Modified Working Electrode by Magnetite Nanocomposite for Electrochemical Sensor Application

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Abstract. In this research, magnetite (Fe_3O_4) has been successfully composite with graphene by a sonochemical method. The formation of the nanocomposite was confirmed by X-ray diffraction (XRD). The XRD pattern showed the magnetic phase of crystalline Fe_3O_4that could be attributed to the cubic structure. However, the graphene peak did not appear in the XRD pattern of the nanocomposite. The crystallite sizes of the Fe_3O_4 nanoparticles were estimated about 10 nm. Furthermore, the morphology of the nanocomposite was investigated using scanning electron microscope (SEM). The SEM image showed the interaction and decoration of graphene sheets with Fe_3O_4.Meanwhile, the synthesized graphene-Fe_3O_4 nanocomposite can be separated by applied an external magnetic field, thus demonstrating the magnetic properties of the nanocomposite. A working electrode was fabricated by modified a surface of carbon paste electrode (CPE) with the graphene-Fe_3O_4 nanocomposite. The modified electrode was characterized using cyclic voltammetry (CV) to evaluate electrochemical properties. By Modifying the surface of the working electrode with graphene-Fe_3O_4 nanocomposite, it can be increased the oxidation and reduction peak current that refer to excellent electron transfer materials. Therefore, the results of this research showed that the use of the graphene-Fe_3O_4 nanocomposite is very feasible for electrochemical sensor.

Keywords. Electrochemical sensor, graphene, magnetite, nanocomposite, and sonochemical method.

1. Introduction

Electrochemical sensors are a device to detect and analyze a specific compound by measured the chemical signals produced. The chemical signals can be measured by analyzing current, potential, or

conductance changes [1]. Electrochemical sensors have been applied for many analysis, such as in clinical [2], environmental [3], [4], biological [5], pharmaceutical, and process control in food processing [6]. The attraction of applying electrochemical sensors based on their high sensitivity, good selectivity, inexpensive, the simplicity of operation, simple pretreatment procedure, and fast analytical time.

Nowadays, many researchers are focusing to improve the analytical performance of electrochemical sensors. Highly sensitivity is one of the main keys to obtain more precise detection results. Applying nanomaterials to electrochemical sensors have found able to enhance the effective surface area of electrodes and accelerate electron transfer across the electrode surface, thus improve the sensitivity and the stability of analytical response [2]. Moreover, nanomaterials exhibit fabulous in optical, electrical, mechanical, catalytic, thermal, and magnetic characteristics by comparing with bulk materials.

Magnetite nanoparticles (Fe_3O_4) is one of the nanomaterials that has attracted much research and has been using in various applications, such as magnetic resonance imaging (MRI), drug delivery, cell labeling, hyperthermia, removal of contaminants from water, and biosensing [7]. This is because of their superparamagnetic property, large surface area, biocompatibility, and low toxicity. However, high energy surface of Fe_3O_4 leads it to agglomerate in clusters and Fe_3O_4 have poor conductivity. Therefore, composing Fe_3O_4 with a material with high electrical conductivity is an effort to produce new material that can reduce agglomeration, increase the conductivity, and enhance detection signal. Graphene is one of good material for electrochemical sensors because of its unique structural and catalytic properties, high electrical and thermal conductivity, large surface area, and high loading of biocatalysts [8], [9]. Due to its unique properties, graphene is very competent to develop in biological applications and energy storage, like fuel cells, batteries, and supercapacitors [10]. Accordingly, composing Fe_3O_4 with graphene can integrate the advantages possessed of Fe_3O_4 and graphene and may offer great application potential in electrochemical sensors.

Magnetite (Fe_3O_4) have been composite with multi-walled carbon nanotube (MWCNT) by using coprecipitation-ultrasonic irradiation [10] and sonochemical method [11]. In this work, a sonochemical method at room temperature was used to synthesize graphene-Fe_3O_4 nanocomposite. The graphene-Fe_3O_4 was prepared using graphene powder, $FeCl_3.6H_2O$, and $FeCl_2.4H_2O$ as starting materials. The characteristic of graphene-Fe_3O_4 confirmed by XRD, SEM, and CV. The result displayed that modified the surface of the working electrode with graphene-Fe_3O_4 can enhance of reduction and oxidation currents. It was indicated that the graphene-Fe_3O_4 nanocomposite could provide good material for constructing electrochemical sensors.

