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Research Article

Preparation and Caharcterization of Graphene Oxide-Fe_3O_4 from Rice Husk

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ABSTRACT

The article presents of preparation Graphene Oxide (GO) Fe_3O_4 nanocomposites. This work describes the syntesis of Graphene Oxide (GO) by Modified Humme's method and its characterization by X-ray diffraction (XRD), fouriere transform infrared (FTIR), Field emission scanning electron microscopy (FESEM) Scanning electron microscopy (SEM- EDX), and Raman Spectroscopy. This result promising that GO-Fe_3O_4 nanocomposites can be used for applications to degrade pharmacheutical waste in environment.

Keywords: GO-Fe_3O_4, nanocomposites, rice husk,

1. Introduction

The production of carbon from biomass around the world is close to a half teratons[1]. Indonesia is one of the biggest rice producer in the world, it is comparable to the production of rice husk which is not yet sufficient to be utilized properly. In previous study, rice husks has been used to produce silica [2]; [3], biosorbents [4] adsorbents for oil refining [5], composites polyester resin [6]. Rice husks were used as the basic material for graphite production. Graphite will be convinced into graphene oxide (GO) by modified Hummers method [7]. GO and its derivatives are used as a source of material based on nanomaterials and are of particular interest because they have a nanostructure with a very large surface area and superior chemical strength [8].

Nowdays graphene oxide is a material that have a many benefits such as extensive specific surface area, optimal electrical conductivity, and mechanical rigidity [9].GO contains a carbon-based hexagonal ring (C) with sp2 and sp3 C atom hybridization in a 2-dimensional structure containing functional groups containing oxygen (O) atoms such as epoxy, carbonyl, hydroxyl, carboxyl on its surface. The functional groups in the GO layer directly function as a material to stabilize nanoparticles [10]. GO has a function as a stabilizing agent for the preparation of metal nanoparticles, one of is iron (Fe) [11], [12], and [13].

The composites of ferrite and carbon based materials have persuaded extensive scrutiny in recent years due to their simple preparation method, low price, and strong absorption[14]. Hence researcher has been widely used GO nanocomposites for many application for dye removal [15] and [16], heavy metal removal [17] and [18], drug delivery system [19], sensor [20] and adsorbent [21]. GO nanocomposites hase been prepared by modified Hummers method then co precipitation [22]. The GO nanocomposites were characterized by XRD, FTIR, FESEM, SEM- EDX, dan Raman spectroscopy.

2. Materials and Methods

2.1. Materials and Chemical

Graphite was prepared from rice husk obtained from Pasuruan. Chemical reagents and materials such as sulfuric acid (H_2SO_4 98%), peroxide acid (H_2O_2 30%) hydrochloric acid (HCl 5%), pottasium permanaganate ($KMnO_4$), sodium nitrate ($NaNO_3$) , hydrogen fluoride (HF), ferrous chloride heksahydrate ($FeCl_3.6H_2O$), ferrous sulfate heptahydrate ($FeSO_4.7H_2O$), sodium hydroxide (NaOH), and deionized water (DI) purchased from Merck.Co (Surabaya, Indonesia).

2.2. Methods

In typicall procedure,GO was produced using modified hummer's method [7] from graphite based on rice husk. 5 gr of graphite was added into 2,5 g of $NaNO_3$ and 115 mL of H_2SO_4 (98%), and stirred for 2 h under the ice bath. Then 15 gr of $KMnO_4$ was then added slowly into solution. This mixture was stirrer for 2 h. Next,230 mL of DI was diluted to the mixture, the temperature was kept bellow 100^0C. 700 mL of DI was added to the mixture. 10 mL H_2O_2 was dropped slowly and stirrer for sveeral times. The exchotermic reaction occured and it to cool down. Some of drops of HCl and DI was added and centrifuged for several minutes. Then GO was dried using oven at 60^0C for 24 h to produce the powder of GO.

