

GO-Fe₃O₄ Nanocomposite from coconut shell: Synthesis and characterization

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Abstract. Synthesis and characterization of graphene oxide nanocomposite from coconut shell GO-Fe₃O₄ has been done. Graphene oxide can be prepared using Hummer's method and subsequently, the synthesis of GO-Fe₃O₄ nanocomposite was carried out by ultrasound assisted co-precipitation of iron (II) and (III) chlorides in the presence of GO. The formation of GO and graphene-Fe₃O₄ nanocomposite was confirmed by x-ray diffraction (XRD), Fourier transform-infrared (FTIR), SEM and Raman spectroscopy. The characteristics of GO-Fe₃O₄ as a result of synthesis from coconut shell analyzed using XRD showed that GO characteristics peak in accordance with the characteristics of GO-Fe₃O₄ in (JCPDS No. 88-0315). Analysis using FTIR was seen in 3421 cm⁻¹ (O-H stretching), 1631 cm⁻¹ (C = C aromatic), and 565 cm⁻¹ (Fe-O). Analysis using SEM seen in the presence of Fe, O and C in the EDX analysis confirmed the formation of GO-Fe₃O₄ nanocomposite. Analysis using Raman spectroscopy showed that peaks of Fe₃O₄ were at wavelengths of 396 cm⁻¹ because sp³ carbon was bound to Fe₃O₄ so that the peak band D was not present in GO-Fe₃O₄ spectroscopy.

Keywords: Coconut shell, graphene oxide, nanocomposite GO-Fe₃O₄

1. Introduction

Biomass is a ubiquitous and abundant renewable resource on Earth [1]. Charcoal from biomass is popular adsorbent for air and water purification [2]. Activated carbon (AC), which is sometimes called activated charcoal or active carbon, is used mostly for adsorption in industry and is commonly used owing to its large adsorption capacity, fast adsorption kinetics and relative ease of regeneration [3,4]. AC can be produced from a range of raw carbon resources, such as lignite, peat and coal and biomass resources, such as eucalyptus [5], cherry, car stone, apricot stone, nuts, grape seeds [6], olive and peach stones [7], walnut shell [4], [8], oil palm trunks/sells [9], wood, sawdust, bagasse and coconut shells [10]. Gratuito et al. [11] suggested that coconut shell (AC) is advantageous over carbon made from other materials because of its high density, high purity and virtually dust-free nature [12].

Graphene oxide (GO) is an oxidized derivative of graphene which contains epoxide, hydroxyl, and carboxyl groups [13]. These functional groups lead to the negative charge, hydrophilicity and easy dispersion of GO in aqueous solutions [14]. These properties make GO a great candidate for the removal of different pollutants by degradation. Due to its high surface area and functionalities, GO can be used as an excellent platform to grow various nanoparticles. In addition, GO helps prevent on nanoparticles [15]. GO consists of a hexagonal ring-based carbon network with both sp² and sp³ hybridised carbon atoms in two-dimensional structure that contain copious oxygen functional groups such as epoxy, hydroxyl, carbonyl and carboxyl groups on surfaces and edges [17-20]. These oxygen functional groups serve as activation sites for nucleation and growth of iron precursors to form GO supported iron-containing nanocomposites [20].

Nowadays, Fenton process is becoming more and more important on the degradation of organic pollutant in dye wastewater [21], for its own advantages such as high degradation efficiency, low cost,



eco-friendly and mild conditions [22]. In Fenton system, Fe^{2+} ions are served as catalyst to decompose hydrogen peroxide (H_2O_2) to generate hydroxyl radicals ($\cdot\text{OH}$) which can degrade dyes into harmless chemicals, such as CO_2 and H_2O completely [23]. In order to develop a novel Fenton-like system, some recent studies have investigated different iron solid compounds to replace the soluble Fe^{2+} such as hematite, $\alpha\text{-FeOOH}$, $\beta\text{-FeOOH}$, iron-immobilised zeolites, Fe_3O_4 and so on [24]. Especially, owing to the unique characteristic such as easy preparation, high stability and convenient separation from water solution by external magnetic field, Fe_3O_4 nanoparticles were attracted many attentions in recent years [25].

