 2. Results of FTIR from GO, rGO and rGO/Fe_3O_4

Table 1. Data on XRD Fe_3O_4 and rGO/Fe_3O_4

No.	2θ		d_{hkl}
	Fe_3O_4	rGO/Fe_3O_4	
1.	30,2	30,1	(220)
2.	35,3	35,4	(311)
3.	42,8	43,1	(400)
4.	54,5	53,7	(422)
5.	56,9	57,2	(511)
6.	62,5	62,7	(440)
7.		26,4	rGO

The formed Fe_3O_4 had a cubic crystal plane, and the rGO diffraction peak in the rGO/Fe_3O_4, 2θ composite was identified at 26.4. The presence of graphene diffraction peaks in the rGO/Fe_3O_4 composites was not detected due to the amorphous nature of rGO as explained in an earlier report (B. Wang et al., 2018)
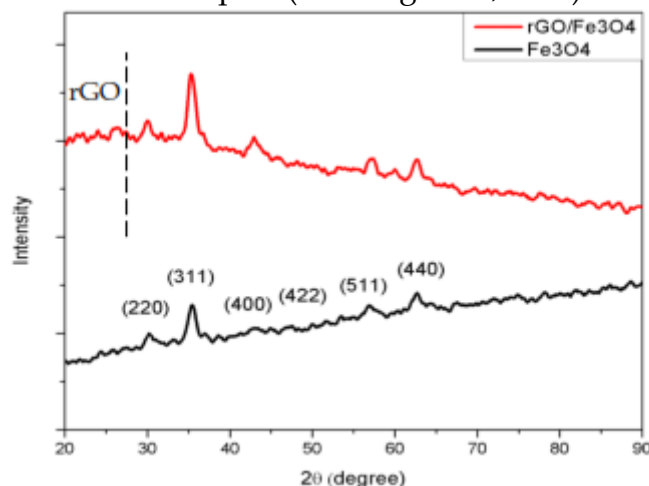

Figure 3. Result XRD Fe_3O_4 and rGO/Fe_3O_4

The ability of rGO/Fe_3O_4 composites to absorb glucose (glucose biosensor) with variations of Fe_3O_4 in the composites was tested by using the UV-Vis spectroscopy (Ultraviolet-Visible Spectroscopy). UV-Vis characterization was carried out by making a composite solution of rGO/Fe_3O_4, then the solution was used to test the absorbable glucose solution by varying the addition of Fe_3O_4.
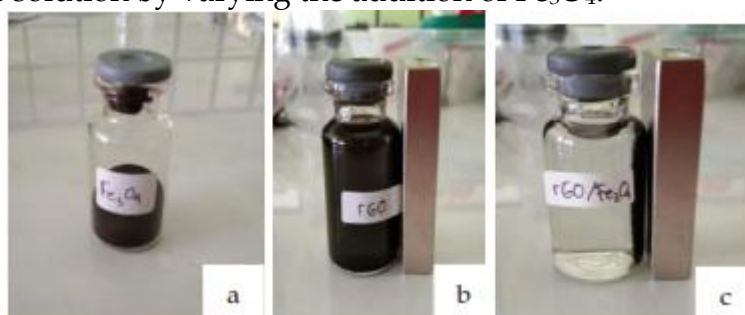

Figure 4. Fe_3O_4 powder (a), rGO solution (b), rGO/Fe_3O_4 solution (c)

The absorbance of glucose in the rGO/Fe_3O_4 composite based on the UV-Vis test results was identified from the appearance of the peaks at a wavelength of 435-440 nm. Pure UV-Vis GOx is shown to had a peak appearing at 275 nm and two light absorption peaks at 375 nm and 452 nm are well distinguished (Figure 4). UV-Vis spectra of rGO/Fe_3O_4 composites show that no absorption peak appeared in the 250-500 nm range, but after the GOx bond with rGO/Fe_3O_4 there was almost no change in the absorption band, similar to the pure GOx. This finding shows that the GOx trapped in the nanocomposite has a secondary structure that does not change and maintains its biological activity (Yu et al., 2014).