GO/Fe_3O_4 nanocomposites were syntesized through a facile chemical process. For the mixture of 0,025 g of GO with 0,556 g $FeSO_4.4H_2O$ and 1,081 g $FeCl_3.6$ H_2O. Then, stirrer and heated up to 40^0C. Black precipitate was produced immediately by adding several drops of NaOH until pH level 10 was reached. Black precipitation on the mixture are separated by magnetic separation using neodymium magnet and washed several times using DI and heated to 60^0C for 48 h.

3. Result and Discussion

XRD showed the graphite 10 after desillaction has a peak of 2θ = 23.1311 with d-spacing of 3.84529 Å. GO formation derived from rice husk from graphite after desillication was characterized by a peak of 2θ 24.3657; 25.6684 with d-spacing of 3.65317 ; 3.47064. Similiar result with the active carbon compound [23]. The peak characteristic of nanocomposite materials of GO- Fe_3O_4 in can be found at two peaks which is at 30°; 36° [24]. The removal of silica conten by HF solution, makes a difractogram of the pattern becomes slightly thinner. Commonly the Figure 1 show that the all characteristic compound are amorphous or crystalline.

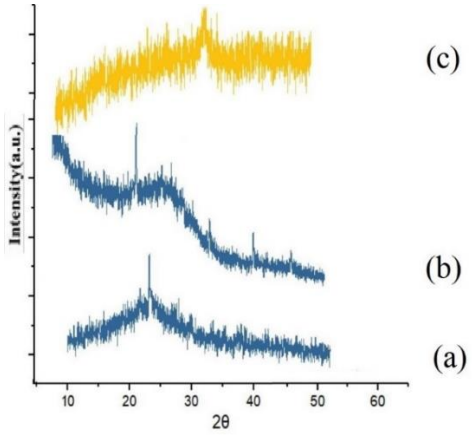


Figure 1. XRD diffraction patterns of graphite after desilication (a); GO after desilication (b); GO-Fe_3O_4(c)

Some data regarding the type of chemical bonding information known by the wave number of the bands that appear in the FTIR spectra.The FT-IR analysis of the samples of graphite desilication, GO, and GO–Fe_3O_4 shows in (Fig. 2) with wavenumber shifts in FTIR for the spectrum range 500 cm-1 – 4000 cm-1. The IR peak of graphite after desilication (A) shows a sharp and broad peak intensity in the area of 1100 cm-1 (streching vibration at CO), 1700 cm-1 (streching vibration at C=O), 3000-3700 cm-1 (streching vibration at C=O), 3000-3700 cm-1 (streching vibration at C=O), OH), and 1600 cm-1 (streching C=C aromatic GO). The functional group in graphite should be C-C, but the results of IR analysis obtained several functional groups such as C-O, C=O, OH, which indicate the presence of impurities in graphite after desilication from rice husks. The number of waves in the 798 cm-1 region which shows an aromatic structure. Peak of GO-based graphite after desillication and GO-Fe_3O_4 did not show significant changes with IR graphite results. The addition of a new functional group at a wave number of 572 cm-1 indicates a characteristic Fe-O peak in Fe_3O_4. And the reduction in the sharpness of the GO-Fe_3O_4 peak in the 3000 cm-1 (OH) region of the C=O functional group indicated the presence of COO- after coating with Fe_3O_4. The characterization using FTIR aims to ensure the formation of functional groups and testing using this FTIR

has not been able to directly compare whether GO has been formed after the synthesis process. Therefore, several additional characterizations were carried out, including using XRD and Raman instruments. The results of the FTIR above can be concluded that there is the formation of several OH, C=O, and C-O functional groups containing oxygen. This indicates that the synthesis of GO based on graphite from rice husk has been formed. The additional wave number of 572 cm-1 indicates the characteristic Fe-O peak in GO-Fe_3O_4.

