Synthesis and characterization of reduced graphene oxide-iron oxide nanocomposite as a potential fuel cell electrocatalyst

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Abstract. Driven by the high demand for commercialization of fuel cell (FC) technology, a design of potential oxygen reduction reaction electrocatalyst based on reduced graphene oxide (rGO) and iron oxide (Fe3O4) nanocomposite has been described and denoted as rGO/Fe3O4. The nanocomposite was synthesized by means of facile one-pot process. The resultant rGO/Fe3O4 was physically and electrochemically characterized by using Fourier Transform Infrared Spectroscopy (FT-IR), X-Ray Diffractrogram (XRD), Scanning Electron Microscopy (SEM), Cyclic Voltammetry, (CV) and Electrochemical Impedance Spectroscopy (EIS). The FTIR analysis shows the formation of rGO/Fe3O4 from the presence of C=C, C-C and Fe-O bonds in the spectrum of the indicating the synthesis material is successfully obtained. XRD analysis also confirms the presence of rGO and Fe3O4 in the composite by hematite structure indexed peak of diffractogram. Scanning Electron Microscopy (SEM) image depicts the attachments Fe3O4 onto the surfaces of rGO. The composite was then dissolved in the solvent and drop-casted on the glassy carbon electrode (GCE) for electrochemical analysis. Cyclic Voltammetry (CV) shows increment in current responses of nearly two and half folds for rGO/Fe3O4/GCE compared to bare GCE. Electrochemical Impedance Spectroscopy (EIS) shows a stable electron transfers process with lower charge transfer resistance (Rct) of the nanocomposite modified electrode which due to the synergistic effect between rGO and Fe3O4. The results of the analysis show the compound could be a promising candidate as an electrocatalyst for fuel cell.

Keywords: fuel cell, oxygen reduction reaction, magnetite, graphene, iron oxide
1. Introduction
Roughly 65 % of the world’s energy production is reported to base on non-renewable resources especially fossil fuel [15]. In urge of controlling fossil fuels depletion, fuel cell has been invented to overcome the issue. Platinum which has been used as the electrocatalyst in the system of fuel cell, however has resulted in lacks of performances despite being the better electrode amongst other materials [11]. To add on, it has heavy cost consumption since the metal is precious and this will eventually cause economical rises in costing.

Graphene is a two-dimensional carbon known for its unique structure and physicochemical properties such as possession of sp² hybridization, large surface area and good conductor [1,6]. In addition, graphene has great amount of favorable edge carbons electrochemically which assist electron transfer between molecules to an electrode substrate in low overpotential condition [5]. Chemical reduction of graphene oxide makes the substance to exist as a compound between graphene and graphene oxide [10].

Magnetic nanoparticles, also known as magnetite consist of iron (III) oxide nanoparticles (Fe₃O₄) on the other hand could be prepared in a simple method. The nanoparticles possess strong magnetism which makes it useful in various applications [4]. On the other hand, Fe(II) and Fe(III) elements possesses strong tendency on undergoing hydrolysis and hence fabricate oxidation groups [20]. Combination of magnetite with other material gives the compound better characteristics and hence enhanced performance which makes the nanocomposite as most preferred in most studies.

Unification of the materials into a composite helps to enhance the catalytic activity through the increase in surface area of the nanocomposite contributed mainly from graphene. Addition with metal oxide compound gives significant stability and indirectly adds up surface area of the nanocomposite [20]. Recent studies show that Fe₃O₄ combined with carbon-related materials such as graphene increase the performances of that material in various fields such as biosensors, determinations and environmental remediation [14,19]. The nanocomposite have been used in determining amino acids in sugarcanes and as substrate in enzyme immobilization [18]. Usage of the nanocomposite in the field of electrochemistry is being pioneer approach, where the material can be used directly without any addition of other element for stability and endurance.