2. Materials and methods

2.1. Synthesis of Graphene-Fe₃O₄ Nanocomposite

The synthesis of the graphene-Fe_3O_4 nanocomposite was started by dispersed graphene into ethanol and ultrasonicated for 10 min. Then, $FeCl_3 \cdot 6H_2O$ and $FeCl_2.4H_2O$ with a molar ratio 2:1 completely dissolved in water and added to the graphene suspension. Subsequently, ammonia solution was added slowly until the pH of the resulting solution maintained at 10 under ultrasonic irradiation for 30 min. The nanocomposite collected by magnetic separation and washed with water and ethanol several times. Finally, the produced nanocomposite was dried in an oven at 100 ºC to get graphene-Fe_3O_4 nanocomposite powder.

2.2. Fabrication of Working Electrode

The bare carbon paste electrode (CPE) as the basic working electrode was prepared by mixed 70 wt% graphite powder and 30 wt% paraffin oil. The mixture of the carbon paste was packed into one end of a glass tube. A copper wire was inserted establish electrical contact. The CPE surface was smoothed by polishing it on a paper surface. To prepare a modified surface electrode (CPE/graphene-Fe_3O_4), 5

µL of 1 mg.mL^{-1} graphene-Fe$_3$O$_4$ nanocomposite solution in ethanol was dropped onto the surface of bare CPE.

2.3. Characterization

The formation of graphene-Fe$_3$O$_4$, namely crystalline phase was analyzed using X-ray diffractometer (XRD). The morphology of graphene-Fe$_3$O$_4$investigated using scanning electron microscope (SEM).Cyclic voltammetry (CV) was used for measuring the electrochemical performance with three-electrode system consisted of the bare CPE or CPE/graphene-Fe$_3$O$_4$as a working electrode, platinum (Pt) wire as a counter electrode and silver/silver chloride (Ag/AgCl) as a reference electrode.

3. Results and discussion

3.1. XRD Analysis

The XRD patterns of the graphene-Fe$_3$O$_4$ nanocomposite in Figure 1 was found to be the characteristic peaks at *2θ* = (30.14°, 35.86°, 43.32°, 53.96°, 57.40°, and 62.92º) corresponding to (220), (311), (400), (422), (511), (440). These peaks are similar to Fe$_3$O$_4$ with spinel inverse cubic structure based on JCPDS card no. 19-0629. The broad peaks suggest that the crystalline size of Fe$_3$O$_4$ nanoparticles are very small and the sharp peak indicate the good crystallinity phase of Fe$_3$O$_4$. Moreover, the Fe$_3$O$_4$ nanoparticles have a fine crystalline quality cause of the absence of other impurity peaks from the XRD patterns. However, the diffraction peak attributed to graphene was no evidence. The XRD patterns only showed a hump between *2θ* = (23° to 28°) indicate the formation of graphene [12].

According to the XRD data, the average crystallite size of Fe$_3$O$_4$ nanoparticles loaded on graphene nanosheets is estimated using Debye-Scherrer formula at *2θ* = 35.86° found to be 10.05 nm. This result was smaller than Shenmin Zhu, and Deosarkar has reported for preparation Fe$_3$O$_4$-graphene nanocomposite by sonochemical co-precipitation method, which was 45 nm and 21.22 nm, respectively [13], [14]. The acoustic cavitation arises from ultrasonic irradiation resulting in local high temperature and pressure instantaneously. These extreme conditions cause the formation of smaller sized particles.
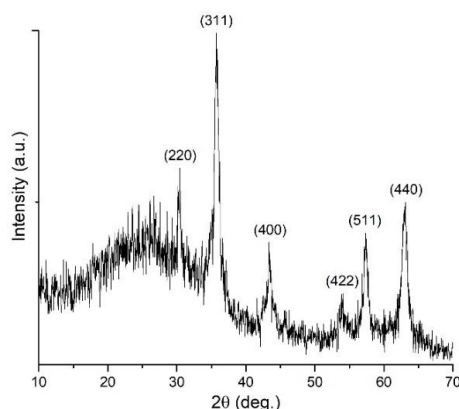

