

SYNTHESIS AND CHARACTERIZATION: COMPOSITE OF GRAPHENE OXIDE BASED PALM KERNEL SHELL WASTE WITH Fe_3O_4

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION: COMPOSITE OF GRAPHENE OXIDE BASED PALM KERNEL SHELL WASTE WITH Fe_3O_4 . In this study, GO- Fe_3O_4 were fabricated by co-precipitation technique and the graphene oxide (GO) were synthesized from an agricultural biomass, palm kernel shell, via Hummer's method. Field Emission Scanning Electron Microscopy and Energy Dispersive Spectrum (FESEM-EDS), Fourier Transform Infra-Red (FT-IR) spectroscopy, X-Ray Diffractometer (XRD), and Raman spectroscopy were used to analysis the successful attachment of Fe_3O_4 onto the surface of GO. Morphology observation showed that Fe_3O_4 were heterogeneously deposited on the surface of GO. FT-IR spectra shows peak that incorporated to oxygenated functional groups and sharp peak at 586 cm^{-1} confirmed to lattice absorption of Fe_3O_4 . The percentage of composition of GO- Fe_3O_4 was characterized by energy dispersive spectroscopy and the results also confirmed in XRD exhibits similar properties with JCPDS 19-0629 for magnetite more dominant than GO. From Raman spectroscopy analysis shows that 1343.82 cm^{-1} (D-band) and 1584.62 cm^{-1} (G-band) and 2698 cm^{-1} (2D-band) indicates GO and GO- Fe_3O_4 were successfully synthesized.

Keywords: Palm Kernel Shell, Hummer Method, Graphene Oxide, GO- Fe_3O_4 Composite, Co-Precipitation

ABSTRAK

SINTESIS DAN KARAKTERISASI: KOMPOSIT OKSIDA GRAFENA BERBASIS LIMBAH KELAPA SAWIT DENGAN Fe_3O_4 . Pada penelitian ini, GO- Fe_3O_4 disintesis dengan teknik *co-precipitation* dan oksida grafena (GO) disintesis dari cangkang kelapa sawit via metode Hummer. *Field Emission Scanning Electron Microscopy and Energy Dispersive Spectrum* (FESEM-EDS), *Fourier Transform Infra-Red Spectroscopy* (FT-IR), *X-Ray Diffractometer* (XRD), and *Raman spectroscopy* digunakan untuk menganalisis adanya dan suksesnya Fe_3O_4 yang melekat pada permukaan GO. Observasi pada permukaan komposit menunjukkan bahwa Fe_3O_4 tersebar merata pada permukaan GO. Spektra FT-IR menunjukkan adanya gugus fungsi beroksigen dan puncak tajam di 586 cm^{-1} , yang merupakan absorpsi dari kisi Fe_3O_4 . Jumlah persentasi komposisi dari Fe_3O_4 dikarakterisasi menggunakan *energy dispersive spectroscopy* dan dari hasil yang diberikan mengkonfirmasi hasil XRD yang menunjukkan sifat yang sama dengan JCPDS 19-0629 yaitu magnetite yang lebih dominan dari pada GO. Dari hasil analisis *Raman spectroscopy* ditunjukan adanya puncak di daerah 1343.82 cm^{-1} (D-band) and 1584.62 cm^{-1} (G-band) dan 2698 cm^{-1} (2D-band) yang merupakan karakterisasi dari GO dan GO- Fe_3O_4 yang telah sukses disintesis.

Kata kunci: Cangkang Kelapa Sawit, Metode Hummer, Oksida Grafena, Komposit GO- Fe_3O_4 , *Co-Precipitation*