In the Fe_3O_4 mass variation of 0.1 gram, the composite was not able to absorb glucose, it can be seen from the absorbance peak that exceeds the peak of pure GOx. In the mass variation of 0.2 grams of Fe_3O_4, the absorbed glucose can be seen from the reduced absorbance peak, and the optimal absorption of glucose is at the variation of the mass of 0.3 grams of Fe_3O_4, with the smallest absorbance peak. It means that the amount of glucose trapped increased. For the mass of > 0.3 grams, the absorption peak

rose again because the rGO/Fe_3O_4 composite was unable to absorb glucose, even glucose that had been trapped or partially bound was released (Karimi Pasandideh et al., 2016).
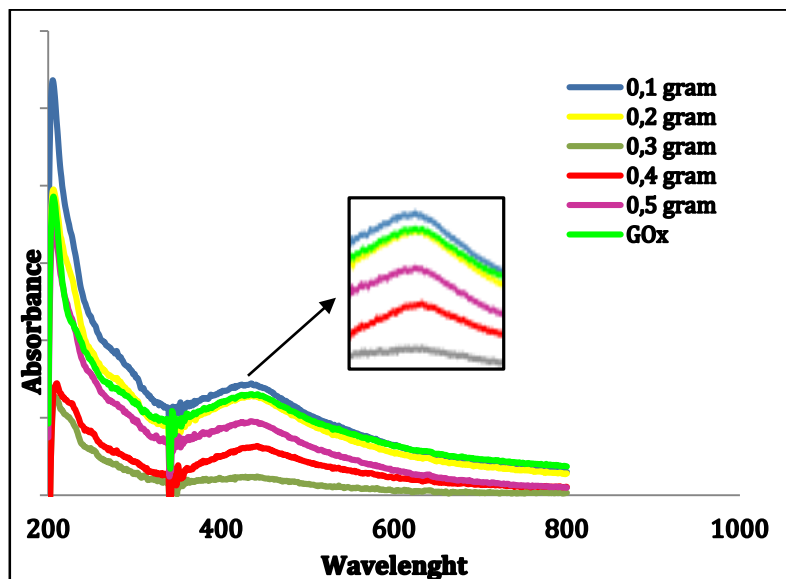

Figure 4. Result UV-Vis from rGO/Fe_3O_4

The ability of the rGO/Fe_3O_4 composite to absorb glucose can be calculated using equation (1).

$$q_e = \frac{(C_o - C_e)}{m} x \, V ………..(1)$$

Where q_e is the absorbance per unit mass, C_o is the initial concentration of the solution, C_e is the residual concentration, m is the mass of the composite and V is the volume of the solution (Karimi Pasandideh et al., 2016).

Table 2. The results of the calculation of the absorbance ability of the rGO/Fe_3O_4 composite

Mass Variation Fe3O4 (g)	Wavelenght (nm)	Absorbtion	*q_e (mg/g)
0.1	435	0.0289	-2.8
0.2	435	0.0257	0.2
0.3	441	0.0048	7.1
0.4	441	0.0127	3.35
0.5	435	0.0191	1.4

*q_e is the absorbance capacity per unit mass

From the calculation of the ability of the rGO/Fe3O4 composite as a glucose biosensor (Table 2), it can be seen that the greater the addition of Fe3O4, the higher the ability of the composite to absorb glucose. Where the highest absorbance value is found in the addition of Fe3O4 of 0.3 grams, with a value of qe = 7.1 mg/g. The results of this calculation are in accordance with the results of UV-Vis, where the addition of 0.3 grams of Fe3O4 obtained the lowest curve, which states that there is glucose trapped in the rGO/Fe3O4 composite. The lower the curve, the more glucose absorbed by the rGO/Fe3O4 composite (Karimi Pasandideh et al., 2016). However, with the addition of Fe3O4 greater than 0.3 grams, there was a decrease in the absorbance capacity, this was because the absorption capacity of the rGO/Fe3O4 composite had reached its maximum point, so it was unable to absorb glucose and instead the trapped glucose could be released again.

CONCLUSION

The developed rGO/Fe$_3$O$_4$ composite cound be used as a glucose biosensor. The absorbance ability was better when the GOx and the residual concentration of the composite solution were smaller. The Fe$_3$O$_4$ material added to rGO did not change the biological activity of rGO, but instead improved the performance of the biosensor by accelerating the electron transfer process. The variation in the mass of Fe$_3$O$_4$ added had the optimum value at 0.3 grams. Beyond the optimum value, it increasd the absorbance peak that lowered the absorbed GOx or releasing back of GOx.

RECOMMENDATION

Research on the rGO/Fe$_3$O$_4$ composite biosensor can be further developed by applying it to other materials, by utilizing the magnetic properties of Fe$_3$O$_4$ material.

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