2. Experimental Method

2.1 Materials

The graphite used in this experiment was prepared using coconut shell obtained from Surabaya Indonesian. The preparation of GO used graphite of the coconut shell, sulfuric acid (H_2SO_4 , Merck, 98%), peroxide acid (H_2O_2 , Merck, 30%), hydrochloric acid (HCl , Merck, 5%), potassium permanganate (KMnO_4 , Merck), sodium nitrate (NaNO_3 , Merck), hydrogen fluoride (HF , Merck), Iron(II) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Merck), Iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Merck), sodium hydroxide (NaOH , Merck), methanol (CH_3OH , Merck) and deionized water (DI water).

2.2 Instrumentation

The instrumentals used were X-Ray Diffraction (XRD), Infrared Tracer-100 (IR), Raman spectroscopy and Scanning Electron Microscopy (SEM). XRD was used to measure the crystallinity of graphite and GO, IR and Raman was used to know the functional groups of graphite and GO, and Scanning Electron Microscopy (SEM) used to determine the morphology of $\text{GO-Fe}_3\text{O}_4$.

2.3 Procedure

Preparation of graphite

Graphite was produced from coconut shell. First these waste was washed and inserted in vial and dried using oven for 24 hours. After that furnace at 550°C for 3 hours. These three materials contain high silica. Hence silica was removed using hydrogen fluoride (HF). 10 g of graphite was dissolved using 30 mL HF 40%, heated and stirred for 3 hours. After that the suspension was washed using distilled water and dried. Graphite was then analyzed using XRD and IR instruments.

Preparation of graphene oxide (GO)

GO was prepared according to modified Hummers method. Graphite 5 g was added 2.5 g NaNO_3 and 115 mL H_2SO_4 (98%), the rate of addition was controlled carefully. Avoiding a sudden increase of temperature reaction was performed on ice bath. The stirring was continued for 2 h at temperatures below 20°C . Then 15 g of KMnO_4 was slowly added to the reaction, with stirring for 2 h. The ice bath was removed and then the reaction was covered by aluminum foil, stirring for 30 minutes to form a brown paste. After that, the reaction mixture was diluted with 230 mL of DI and the temperature was kept below 100°C . The mixture was stirred for 1 hour, and further diluted to approximately 700 mL of DI water. After that 10 mL of 30% H_2O_2 was added to the mixture which changed its color to brilliant yellow. The resultant was centrifuged and washed several times with 5% HCl aqueous solution and DI water. Finally the resulting solid was dried at 60°C for 24 h where a loose brown powder, was obtained. GO was analyzed using XRD and IR instruments.

Preparation of $\text{GO-Fe}_3\text{O}_4$ nanocomposite

In a typical process, 0.025 g of GO was dispersed in 50 mL of distilled water by ultrasonic treatment for 15 min, and then 100 mL of $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (0.556 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.081 g) mixed water solutions were slowly added to the GO solution. And stirred and heated up to 40°C . After that, several drops of NaOH was put into the mixture until the pH was 10, followed by stirring for a further 30 min at 80°C . After cooling to room temperature, the product ($\text{GO-Fe}_3\text{O}_4$ nanocomposites) was washed with distilled water three times and dried in a vacuum at 80°C . In comparison, bare Fe_3O_4 nanoparticles were prepared by the similar process as $\text{GO-Fe}_3\text{O}_4$ nanocomposites except the addition of GO.

3. Result and Discussion

X-ray diffraction (XRD) was taken to confirm the formation of various phases. Comparison result between the XRD patterns before and after desilication process was shown in Figure 1. Neither of graphite patterns or GO patterns has the broad patterns in Figure 1 before graphite desilication, its meant that there is silica content. After the silica on the graphite base material was removed by HF solution, the diffractogram pattern becomes slightly thinner and the pattern not widened such as before the silica removal. The widening diffractogram pattern is likely to be debated because the crystals of graphite and GO are still covered by silica having the same peak as graphite and GO.