INTRODUCTION

Graphene oxide (GO) is a single layer of sp^2 carbon atom arranged in a honeycomb lattice structure. GO is a water soluble nanomaterial that has a hydrophilic character due to various oxygen functional groups such as epoxides, carboxylic groups [1], [2]. GO has unique properties such as relatively large surface area, high electrical conductivity, chemical inertness stability, high porosity, and strong mechanical strength [1,3–6]. It is started promoting material for any application from energy, environment to health [7–10]. Therefore, the development of methods and resources to synthesize GO has attracted attention. GO could obtain by the oxidation of graphite through Staudenmaier [11], Brodie [12], Hummers-Offeman/ Hummers Method [13], chemical vapor deposition or epitaxial growth, etc. [7,14]. One of the most widely method to produce GO is chemical exfoliation or using an oxidizing agent. This method was an applicable for large scale production of GO because could produce large quantities of GO powder, which is dispersed either polar or non-polar solvent. The Hummer method is a chemical oxidation method, which is simple and applicable to produce GO. Compare to other method, Hummers method provide larger interlayer distance and higher C/O atomic [15]. The use of $KMnO_4$ as a strong oxidant, helps to ensure the reaction only in a few hours, the absence of chlorate could eliminate the possibility of ClO_2 explosion and acid mist formation is reduced due to the use of $NaNO_3$ as a substitute for HNO_3 [16,17].

Commonly, the sources for preparation GO from graphite and organic compounds. Utilization of agricultural biomass, such as coconut shell [18], Dead neem leaves [19], Wood, leaf, bagasse, sawdust, bagasse [19–21], oil palm trunks [22] could be an alternative precursor carbon for preparation of GO. The utilization of palm kernel shell (PKS) to explore the resources of precursor carbon was chosen because of has a high carbon content [23]. The proximate carbon content of PKS comparing with other biomass are shown in Table 1. Moreover, the characteristic of PKS appropriate as precursor due to its porous surface, high mechanical strength, high chemical stability, various surface functional groups, and insolubility in water [24].

The decorating GO with inorganic material to optimize the catalytic, magnetic, and optoelectronic properties of GO has been develop in environmental applications [31–34]. Magnetite nanoparticles (Fe_3O_4) is a magnetic core owning that a low-cost, low toxicity, easy to synthesize and good biocompatibility. The

Table 1. Summary report of carbon content in biomass

Biomass	Carbon content (wt %)
Coconut shell and fiber	20.96 ^[25,26]
Oil palm wood	9.63 ^[27]
Sugarcane bagasse	44.17 ^[28]
Waste corn cob	30.4 ^[29]
Rice husk	37.6 ^[30]
Palm kernel oil	48.68 ^[24]

magnetic properties of Fe_3O_4 decorated in GO can provide an efficient way for separation without filtering when used as an adsorbent [35]. Various procedures have been developed to fabricate magnetic graphene, including in-suit co-precipitation [33], covalent bonding [36] and solvothermal method [37], hydrothermal treatment [32], sol-gel procedure [38], chemical vapour deposition [39] and self-assembly [40]. Recently, application Fe_3O_4 decorated in polymer and other material as adsorbent have been reported. Ma et al. prepared $SiO_2@Fe_3O_4$ for the removal of atrazine [41]. Kalantari et al. utilized Fe_3O_4 /talc nanocomposite for removal of Cu(II), Ni(II), and Pb(II) ions [42]. Mollahosseini et al. developed polypyrrole / Fe_3O_4 for the removal of Al^{+3} ions[43].

In this work, we report a simple strategy to prepare a GO- Fe_3O_4 using two step methods without using any molecular binder or linker. To the best of our knowledge, synthesis GO from PKS composite with Fe_3O_4 has not been reported yet. The Hummer method was used to oxidation graphite from PKS and then composited with Fe_3O_4 by co-precipitation method. Those methods were simple and low cost and the composite can be applied as adsorbent candidate. Moreover, the relationship between morphologies and structure has been studied by X-ray Diffraction (XRD), Fourier Transform Infra-Red (FT-IR), Raman spectroscopy, and Field Emission Scanning Electron Microscopy-Energy Dispersive Spectrum (FESEM-EDS).

EXPERIMENTAL METHOD

Materials and Instruments

Palm kernel shell waste was used as precursors for GO synthesis. Potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), sulfuric acid (H_2SO_4 95%), peroxide (H_2O_2 30%), hydrochloric acid (HCl 37%), Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), iron (II) sulfate ($FeSO_4$), and ammonium hydroxide (NH_4OH 25%) were purchased from Merck. All other chemicals and reagents

used in the experiments were analytical grade. Distilled water was used throughout the experiment.