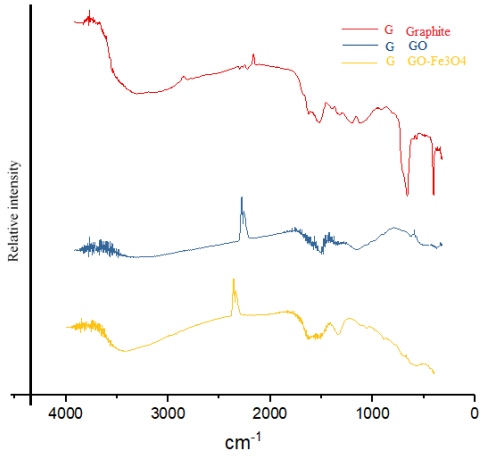


Figure 2. FTIR spectra of graphite, GO, and GO-Fe_3O_4

The Raman instrument was used to characterize the typical carbon (C) structure, which exhibits double bonds in sp2 orbitals and single bonds in sp3 orbitals. Raman spectoscopy widely used to determine the significant changes in the C atomic structure between GO and GO-Fe_3O_4. In Raman there are 2 distinctive bands, namely the D-band and G-band. The D-band shows the mode of structural defects in C sp2 hybrids, while the G-band Raman is first order of all C sp2 hybrid materials. The results of the Raman test on GO and GO-Fe_3O_4 can be seen in Figure 3.

Figure 3 exhibited the result of GO characterized by Raman, showing the G-band of the E2g vibrational mode in the sp2 C orbital, namely in the 1597 cm-1 region and the D-band at 1346 cm-1 indicating the sp2 C conversion. The results obtained in this study close to the results of the literature [25] which states that the intensity of the D-band in GO is 1331 cm-1 and the intensity of the G-band is 1570 cm-1. Therefore, based on the similarity of the data, it is possible that the typical C atomic structure of the graphite-based GO compound after the desilication has been carried out formed. Meanwhile, for GO-Fe3O4 catalyst there was a decrease in the peak intensity of the G-band. This is probably due to the addition of nanocomposite (Fe_3O_4) into the GO structure, and the conversion of C sp2 orbitals into C sp3.

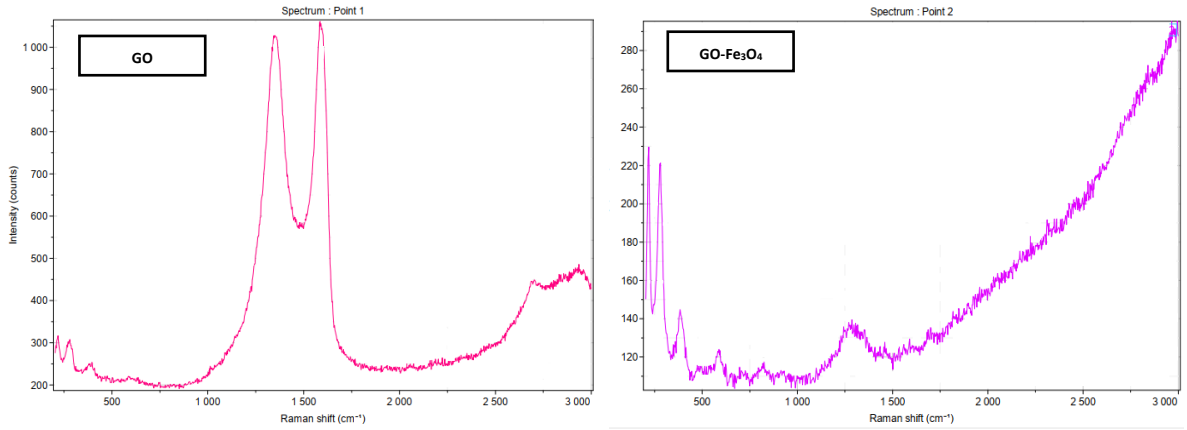
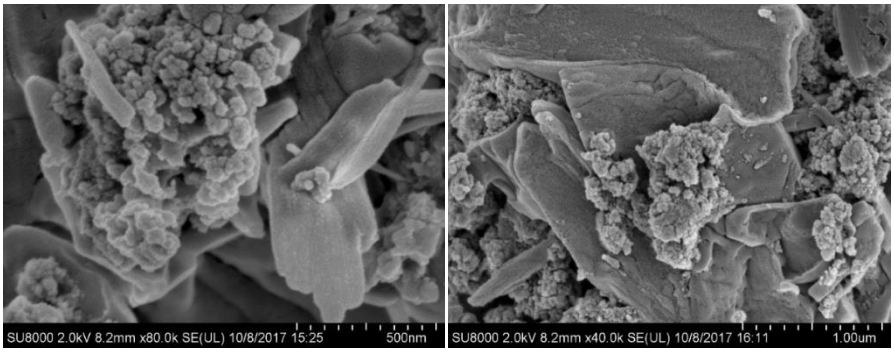