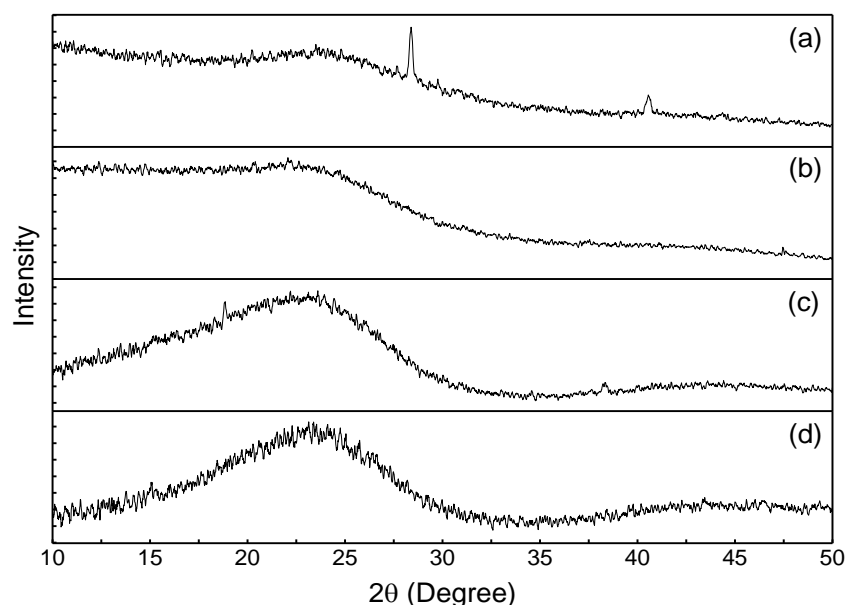


Figure 1. XRD diffraction patterns (a) and (b) graphite and GO before desilication, and (c) and (d) graphite and GO after desilication

GO was made from graphite derived from coconut shell. GO was synthesized using modified Hummer's method. The concentrated sulfuric acid was used to exfoliate the number of layers from the graphite flakes, KMnO_4 was used as oxidizing agent. The addition of KMnO_4 must be slowly done to avoid the exothermic reaction and the bumping. The temperature must be maintained under 20°C . The results were suspension. After adding by water, the temperature of suspension increased, and the colour turn from brown to brilliant yellow. After adding by H_2O_2 , indicating the GO formation. Figure 1 showed commonly the characteristic of graphite pattern before treatment by HF solution defined peaks at 23.11° [26] and 38° [27]. The result of characteristic of graphite from coconut shell 23° for graphite and 43° for GO. After oxidation, the characteristic graphite pattern was so small broad such as coconut shell at 23.11° . Commonly the GO pattern from commercial graphite was defined at $10-11^\circ$, but it was different thing if we used graphite from waste, although based on [28] that XRD spectrum of GO nanoplatelets from carbonized agro waste was 26.60° .

To compare the structural properties of $\text{GO-Fe}_3\text{O}_4$ nanocomposites synthesized with GO, XRD analysis was performed and shown in Figure 2. $\text{GO-Fe}_3\text{O}_4$ nanocomposite XRD patterns were found to be equivalent to magnetic. The peak characteristic of $\text{GO-Fe}_3\text{O}_4$ in (JCPDS No. 88-0315), which is at 30° ; 35° ; 43° and 57° . The XRD pattern shows all Fe_3O_4 nanoparticle peaks that are in accordance with those reported in the literature [30,31]. $\text{GO-Fe}_3\text{O}_4$ nanocomposite particle size of 19.53\AA or 1.95 nm uses the Scherrer equation. This shows the results of nano-sized synthesis.