The morphology of GO and GO- Fe_3O_4 composite were examined using a Field Emission Scanning Electron Spectroscopy (FESEM, Thermo Scientific Quattro S). The surface functional group were analyzed using Fourier Transform Infra-Red spectroscopy (FT-IR, Perkin Elmer) with attenuated total reflectance method at a resolution of 4 cm^{-1} in the range of $400\text{ cm}^{-1} - 4000\text{ cm}^{-1}$. X-Ray diffraction analysis was investigated using a Shimadzu XRD 7000 diffractometer (Shimadzu, Japan) with an acceleration voltage of 40 kV and current of 40 mA, in scanning range $10 - 60^\circ (2\theta)$. The graphitic character was measured using Micro confocal hyperspectral 3D imaging Raman Spectrophotometer (LabRAM HR Evolution, HORIBA, 800 mm Spectrometer Focal Length) at room temperature.

Method and Procedure

Preparation and Carbonization

The carbonization was conducted in a furnace under nitrogen gas. The palm kernel shell was crushed into granular particles and was washed several times with distilled water to remove dust and impurities. Then, it was dried in an oven at 80°C for 24 h. After that it was heated at 700°C for 3 h. Finally, the graphite based palm kernel shell was ground into powder and sieved to obtain a particle size of $250\text{ }\mu\text{m}$ using a 60 mesh sieve.

Synthesis GO by Hummer's method

Hummer method was used to synthesis GO [44]. About, 5 g of carbon based palm kernel shell was mixed with 120 ml H_2SO_4 under stirrer on an ice bath ($\sim 5^\circ\text{C}$) for 30 min. Then, 2.5 g NaNO_3 was added for 30 min. After another 30 min, 15 g of KMnO_4 was added slowly in the mixture with stirring on the ice bath for 3 h until the solution became dark green. During the reaction, the temperature was maintained below 5°C with constant stirring. The 230 mL of distilled water was added slowly and after 15 min the additional 400 mL distilled water was added. Afterward, 30 mL of 30% H_2O_2 was added to neutralize the remaining unreacted KMnO_4 until it produced visible bubbles. The precipitate was washed with 800 mL of 5% HCl using centrifugation and then continued with distilled water until it reached a neutral pH. The final product was dried at 105°C for 12 h.

Fabrication of GO- Fe_3O_4 composite

The GO- Fe_3O_4 composite was synthesized by co-precipitation method [45,46]. 2 g of GO was mixed with $\text{FeCl}_3 \cdot 5\text{H}_2\text{O}$ and Fe_2SO_4 with a 2:1 mole ratio, respectively. The mixture was dispersed in 50 mL distilled water under stirrer. Then, the mixed solution was heated at 80°C and added drop wise 250 mL of 30% NH_4OH under stirring for 1.5 h to make pH 10. The resultant was washed with distilled water using centrifugation until it reached a neutral pH and dried at 80°C for 24 h.

RESULTS AND DISCUSSION

GO from palm kernel shell was produced by The Hummer method. The synthesis process of GO begins with the addition of concentrated sulfuric acid and KMnO_4 as an oxidizing agent. It was used to intercalate the graphite layers from flakes. The intercalation will cause the distance between graphite layer to become larger and weaker. Furthermore, the penetration of KMnO_4 very effective for oxidizes graphite. During the process the temperature must be maintained under 5°C to prevent increasing and bumping due to exothermic reaction. After the oxidation process is complete, the mixture was dilute with water and continue adding H_2O_2 to reduce residual MnO_4 and MnO_2 . The suspension color will turn from brown to brilliant yellow, indicating the formation of GO. The results are then wash using HCl to remove the residual metal ion. Due to the functionalization of GO that stabile in the aqueous suspension, Fe^{2+} and Fe^{3+} were added to fabricate GO- Fe_3O_4 composites [47]. The Iron compound could form crosslinking with oxygen functionalities on the surface of carbon [46,48]. Figure 1 shows the magnetic properties of GO- Fe_3O_4 . The GO- Fe_3O_4 composite was characterized using FESEM-EDS, XRD, FT-IR, and Raman spectroscopy.