Through this paper, rGO/Fe₃O₄ was aimed to be a promising electrocatalyst especially as a substitute for platinum electrodes in fuel cell. Through this study, the economic issues regarding costings of ongoing energy production using platinum could be curbed as the synthesized nanocomposite is relatively cheaper in sense production costings.

2. Materials and Methods
2.1 Reagents and Chemicals
Graphite powder was used for the synthesis of graphene oxide through the oxidation process based on the modified Hummers method [3]. Other chemicals required for Hummers method is sodium nitrate (NaNO₃), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂), concentrated sulphuric acid (H₂SO₄), hydrazine hydrate and hydrochloric acid (HCL). Chemicals required to prepare magnetic iron (II,III) oxide is iron (III) 6-hydrate, iron (II) 4-hydrate, potassium hexacyanoferrate (II), potassium hexacyanoferrate (III), and ammonia solution. All chemicals were purchased from Sigma Aldrich, USA. For the purpose of diluting and washing the substances, deionized water of 18.2 mΩcm is used.

2.2. Synthesis of reduced graphene oxide/ Fe₃O₄ Magnetite Nanoparticles (rGO/Fe₃O₄)
Synthesis of graphene oxide (GO) was done following the modified Hummers’ method [3,7]. Approximately 1 g of graphite was put in into a mixture of 0.5 g of sodium nitrate and concentrated sulfuric acid then placed in ice bath condition and stirred for 30 minutes. KMnO₄ was put into the solution while the reaction temperature does not exceed 98 °C and stirred for 2 hours. The solution then diluted with 100 mL deionized water. The reaction was stalled using 10 mL hydrogen peroxide
(H$_2$O$_2$) and the solution was filtered using a vacuum filtration system. The precipitate then dried for approximately 12 hours at 60 °C.

The amalgamation of reduced graphene oxide/iron oxide (rGO/Fe$_3$O$_4$) nanocomposite is done by in-situ method, where magnetite will be decorated on reduced graphene oxide (rGO) using the GO powder which was synthesized using Modified Hummers’ method. Approximately 0.7 g of graphene oxide is added into 450 mL of deionized water. The aqueous solution of ferric chloride (Fe$_3$$^{3+}$) and ferrous chloride (Fe$_2$$^{2+}$) was prepared in a molar ratio of 2:1 in another different beaker. The solution was then added slowly into the GO solution at room temperature while ammonia solution being added ensuring pH 10 of the mixture. The solution was then heated at 90°C with 10 mL of hydrazine hydrate (N$_2$H$_4$) with constant stirring for 4 hours. Hydrazine hydrate was added as reducing agent for reduced graphene oxide (rGO) by eliminating excess O-H functional groups in the compound. The mixture then cooled down till reaching room temperature roughly and then filtered. Black precipitate was washed with deionized water several times to neutralize the pH. The precipitate was then dried at 70°C for 12 hours to obtain rGO/Fe$_3$O$_4$ in powder form.

2.3. Physical and Electrochemical Characterization

The existence of functional groups in a compound or nanocomposite was determined using Fourier Transform Infrared Spectroscopy (FT-IR) Perkin Elmer Spectrum 100. X-Ray Diffraction (XRD) pattern was studied using Rigaku Miniflex II while surface morphology of compound was analyzed using Scanning Electron Microscope (SEM) JEOL JSM 6360LA. The percentage of sample degradation or loss through heat was determined using Thermo-Gravimetric Analysis (TGA) Metler Toledo at the temperature range of 30 °C to 900 °C. Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) was studied using Potentiostat/Galvanostat Autolab PGSTAT302N and obtained data analyzed using Nova 1.11 software. Electrochemical characterization begins with Glass Carbon Electrode (GCE) as itself and also modified with samples as the working electrode, with 3.0 M Ag/AgCl reference electrode. Platinum wire electrode acts as counter electrodes in the system.