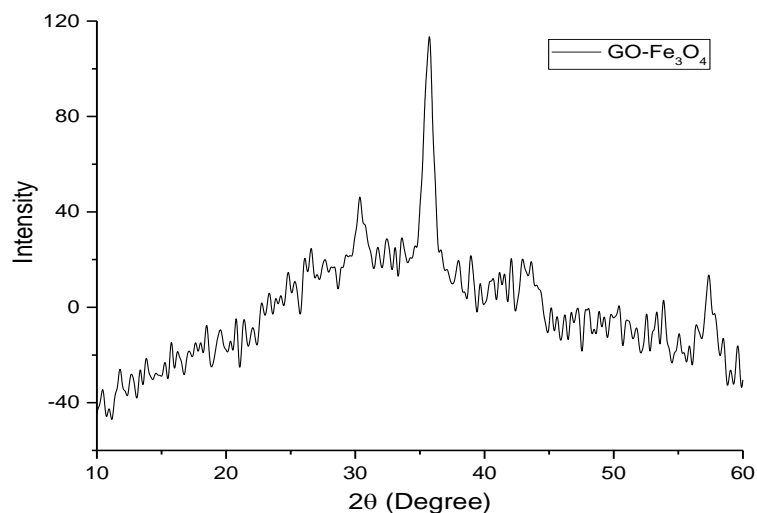


Figure 2. GO-Fe₃O₄ XRD diffraction pattern

Figure 3 showed the IR spectrum of GO from coconut shell. The bands coconut shell of graphite are 3620 cm⁻¹ (OH stretch), 1612 cm⁻¹ (C = C aromatic), 1238 cm⁻¹ (stretching CO), and 829 cm⁻¹ (stretching CC), while the GO spectrum is 3593 cm⁻¹ (OH stretch), 1722 cm⁻¹ (C = O stretch), 1283 cm⁻¹ (CO stretch) and 822 cm⁻¹ (CH stretch). This can also be distinguished by functional groups such as carboxyl, hydroxyl, and epoxy on GO. GO is also stable at the transmission peak at a wavelength of 1722 cm⁻¹ which indicates the stability of the functional group (C = O). GO-Fe₃O₄ nanocomposite spectrum shows 3421 cm⁻¹ (O-H stretch), 1631 cm⁻¹ (C = C aromatic), and 565 cm⁻¹ (Fe-O). The GO-Fe₃O₄ nanocomposite IR spectrum showed a shift in the O-H peak from 3593 cm⁻¹ to 3421 cm⁻¹ which showed loading of Fe₃O₄ nanoparticles on GO [31]. Also the IR GO spectrum shows a characteristic peak at 1722 cm⁻¹ which indicates the presence of a carboxylic acid functional group which shifts to 1631 cm⁻¹ due to the formation of -COO- after Fe₃O₄ nanoparticles are composed. Furthermore, the characteristic peak at 565 cm⁻¹ is indicated by Fe-O, which confirms the presence of Fe₃O₄ [32].