Figure 1. GO- Fe_3O_4 composites images

Morphology Analysis

The surface morphology of the GO and GO- Fe_3O_4

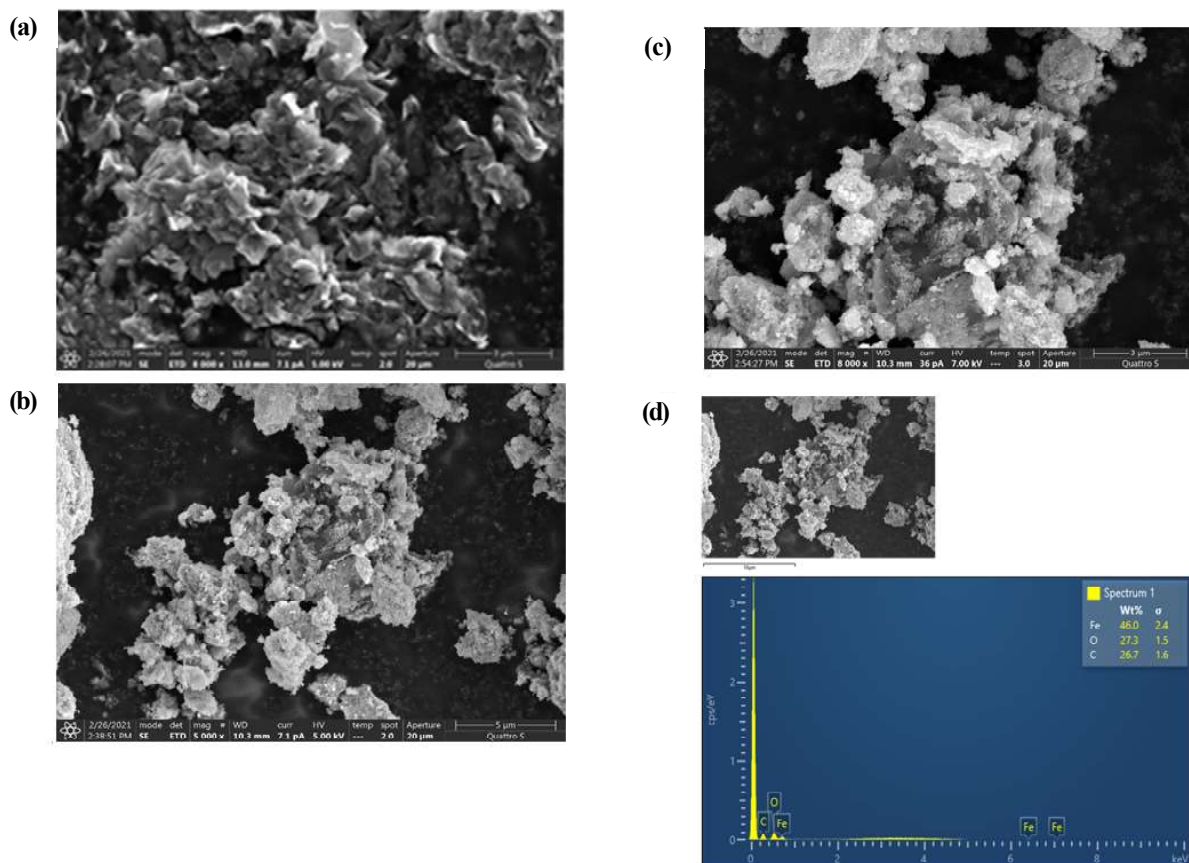


Figure 2. (a) SEM image of GO, (b) GO-Fe₃O₄ with magnification 5.000x, (c) GO-Fe₃O₄ with magnification 8.000x and (d) EDX result of GO-Fe₃O₄

composite is shown in Figure 2. Figure 2(a) display the images of the structure of flakes and thin layers with a large surface area. It had some ripples and wrinkles on the edge due to the oxidation process. This is showed the characteristic of graphite exfoliation that form GO sheets [49–51]. The SEM images in Figure 2(b) and (c) showed the bright dots of Fe₃O₄ particles. In the higher magnifications in Figure 2(c) observed that Fe₃O₄ heterogeneously deposited on the surface of GO. The composition of GO-Fe₃O₄ was further characterized with EDS, the result as shown in Figure 2(d). The EDS indicated the presence of atomic iron, carbon and oxygen in Fe₃O₄, which is the percentage of Fe more dominant than another element. This becomes evidence that Fe₃O₄ effectively combined on the surface of GO.

