Synthesis and Characterization of Fe$_3$O$_4$@rGO Composite with Wet-Mixing (ex-situ) Process

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Abstract. Fe$_3$O$_4$rGO composite synthesis has been successfully made in three stages. First, synthesis of Fe$_3$O$_4$ particles from the iron sand with coprecipitation method. Second, the synthesis of rGO from coconut shell by ultrasonication method. Third, the synthesis of nanocomposite Fe$_3$O$_4$rGO using a wet mixing method by mixing Fe$_3$O$_4$, rGO, and alcohol. The XRD characterization results show that the phase structure of the Fe$_3$O$_4$rGO composite is successfully formed. The presence of FTIR supports this results in the form of wave absorption patterns identified as having Fe-O, C = O and C = C bonds which state that Fe$_3$O$_4$ surface modification has been successfully carried out using rGO. Also, the results of the VSM characterization showed that the saturation magnetization in the sample was 23.5 emu/g. This value is high, and the increasing rGO in the composites, the magnetic components become relatively lower which results in full magnetization values decreasing, and the results of TEM characterization show that Fe$_3$O$_4$rGO nanocomposites have successfully formed core-shell formations.

1. Introduction

Magnetite (Fe$_3$O$_4$) is one of the iron dioxides in addition to maghemite ($\gamma$-Fe$_2$O$_3$) and hematite ($\alpha$-Fe$_2$O$_3$). Magnetite is known as black iron oxide, which is the most powerful magnetic oxide of the metal [1]. Broadly speaking magnetite nanoparticles are used in the separation of proteins or enzymes, drug administration and DNA purification (Deoxyribonucleic Acid). Besides that, it is also used to remove catalysts and toxic elements from industrial waste [2].

In the last few years, a lot of research has been done on the combination of materials with each other. One of the materials that can be coated on magnetic materials is reduced graphene oxide (rGO). Advantages such as electrical, thermal and mechanical properties and a large cross-sectional area make reduced Graphene Oxide (rGO) selected as a coating material on Fe$_3$O$_4$. The O-H bond formed in rGO can act as a center of polarization so that it can produce a greater absorption intensity [3].

Reduced Graphene Oxide Material (rGO) is graphene oxide where carbon atoms from graphene undergo oxidation and reduction. In the oxidation process, several oxygens and hydrogen atoms bind to carbon atoms, the result of this oxidation process called graphene oxide. While in the reduction process, there is the release of several hydrogen and oxygen bonds from graphene oxide so that a structure that almost resembles graphene is obtained. The result of this reduction process is called Reduced Graphene Oxide (rGO) [4]. In this research on the synthesis of Fe$_3$O$_4$rGO nanocomposite using the wet mixing method. The wet mixing method is a mixing process where matrix and filler powders are mixed first with a polar solvent. This method is used if the material (matrix and filler) used is easily oxidized. The mixing of Fe$_3$O$_4$ and rGO will later form Fe$_3$O$_4$ @ rGO core-shell [5].
Qin et al. (2014) performed the synthesis and characterization of Fe$_3$O$_4$@rGO nanoparticle composites using the coprecipitation method and reduction which showed that Fe$_3$O$_4$ had a higher adsorbent capacity of 3.7 times and the adsorption rate was thirty times faster [6]. Then Vuong Hoan et al. (2016) also performed Fe$_3$O$_4$@rGO nanocomposite synthesis using the in-situ method which resulted in excellent adsorption of heavy metal ions which showed that this was a potential adsorbent for water sources contaminated by heavy metals [7]. Liang et al. (2016) also carried out the synthesis of Fe$_3$O$_4$@rGO composites using the hydrothermal method on the effect of loading Fe$_3$O$_4$ on the performance of Fe$_3$O$_4$@rGO composites for lithium-ion batteries by making the best component ratio for cycling performance [3,8]. In this study, the synthesis of Fe$_3$O$_4$ derived from iron sand using the co-precipitation method and the synthesis of rGO using ultrasonication and Fe$_3$O$_4$@rGO composite synthesis using the wet mixing method; Furthermore Fe$_3$O$_4$@rGO was characterized, XRD for analysis of its crystal structure and phase, FTIR for functional group analysis, VSM for analysis of its soft magnetic properties and microstructure with TEM.

2. Materials and Method

Synthesis of Fe$_3$O$_4$@rGO composite was initiated by mixing Fe$_3$O$_4$ powder, and rGO powder and then alcohol was added to the mixture. Furthermore stirring using a magnetic stirrer hot plate, refers to a previous study conducted by Munasir et al. [9]. After going through a stirring process, a slurry will be formed and the drying process will be carried out at room temperature and will produce the powder. The result of the combination of the two particles will be obtained Fe$_3$O$_4$@rGO composite which is ready to be characterized.

2.1 Materials

The material used for the formation of Fe$_3$O$_4$@rGO composites is Fe3O4 made from iron sand [9], rGO made from coconut shell through the Hammers process and calcination treatment [10] and on Fe$_3$O$_4$@rGO composite formation which requires a polar solution. The polar solution used is alcohol (n-butanol).