Figure 3. Raman spectra of GO, and GO-Fe_3O_4

FESEM analysis purpose to determine the morphology and surface state of GO composites with nano Fe_3O_4 and the distribution of Fe_3O_4into GO sheets. Tests using the FESEM instrument can see the topography of the catalyst on the surface as well as into the catalyst sample with a magnification of up to 300,000 x with the energy used in the range of 2.0 kV. Morphological results using FESEM on the catalyst surface shown in Figure 4 (a) and 4 (b) show the morphology of GO-Fe_3O_4. The GO in Figures 4 (a) and (b) are shown in the form of a thin sheet like fine structure with a soft edge surface (Chimezi et al., 2016). Small round lumps on the GO surface indicate the presence of Fe3O4 composite into the GO thin sheet. The lumps on the surface of the GO morphology are thought to be caused by the addition of composites or

intercalation of Fe_3O_4. The GO sheets were partially separated from each other due to the addition of Fe_3O_4, and the distribution of Fe_3O_4 on the GO sheets was evenly distributed. Meanwhile, the size of Fe_3O_4 ranges from 30-39 nm. For more details can be seen in Figure 4. Analysis using FESEM can only provide information about the topography on the surface of the catalyst but is not able to explain what elements are contained in the catalyst. Therefore, further testing was carried out using the SEM-EDX instrument to ascertain the percentage distribution of Fe_3O_4 nanoparticles on GO sheets.

The test using SEM-EDX aims to determine the morphology and surface state of GO composites with nano Fe_3O_4 and the distribution of Fe_3O_4 into GO sheets. Tests using the SEM-EDX instrument can see the topography of the catalyst on the surface as well as into the catalyst sample with a magnification of up to 10,000 x with the energy used in the range of 20.0 kV. Morphological analyzed using SEM-EDX on the surface of the catalyst showed theris a presence of white spheres on the GO sheet. For more details can be seen in Figure 5.



(a) **(b)**

Figure 4. FESEM of GO-Fe_3O_4 with magnification of 40,000x (a), 60,000x (b)

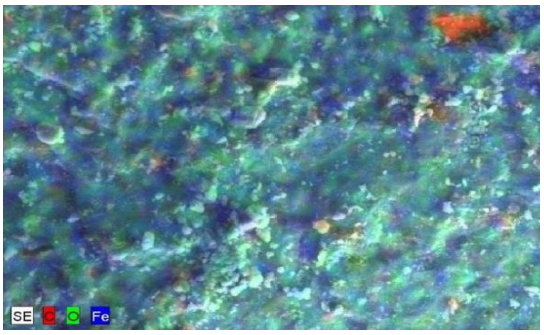


Figure 5. SEM_EDX of GO-Fe_3O_4

4. Conclusion

Graphene oxide has been successfully synthesized by utilizing rice husk. The magnetite GO-Fe_3O_4 was prosperous, and exhibited good result founded on characterized by XRD, FTIR, Raman spectroscopy, FESEM and SEM-EDX.

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