FT-IR Analysis

The FT-IR spectrum of carbon, GO, Fe₃O₄ and GO-Fe₃O₄ are presented in Figure 3. Figure 3 shows the position of the absorption peaks of GO in the FT-IR spectrum. In GO spectrum exhibited strong and broad absorption peak at 3450 cm⁻¹ correspondings to stretching vibrations from hydroxyl groups (-OH). The absorption

peak at 1720 cm⁻¹ and 1625 cm⁻¹ can be attributed to carboxyl vibrations (-COOH), 1270 cm⁻¹ (CO-H), 1148 cm⁻¹ (C-O vibrations), 1030 cm⁻¹ (C-O-C). It result indicated that the various oxygenated functional groups incorporated in the GO structure and were similar to Ain et al, (2019) [35]. The FT-IR spectra of Fe₃O₄ showed the band at 750-400 cm⁻¹, corresponding to Fe-O vibration. Compared to the FT-IR spectra of GO the spectra of GO-Fe₃O₄ showed the intensity of -OH stretching vibrations decreased at 3450 cm⁻¹, 1637 cm⁻¹ and 1625 cm⁻¹ are contributed the stretching vibrations of C=O (Carbonyl /

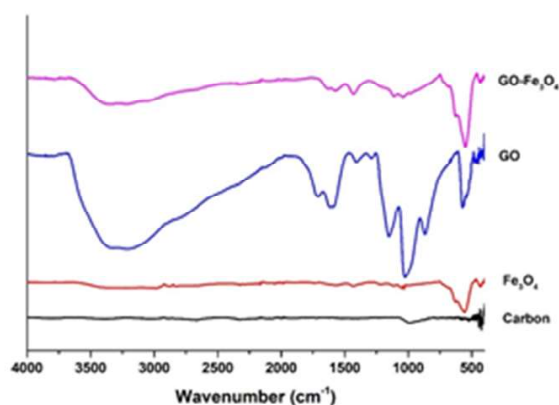


Figure 3. FT-IR spectra of GO-Fe₃O₄, GO, Fe₃O₄ and Carbon

Carboxyl), and 1130 cm^{-1} is attributed to C-O stretching vibrations of epoxy group. Those characteristic peak related to the existence of surface hydroxyl and water molecules [35,46,52,53]. However, there is sharp peak at 586 cm^{-1} confirmed to lattice absorption of Fe_3O_4 . This is assumed that Fe_3O_4 particles have been decorated on the surface of GO thought strong interaction oxygen atom with Fe_3O_4 particles [51,54].

X-Ray Diffraction Analysis

The identification of diffraction spectra using XRD has aims to determine the crystallinity of sample whether it is Fe_3O_4 , graphite, and graphene oxide. The X-Ray diffraction pattern of carbon, GO, Fe_3O_4 and GO- Fe_3O_4 was appeared in Figure 4. The diffraction spectra was compared with the XRD JCPDS database. In Figure 4, the characteristic X-Ray diffraction spectra of graphite was exhibited (002) reflection at 23.80° and 26.40° (2 θ) match with JCPDS-No: 75-1621. It was conducted to the high graphite structure [15]. While, the XRD diffractogram of GO shows dominant peak 2 θ at 26.6 (002) and 42.5 (100). These peak probably indicated impurity in the sample and high crystallinity of the few layer graphene with functional group [17,55,56]. The XRD pattern of Fe_3O_4 as shown in Figure 3 exhibit peak at 29.8 (220), 35.2 (311), 43.1 (400), 53.9 (422), 57.2 (511) and 57.14 (511) match with JCPDS file no. 19-0629 for the magnetite. Whereas for the XRD diffractogram of GO- Fe_3O_4 composite show similar pattern with Fe_3O_4 and no typical of carbon was observed, which is indicating the existence of Fe_3O_4 on GO. This implies that the presence