Figure 1. XRD patterns of the graphene-Fe$_3$O$_4$ nanocomposite

3.2. Morphological Analysis

Figure 2.a presented the SEM image of the graphene-Fe$_3$O$_4$ nanocomposite. The SEM image showed some aggregation of Fe$_3$O$_4$because of their surface energy interaction and plenty of Fe$_3$O$_4$ nanoparticles attached to the graphene nanosheets. The agglomeration size distribution of the Fe$_3$O$_4$ nanoparticles was estimated about 8 nm to 10 nm, as shown in the Figure 2.b. The attachment Fe$_3$O$_4$ nanoparticles between the layer graphene nanosheets can reduce the aggregation of Fe$_3$O$_4$ nanoparticles. The distribution of Fe$_3$O$_4$ nanoparticles on the layer graphene lead to the formation of

porous nanocomposite with a large amount of void space. That porous nanocomposite with several void spaces can enhance the cyclic performance [14].
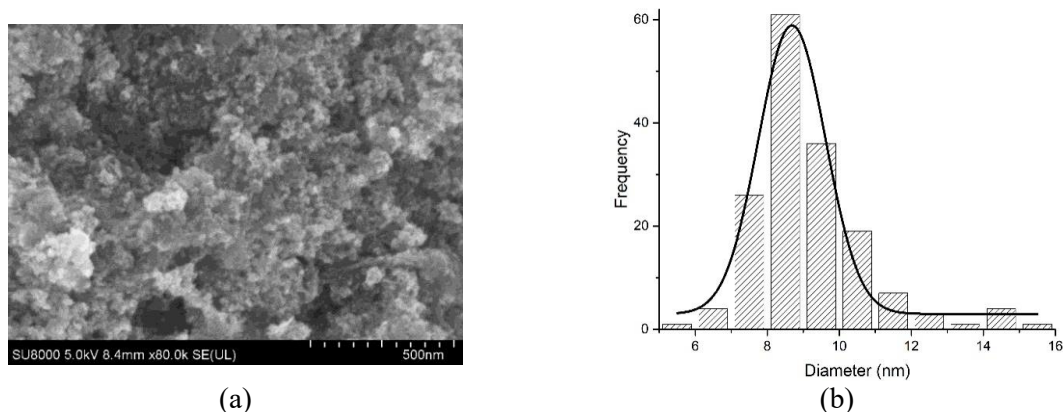

(a)   (b)

Figure 2. (a) SEM image of the graphene-Fe$_3$O$_4$ nanocomposite and (b) the agglomeration size distribution of the Fe$_3$O$_4$ nanoparticles

3.3. Magnetic Properties
The magnetic properties of graphene-Fe$_3$O$_4$was investigated by looking at the attraction when placing near a permanent magnet. For the experiment, the graphene-Fe$_3$O$_4$was dispersed into ethanol (1 mg/mL^{-1}) via ultrasonication. Then, this suspension attracted using a magnet for 5 min. The experiment resulted that graphene-Fe$_3$O$_4$can be uniformly and dispersed stably in ethanol. After 5 min, graphene-Fe$_3$O$_4$ attracted to the vial wall near to magnet and separated from the solvent. Although the Fe$_3$O$_4$ particles attached to the graphene sheets, the nanocomposite still has an excellent magnetic response. It is indicating that the graphene-Fe$_3$O$_4$ has easy recycling attributes and useful for magnetic separation application [15], [16].

3.4. Electrochemical Properties
Cyclic voltammetry has done to study the electrochemical properties. Figure 3.a displayed a CV diagram of the bare CPE and CPE/graphene-Fe$_3$O$_4$ electrode in 0.01 M K$_3$[Fe(CN)$_6$]/ K$_4$[Fe(CN)$_6$]-0.1 M NaCl at the scan rate of 100 mVs^{-1}. A couple of redox peaks corresponding to the reduction and oxidation of [Fe(CN)$_6$]$^{3-/4-}$ were observed for all sample electrode indicating a reversible electron transfer process. Both anodic (I_{pa}) and cathodic(I_{pc}) peak current were increased after the bare CPE was modified. The I_{pa} was increased until 76.58 % and I_{pc} also increase until 346.96 % from the bare CPE. The data saw that applying nanomaterial as the electrode surface can enhance the redox currents. Besides that, the peak-potential separations (ΔE_p) getting smaller and the I_{pa} and I_{pc} moving closer to each other reveal to the better transfer electron media.