3. Results and Discussion

3.1 Physical Characterization

Fourier Transform Infrared Spectroscopy (FT-IR) facilitates to identify the functional group of the synthesized compound. The spectrum of graphite (Figure 1a) shows no peak indicating there is no functional group available hence proving that it is pure compound. Peak 3406 cm$^{-1}$ in GO (Figure 1c) spectrum shows the presence of O-H groups which disappear in the spectrum of rGO and rGO/Fe$_3$O$_4$ (Figure 1b and 1e), indicating the reduction of functional group took place. Presence of other peaks at 1750 cm$^{-1}$ (C=O) and 1220 cm$^{-1}$ (C-O) in GO spectrum was not visible in rGO affirming the reduction in functional groups [21].

In X-Ray diffractogram of Figure 2(c) showing the spectrum of rGO/Fe$_3$O$_4$ there are a total of five peaks observed; at 30.3°, 35.2°, 43.3°, 57.4°, and 62.9°, in which corresponds to (220), (311), (400), (511), and (440) respectively. The obtained peaks were identical to the value in XRD standard value card (ICPDS 19-0629) which verify that the desired product was acquired. The pattern of rGO (Figure 2a) shows the peaks of Fe$_3$O$_4$ with smaller crystallization when compared to rGO/ Fe$_3$O$_4$ with few added peaks, suggesting that Fe$_3$O$_4$ (Figure 2b) in the compound embedded on rGO layers completely [12].
Figure 1: FT-IR spectra of (a) graphite, (b) graphene oxide, (c) reduced graphene oxide, (d) Fe$_3$O$_4$ and (e) rGO/Fe$_3$O$_4$.

Figure 2: XRD images of (a) rGO, (b) Fe$_3$O$_4$ and (c) rGO/Fe$_3$O$_4$.

Scanning Electron Microscope (SEM) helps to analyse the morphological structure of electrocatalyst synthesized. Figure 3(a) represents the image of graphene oxide, which has smoother surfaces compared to Figure 3(b) of rGO which represents as crumpled sheets with wrinkled surfaces, indicating the compound has increased surface area than GO affirming the reduction in functional groups. Figure 3(c) shows a cloudy-like surface of Fe$_3$O$_4$, which was also present in Figure 3(d). From this morphological images, it is concluded that the compound was successfully synthesized with larger surface area and more active sites in order for increased catalytic activity, as can be observed in Figure 3(d) of rGO/Fe$_3$O$_4$, where co-existence of both Fe$_3$O$_4$ and rGO sheet can be observed. In addition, Fe$_3$O$_4$ easily grafted on defected sites of rGO due to less agglomeration [4].
3.2. Electrochemical Characterization

Cyclic Voltammetry (CV) was done to study the electrochemical efficiency of the product. Glassy Carbon Electrode (GCE) was used and later modified with other nanocomposites such as GO, rGO, Fe$_3$O$_4$ and rGO/Fe$_3$O$_4$. The scan rate used in this study is at 50 mV standard for all analysis done. The voltammogram in Figure 4(a) shows rGO/Fe$_3$O$_4$ possess many significant current responses compared to bare GCE and GO or rGO alone. Peak potential separation ($\Delta E_P = E_{Anodic peak} - E_{Cathodic peak}$) of nanocomposite is identical to GCE and other modified electrodes at value of $\Delta E_P = 150$ mV even though it is shifted might be due to electron kinetics [16], suggesting that the electron transfer is rapid and stable with the reversible process [13,17].