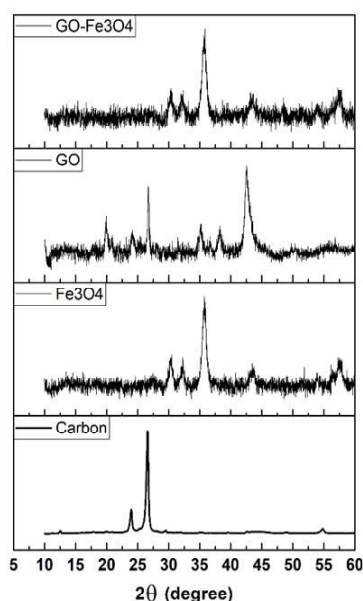


Figure 4. XRD pattern of GO- Fe_3O_4 , GO and Fe_3O_4 and Carbon

of GO does not change the orientations of Fe_3O_4 and may be due to low intensities of GO. It is match with the result of EDS that shows composition of Fe higher than carbon. This result similar with lie et al, 2015 [57].

Raman Spectroscopy Analysis

Raman spectra Fe_3O_4 , GO and GO- Fe_3O_4 were shown in Figure 5. Raman is a non-destructive analysis to investigate the structure and quality of carbon material. Figure 5 shown the Raman spectrum of characteristic peak responds of Fe_3O_4 at 219, 284 and 400 cm^{-1} . However, GO has peak at 1343.82 cm^{-1} (D-band) and 1584.62 cm^{-1} (G-band) and 2698 cm^{-1} (2D-band), which is an intrinsic property of GO [16,58]. The D-band is attributing to a breathing mode of κ -point phonons of A_{1g} symmetry, which is related to carbon atoms in planar terminations of disordered graphite, while the G-band is assigned to E_{2g} phonon of vibration C sp^2 atoms in the 2D hexagonal lattice. The amount of disorder in the crystal structures of carbon material could measure from the intensities of I_D/I_G [16]. The quality of GO could be seen from the intensity ratio I_D/I_G , according to Kaniyoor et al, (2012), the good quality of GO is less than 2 [59], while in this report GO based palm kernel shell has a ratio of 1.03. The increased intensity ratio I_D/I_G proportional to the integrated degree of disorder that may be caused by folding or twisting of a few layer graphene sheet [60], which is distributed on the surface. Comparing with GO- Fe_3O_4 , the Raman spectra display a

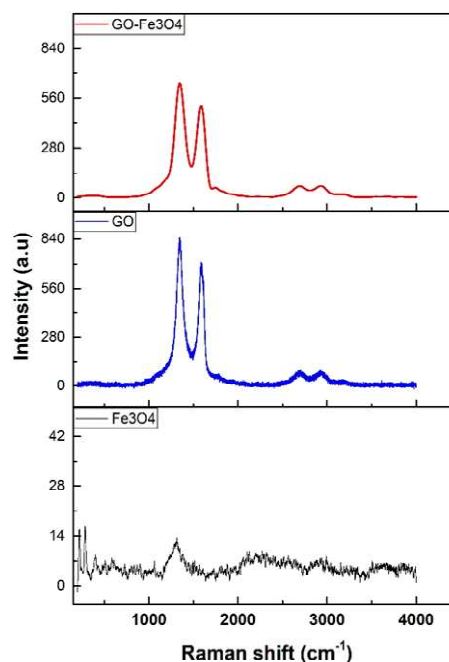


Figure 5. Raman spectra of GO- Fe_3O_4 , GO and Fe_3O_4

decreased intensity in the D and G band compared to GO, but increase intensity ratio of D band to G band (1.17). These phenomena showing decrease in size of the sp^2 domains along with an increased disorder in the sample [34,48,51], which may because the Fe_3O_4 are well embedded inside the GO, which is similar to the previous study [58].

CONCLUSION

The fabrication of the GO based palm kernel shell composite with Fe_3O_4 was successfully synthesized using the co-precipitation technique. The FESEM-EDS observation shows that Fe_3O_4 was deposited in the ripple and wrinkles of GO surface with percent composition of atom Fe higher than carbon. Therefore, the XRD spectra confirmed peak that match with JCPDS file no.19-0629 for magnetite and Raman spectra shows a decreased intensity ratio in the D, G and 2D band with an increase the intensity ratio I_D/I_G . The GO- Fe_3O_4 also confirms in FT-IR, that the appearance of oxygenated functional groups such as hydroxyl, carboxyl, alcohol, and epoxy and shows the peak at 586 cm^{-1} .

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