The effective surface area (A) was determined using Randles-Servcik equation for a reversible process as follow [9]:

$$Ip = \left(2.69 \times 10^5\right) n^{3/2} A \cdot D^{1/2} \cdot v^{1/2} \cdot C \qquad (1)$$

where I_p (A) is the peak current, n is the number of electron transfer in the reaction, A (cm^2) is the effective surface area of electrode, D (cm^{2}s^{-1}) is the diffusion coefficient of the reduced, C (mol cm^{-3}) is the bulk concentration of the reduced form, and v(V s^{-1})is the scan rate. For this calculation, $n = 1$, $D = (7.6 \times 10^{-6})$ cm^{2}s^{-1}, $C = 10^{-5}$ molcm^{-3}. It was calculated that the effective surface area of CPE/graphene-Fe$_3$O$_4$ (0.0436 cm^2) > bare CPE (0.0247 cm^2). The result indicated that the use of nanomaterial for modified surface electrode could improve the electroactive surface area of the electrode.
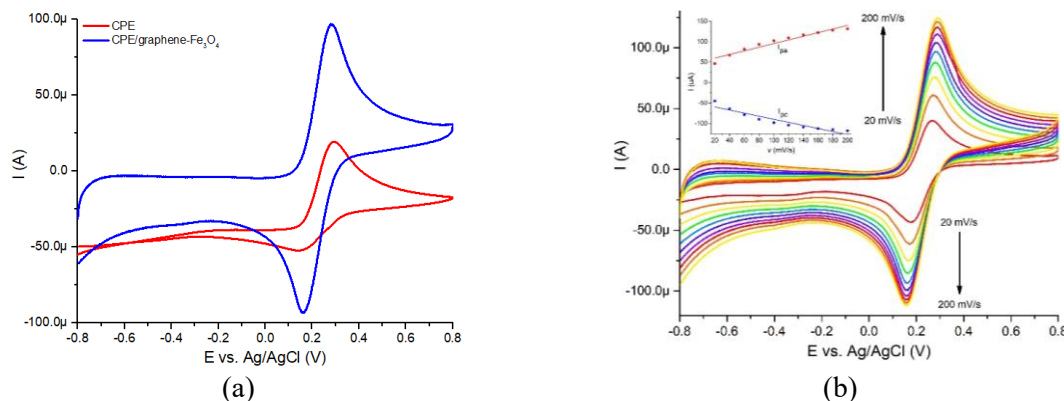
(a)   (b)

Figure 3. (a) CVs of the bare CPE and CPE/graphene-Fe$_3$O$_4$ electrode and (b) effect of scan rate from CPE/graphene-Fe$_3$O$_4$ modified electrode at scan rate (20, 40, 60, 80, 100, 120, 140, 160, 180, and 200) mV·s^{-1}, and (inset) plot of the relationship between anodic and cathodic peak current with scan rate

The effect of scan rate from CPE/graphene-Fe$_3$O$_4$ modified electrode shown in Figure 3.b. From the CV diagram, the anodic (I_{pa}) and cathodic (I_{pc}) peak current were increased linearly by increasing in the scan rate (v) from 20 mVs^{-1} until 200 mVs^{-1}. The plot of the relationship between anodic and cathodic peak current with scan rate inserted in Fig 4b. The linear line equation of I_{pa} (μA) = 0.4452 v + 50.712 (mVs^{-1}), R = 0.9411, and I_{pc} (μA) = –0.3754 v –52.086 (mVs^{-1}), R = 0.8953. It may suggest that the mass transfer of electrochemical kinetics in the electrode mainly diffusion controlled [17]. It can also declare that the combination of Fe$_3$O$_4$ and graphene for the modified surface electrode provided an excellent mediated transfer between the electrode and electrolyte, thus leading to the promotion of the electron transfer rate. The graphene-Fe$_3$O$_4$ nanocomposite is offering better performance when applied as a working electrode in the electrochemical sensor.

4. Conclusions

Graphene-Fe$_3$O$_4$nanocomposite synthesized by a simple, effective sonochemical method at room temperature. The nanocomposite has a good crystallinity with well size and shape of Fe$_3$O$_4$ nanoparticles decorated graphene nanosheets. It also exhibits an excellent magnetic response. The electrochemical studies demonstrated the graphene-Fe$_3$O$_4$ nanocomposite could improve the electroactive surface area of the electrode and mediated electron transfer between electrode and electrolyte. It was due to the integration of the unique properties of Fe$_3$O$_4$ and graphene. Graphene-Fe$_3$O$_4$ nanocomposite can lead to the promotion of the electron transfer rate and enhancement the redox currents, so it was generated higher sensitivity of output signal. Accordingly, graphene-Fe$_3$O$_4$ nanocomposite would provide a great promising material to apply in the development of high-performance electrochemical sensors, including biosensor based on electrochemical procedure.