Electrochemical Impedance Spectroscopy was conducted to ascertain the electron transfer betwixt the electrolyte and the electrode surface. As seen in Figure 4(b), the charge transfer resistance ($R_{ct}$) decreases as the bare GCE electrode is casted with electrocatalyst from GO to rGO/Fe$_3$O$_4$ on GCE. $R_{ct}$ symbolizes the kinetic resistance of charge transfer in redox reaction between electrode and electrolyte. The Nyquist plot is the most typical in EIS analysis. $R_{ct}$ that represents the semicircle in the Nyquist plot becomes smaller as the value of $R_{ct}$ is smaller. The rGO/Fe$_3$O$_4$ modified electrode possesses discrete and incomplete semicircle compared to bare GCE electrode, hence providing data that $R_{ct}$ is higher in bare GCE compared to the modified electrode [2,8]. Table 1 tabulates the data of $R_{ct}$ obtained from the software based on Nyquist plots of experimented electrodes. Lower $R_{ct}$ indicates the less resistance in electron transfer between the electrode surface which was supported with analysis results of CV [9].
Figure 4: (a) Cyclic Voltammogram (CV) and (b) Electrochemical Impedance Spectroscopy (EIS) comparison for non-modified glassy carbon electrode (bare GCE), and modified GCE with GO/GCE, rGO/GCE, and rGO/Fe$_3$O$_4$/GCE at scan rate of 50 mV/s in 5.0 mM K$_4$[Fe(CN)$_6$] of 1.0 M KCl.

Table 1: $R_{ct}$ value of bare GCE, GO/GCE, rGO/GCE, and rGO/Fe$_3$O$_4$/GCE.

| Electrodes          | $R_{ct}$ (Ωcm$^2$) |
|---------------------|--------------------|
| Bare GCE            | 1386.03            |
| GO/GCE              | 598.58             |
| rGO/GCE             | 476.25             |
| rGO/Fe$_3$O$_4$/GCE | 160.18             |