2.2 Synthesis and Characterisation

Stages in the process of preparing Fe3O4 nanoparticles from the iron sand base material, using the co-precipitation method. This method, proven to be chosen because the process is relatively easy, inexpensive and requires a relatively short time [9]. And for rGO particles using the ultra-sonication method. This method also aims to minimize and homogenize particle size. In the final stage, the process of Fe$_3$O$_4$@rGO composite formation was carried out using the wet mixing method. This method was chosen to avoid further oxidation. In this process, giving polar solvents (n-butanol) is to facilitate the process of mixing the material and to coat the surface of the material so that the oxidation process does not occur in the material. Characterization including XRD test is used to characterize the crystal structure, FTIR test functions to determine functional groups, the vibration of functional groups by infrared waves; VSM test to see the nature of magnetization by the applied external magnetic field; and TEM test to see the core-shell formation pattern and particle size [11].

3. Result and Discussions

3.1. X-Ray Diffraction Analysis

The XRD test results showed that there was a diffraction peak of rGO nanoparticles at an angle of 2 pada at an angle of 23.40 ° and a diffraction peak of Fe$_3$O$_4$ nanoparticles at 30.4 °, 35.8 °, 43.4 °, 53.7 °, 57.5 ° and 63.0 ° which corresponded to the crystal respectively (220), (311), (400), (422), (511) and (440) which also show unchanged peaks of Fe$_3$O$_4$. The synthesized Fe$_3$O$_4$@rGO nanocomposite peaks of diffraction formed were also compared with previous studies. For example in Vuong Hoan et al., 2016 also obtained diffraction peaks of Fe$_3$O$_4$@rGO nanoparticles at 30.1 °, 36.0 °, 43.0 °, 58.0 °, 63.0 ° [7]. Based on the results obtained, it shows that the composite has been successfully formed with the appearance of the characteristic peaks of Fe$_3$O$_4$ and rGO.
3.2. Fourier-transform Infrared Spectroscopy Analysis

Based on the FTIR test results of the synthesis of Fe$_3$O$_4$, rGO and Fe$_3$O$_4$@rGO particles, the wave absorption patterns are typical of both (see Figure 2). Fe-O group vibration found at wave number 580 cm$^{-1}$ indicates an indication of particles Fe$_3$O$_4$ and C = O bonds at wave number 1750 cm$^{-1}$ and C = C bond at wave number 1680 cm$^{-1}$ states that surface modification of rGO has succeeded do. In the Vuong Hoan et al. (2016) study Fe-O found at wave number 578 cm$^{-1}$ indicated an indication of particles Fe$_3$O$_4$ and C = O bonds at wave number 1730 cm$^{-1}$ [7]. The functional groups resulting from these characterizations are similar to the characteristics of the Fe$_3$O$_4$@rGO nanocomposite functional group obtained from the reference [9,10].

3.3. Vibrating Sample Magnetometer

Based on the results of the VSM test of Fe$_3$O$_4$@rGO composite synthesis, the saturation magnetization value in the sample was around 23.5 emu / g (see Figure 3). This value is high, because
in Prasad et al., 2017 for Fe$_3$O$_4$ and Fe$_3$O$_4$@rGO nanocomposite was 15.3 emu/g and 12.6 emu/g [5]. With the increase in rGO in the composite, the magnetic component is estimated to be relatively lower which results in a decrease in the full magnetization value, and this is because of the shell-rGO thickness increases. When the magnetite sample is covered by rGO (shell), the interaction between particles will be weakened so that the aggregation between particles also decreases, so the coercivity and magnetization of magnetite Fe$_3$O$_4$ (core) material will also decrease, in the formation of Fe$_3$O$_4$ @ rGO. [10,11].

3.4 Transmission Electron Microscopy

Based on the results of the Fe$_3$O$_4$@rGO nanocomposite TEM test, it was seen that the particles of Fe$_3$O$_4$ were black and rGO was light gray, and it was observed that the rGO enveloped the Fe$_3$O$_4$ particles as a whole. Also, Fe$_3$O$_4$@rGO particles appear round in shape and agglomeration between particles occurs. In the study of Cao et al., 2015 it was also seen that the particles of black Fe$_3$O$_4$ and light gray rGO particles were observed to envelop the entire Fe$_3$O$_4$ particles [5]. Besides, Fe$_3$O$_4$@rGO particles appear round in shape, and there is agglomeration between other particles of rGO (see Figure 4). Based on TEM comparison images from previous studies, it can be said that the results of TEM experiments obtained can be stated to form core-shell formations [12].

4. Conclusion

Fe$_3$O$_4$ and rGO composites were successfully synthesized by the wet-mixing (ex-situ) method, this was confirmed by the results of the characteristic diffraction pattern with magnetite Fe$_3$O$_4$ crystal field
peaks and functional group profiles: Fe-O, C = O and C = C belongs to Fe₃O₄ and rGO; this indicates that the surface modification process of Fe₃O₄ has been successfully formed by rGO (as shell). Fe₃O₄ and rGO composites are soft magnetic and have built the core-shell structure of Fe₃O₄@rGO.

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