References

[1]   A. Chaubey and B. Malhotra, "Mediated biosensors," *Biosens. Bioelectron.*, vol. 17, no. 6–7, pp. 441–456, 2002.
[2]   C. I. Justino, T. A. Rocha-Santos, and A. C. Duarte, "Advances in point-of-care technologies with biosensors based on carbon nanotubes," *TrAC Trends Anal. Chem.*, vol. 45, pp. 24–36, 2013.
[3]   N. L. W. Septiani, B. Yuliarto, H. K. Dipojono, and others, "Multiwalled carbon nanotubes–zinc oxide nanocomposites as low temperature toluene gas sensor," *Appl. Phys. A*, vol. 123, no. 3, p. 166, 2017.
[4]   Yuliarto B, Ramadhani M, Nugraha F, Septiani N L W, and Hamam K A, "Enhancement of SO$_2$ gas sensing performance using ZnO nanorod thin films: the role of deposition time," *Springer US*, vol. 54, pp. 4543–4554, 2017.

[5] P. Bollella *et al.*, "Beyond graphene: electrochemical sensors and biosensors for biomarkers detection," *Biosens. Bioelectron.*, vol. 89, pp. 152–166, 2017.

[6] Y. Song, Y. Luo, C. Zhu, H. Li, D. Du, and Y. Lin, "Recent advances in electrochemical biosensors based on graphene two-dimensional nanomaterials," *Biosens. Bioelectron.*, vol. 76, pp. 195–212, 2016.

[7] T. A. Rocha-Santos, "Sensors and biosensors based on magnetic nanoparticles," *TrAC Trends Anal. Chem.*, vol. 62, pp. 28–36, 2014.

[8] F. He, Z. He, J. Xie, Y. Li, and others, "IR and Raman Spectra Properties of Bi_2O_3-ZnO-B_2O_3-BaO Quaternary Glass System," *Am. J. Anal. Chem.*, vol. 5, no. 16, p. 1142, 2014.

[9] H. Teymourian, A. Salimi, and S. Khezrian, "Fe_3O_4 magnetic nanoparticles/reduced graphene oxide nanosheets as a novel electrochemical and bioeletrochemical sensing platform," *Biosens. Bioelectron.*, vol. 49, pp. 1–8, 2013.

[10] R. Rahmawati, M. G. Permana, B. Harison, B. Yuliarto, D. Kurniadi, and others, "Optimization of Frequency and Stirring Rate for Synthesis of Magnetite (Fe_3O_4) Nanoparticles by Using Coprecipitation-Ultrasonic Irradiation Methods," *Procedia Eng.*, vol. 170, pp. 55–59, 2017.

[11] R. Rahmawati *et al.*, "Preparation of MWCNT-Fe_3O_4 Nanocomposites from Iron Sand Using Sonochemical Route," in *IOP Conference Series: Materials Science and Engineering*, 2017, vol. 202, p. 012013.

[12] B. Jaleh, A. Khalilipour, S. Habibi, M. Niyaifar, and M. Nasrollahzadeh, "Synthesis, characterization, magnetic and catalytic properties of graphene oxide/Fe_3O_4," *J. Mater. Sci. Mater. Electron.*, vol. 28, no. 6, pp. 4974–4983, 2017.

[13] J. Zhu, G. Zhang, S. Gu, and B. Lu, "SnO_2 Nanorods on ZnO Nanofibers: A New Class of Hierarchical Nanostructures Enabled by Electrospinning as Anode Material for High-Performance Lithium-Ion Batteries," *Electrochimica Acta*, vol. 150, pp. 308–313, Dec. 2014.

[14] M. Deosarkar, S. Pawar, and B. Bhanvase, "In situ sonochemical synthesis of Fe_3O_4–graphene nanocomposite for lithium rechargeable batteries," *Chem. Eng. Process. Process Intensif.*, vol. 83, pp. 49–55, 2014.

[15] K.-K. Cheng *et al.*, "Sugarcane bagasse hemicellulose hydrolysate for ethanol production by acid recovery process," *Biochem. Eng. J.*, vol. 38, no. 1, pp. 105–109, 2008.

[16] D. Yang *et al.*, "In situ synthesized rGO–Fe_3O_4 nanocomposites as enzyme immobilization support for achieving high activity recovery and easy recycling," *Biochem. Eng. J.*, vol. 105, pp. 273–280, 2016.

[17] J. Salamon *et al.*, "One-pot synthesis of magnetite nanorods/graphene composites and its catalytic activity toward electrochemical detection of dopamine," *Biosens. Bioelectron.*, vol. 64, pp. 269–276, 2015.