4. Conclusions

Physical and electrochemical characterization on rGO/Fe$_3$O$_4$ were performed and the result obtained shows that it can be a promising electrocatalyst to substitute the platinum-based electrode in commercial usages. The simple facile one-pot synthesis is successfully done and the electrocatalyst is promisingly can be used to substitute platinum in fuel cell application hereafter. Spectrum of GO shows the presence of O-H groups at 3406 cm$^{-1}$ which shrinks in the spectrum of rGO and rGO/Fe$_3$O$_4$ indicating the reduction of functional group occurs. The spectrum of Fe$_3$O$_4$ shows the presence of Fe peak at 580 cm$^{-1}$ which is also found in spectrum of rGO/Fe$_3$O$_4$, indicating the unification of both compounds as a nanocomposite. Morphological images concludes that the synthesis of the nanocomposite was accomplished with larger surface area for increased catalytic activity and uniformly dispersed of rGO/Fe$_3$O$_4$ can be observed. Electrochemically, peak potential separation of nanocomposite is identical to GCE and other modified electrodes at value of $\Delta E_P = 150$ mV when cyclic voltammetry analysis carried out. Even though the peak is shifted possibly due to electron kinetics suggesting that the electron transfer is rapid and stable with the reversible process. Analysis of EIS on modified GCE with rGO/Fe$_3$O$_4$ observed discrete and incomplete semicircle compared to bare GCE electrode indicates that $R_{ct}$ is minimal in nanocomposite-modified GCE compared to the bare GCE electrode. The resultant of lower $R_{ct}$ testifies the less resistance in electron transfer between the electrode surface which supports the results of CV. The fabrication of bare GCE with the compound is expected enhances the kinetics of ORR and proves that it is at practically usable level. The exercise of rGO/Fe$_3$O$_4$ electrocatalyst in an electrode ORR in fuel cell system is then proposed. This will be the subject for the upcoming report.
References
[1] Deng Y, Qi D, Deng C, Zhang X and Zhao D 2008 Superparamagnetic high-magnetization microspheres with an Fe$_3$O$_4$@SiO$_2$ core and perpendicularly aligned mesoporous SiO$_2$ shell for removal of microcysts Journal of the American Chemical Society 130 28
[2] Farhanini Y, Khing N T, Hao C C, Sang L P, Muhamad N B and Md Saleh N 2018 The electrochemical behavior of zinc oxide/reduced graphene oxide composite electrode in dopamine Malaysian Journal of Analytical Sciences 22 227
[3] Hummers W S and Offeman R E 1958 Preparation of graphitic oxide Journal of the American Chemical Society 80 1339
[4] Krishna R, Dias C, Ventura J and Titus E 2016 Green and facile decoration of Fe$_3$O$_4$ nanoparticles on reduced graphene oxide Materials Today: Proceedings 3 2807
[5] Kui L Ü, Guixia Z and Xiangke W 2012 A brief review of graphene-based material synthesis and its application in environmental pollution management Chinese Science Bulletin 57 1223
[6] Liu Y, Guan M, Feng L and Deng S 2013 Facile and straightforward synthesis of superparamagnetic reduced graphene oxide-Fe$_3$O$_4$ hybrid composite by a solvothermal reaction Nanotechnology 24 025604.
[7] Marcano D C, Kosynkin D V, Berlin J M, Sinitskii A, Sun Z, Slesarev A and Tour J M 2010 Improved synthesis of graphene oxide ACS Nano 4 8
[8] Muhamad N B and Yusoff F 2018 The physical and electrochemical characteristic of gold nanoparticles supported pedot/graphene composite as potential cathode material in fuel cells Malaysian Journal of Analytical Sciences 226 921
[9] Yusoff F, Aziz A, Mohamed N and Ghani S A 2013 Synthesis and characterizations of BSCF at different pH as future cathode materials for fuel cell International Journal of Electrochemical Science 8 10672
[10] Yang X, Zhang X, Ma Y, Huang Y and Chen Y 2009 Superparamagnetic graphene oxide-Fe$_3$O$_4$ nanoparticles hybrid for controlled targeted drug carriers Journals of Material Chemistry 86 2710
[11] Wang K, Pei P, Wang Y, Liao C, Wang W and Huang S 2018 Advanced rechargeable zinc-air battery with parameter optimization Applied Energy 225 848
[12] Bhargava R and Khan S 2017 Effect of reduced graphene oxide (rGO) on structural, optical, and dielectric properties of Mg(OH)$_2$/rGO nanocomposites Advanced Powder Technology 28 2812
[13] Yusoff F, Mohamed N, Azizan A, and Ab Ghani S 2016 The perovskite Ba$_0.5$Sr$_0.5$Co$_{0.8}$Fe$_0.2$O$_3$ - MWCNT modified glassy carbon electrode - Its characterization and capacity in oxygen reduction reaction International Journal of Electrochemical Science, 11 5766
[14] Wang W, Cao H, Zhou X and Liu Z 2014 Synthesis of graphene Graphene: Energy Storage and Conversion Applications 6 21
[15] International Energy Agency 2018 Key World Energy Statistics Officials
[16] Wipf D O, Kristensen E W, Deakin M R and Wightman R M 1988 Fast-Scan Cyclic Voltammetry as a method to measure rapid, heterogeneous electron transfer kinetics Analytical Chemistry 60 306
[17] Nicholson R S 1965 Theory and application of cyclic voltammetry for measurement of electrode reaction kinetics Analytical Chemistry 37 1351
[18] Luiz J, Beluomini M A, Sedenho G C and Stradiotto N R 2017 Determination of amino acids in sugarcane vinasse by ion chromatographic using nickel nanoparticles on reduced graphene oxide modified electrode Microchemical Journal 134 374
[19] Xiao-chun W U, Yan Z, Cong-yu W U and Hai-xia W U 2012 Preparation and characterization of magnetic Fe$_3$O$_4$/CRGO nanocomposites for enzyme immobilization Transactions of Nonferrous Metals Society of China 22 162
[20] Moztahida M, Jang J, Nawaz M, Lim S R and Lee D S 2019 Effect of rGO loading on Fe₃O₄: A visible light assisted catalyst material for carbamazepine degradation *Science of Total Environment* **667** 741

[21] Papiya F, Nandy A, Mondal S and Paban P 2017 Co/Al₂O₃-rGO nanocomposite as cathode electrocatalyst for superior oxygen reduction in microbial fuel cell applications: The effect of nanocomposite composition *Electrochimica Acta* **254** 1

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