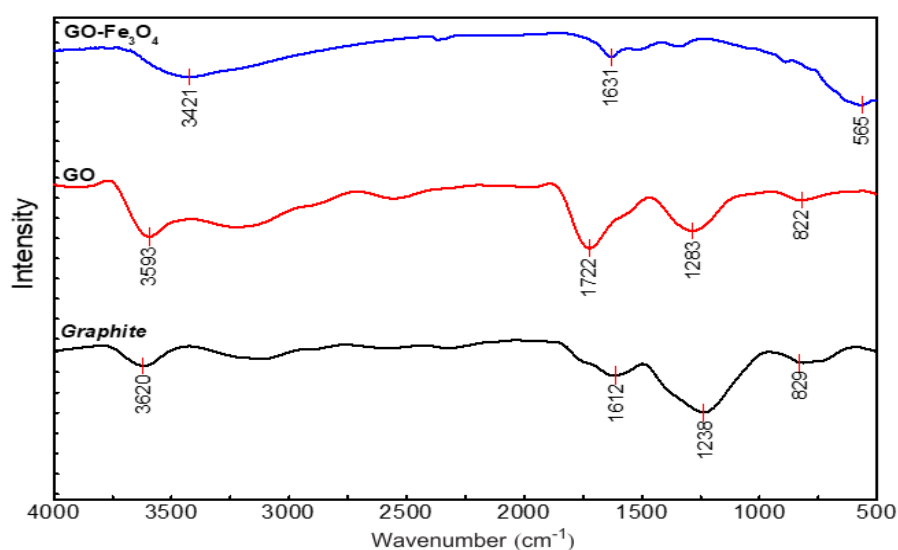


Figure 3. FTIR spectra (a) graphite, (b) GO and (c) GO-Fe₃O₄

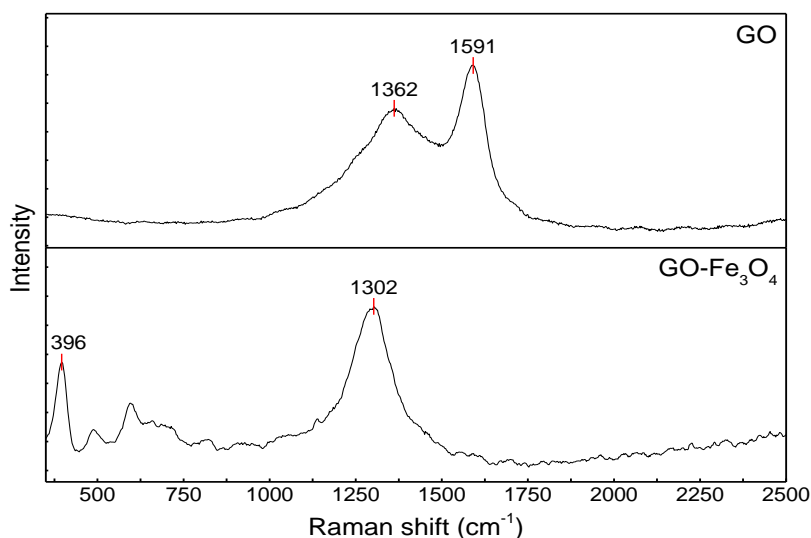


Figure 4. (a) Spectroscopic Raman spectra of GO and (b) GO-Fe₃O₄

The SEM image and EDX analysis of GO-Fe₃O₄ nanocomposite are depicted in Figure 5, it is evident that the Fe₃O₄ nanoparticles are distributed between the layers of the graphene sheets, which lead to the formation of porous GO-Fe₃O₄ nanocomposite with large amount of void spaces. The enhancement in the cyclic performance of GO-Fe₃O₄ nanocomposite as an anode material for lithium-ion batteries takes place because of the porous nanocomposites with several void spaces [34,35]. Furthermore, Fe₃O₄ nanoparticles distributed between the graphene sheets can reduce the aggregation of Fe₃O₄ nanoparticles to a greater extent in the presence of ultrasonic irradiation, which can be of great benefit to cycle life. The presence of Fe, O and C in EDX analysis confirms the formation of GO-Fe₃O₄ nanocomposite.

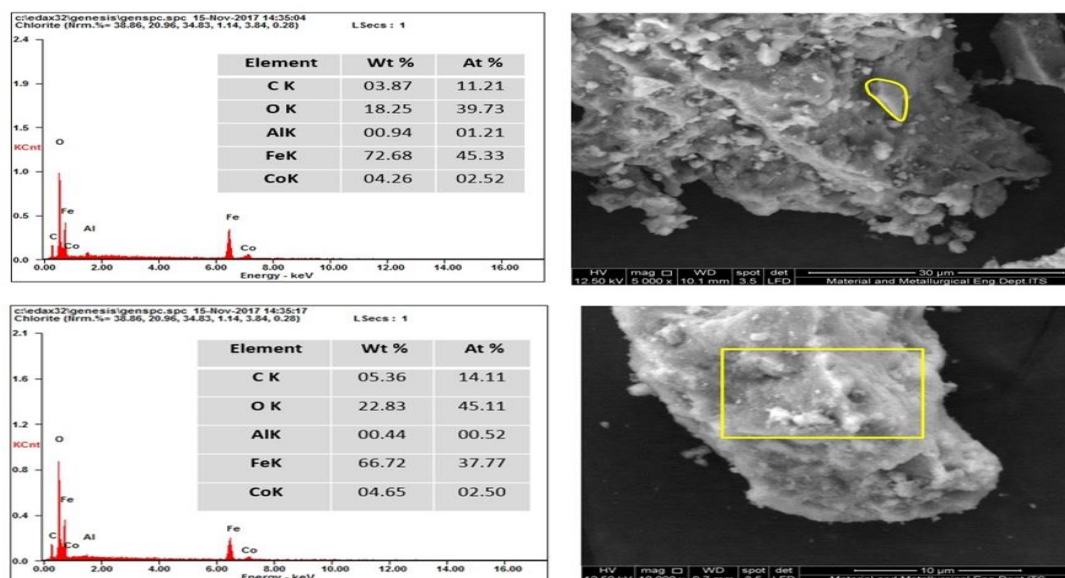


Figure 5. SEM of GO-Fe₃O₄

4. Conclusion

We have successfully demonstrated the synthesis GO from waste environmental using modified Hummers. This study was successfully to confirm the formation of GO-Fe₃O₄ of coconut shell with

characterization of XRD, FTIR, SEM and Raman spectroscopy. From the present study it can be concluded that this research has low cost and effective to decrease much of environmental.

5. References

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