The Bio-sensing Performance and Electrochemical Properties of Non-carbonized Electrospun Nanofibers

Noor Hafizah binti Tahal@Tahar and Dr. Tan Huey Ling

Faculty of Chemical Engineering, Universiti Teknologi Mara

***Abstract* – In this study, there are four samples based on Poly (Acrylic Acid) (PAA) and Polyacrylonitrile (PAN) (PAA/PAN) polymer. The sample with only PAA/PAN act as bare which not included with any other materials. The other three samples were mixed with different types of material which is Gold Nanoparticles (AuNPs), Graphene Oxide (GO) nanoparticles and Iron(III)Oxide (Fe_2O_3) nanoparticles. Firstly, the PAA/PAN based polymer solution undergo electrospinning process producing PAA/PAN, PAA/PAN/AuNPs, PAA/PAN/GO and PAA/PAN/Fe_2O_3 nanofibers. The nanofibers then being analyzed by Cyclic Voltammetry (CV) to check whether there is any redox reaction take places on the nanofibers and to study the electrochemical properties of the nanofibers. It was found that PAA/PAN/GO nanofibers showed the best biosensing performance followed by PAA/PAN, PAA/PAN/AuNPs and PAA/PAN/Fe_2O_3 due to electrochemical properties shown by the obtained data. Both concentration dependence study and scan rate dependence study showed PAA/PAN/GO nanofibers have the highest current detection and highest redox reaction, respectively. Thus, the objectives of this study was achieved.**

***Keywords* – biosensor; electrospinning; nanofibers; cyclic voltammetry; electrochemical properties**

I. INTRODUCTION

Wide applications of biosensors in daily life attract many researchers and lead to a bunch of study about biosensor. The term "biosensor" is referring to a "biological sensor." Biosensor is an analytical device equipped with a biological element (bio-element) and a transducer. Bio-element or also called as bio-receptor binds with the analyte and then convert biological signal into an electrical signal generated by the transducer [1]. Biosensors are quite popular especially glucose biosensor where it being used widely in medical field to detect glucose in the blood. Furthermore, applications of biosensors include in food production industry, agricultural industry, drug manufacturing, environmental industry, industrial process applications and pharmaceuticals manufacturing [2].

Biosensor can be classified into three types piezoelectric biosensors, optical biosensors and electrochemical biosensors [2]. Electrochemical biosensors are quite popular in biosensors due to their sensitivity and selectivity, lower detection limits, faster response times, better long term stability, and low cost [3]. Nowadays, there are lot of researches on biosensor to improve their performances, where they are focusing more to nano-technology. Many approaches are being analyzed where the uses of nanofibers help to increase the sensitivity and stability of the biosensor.

Nanofibers act as a key point to improve the biosensor performance due to their characteristics include having high specific surface area and have small diameters [4]. Moreover, nanofibers are high porosity, easy to produce and basically low cost. These unique characteristics make nanofibers such a desirable material for wide range of applications such as semiconductors, catalysts, filtration, recovery of metal ions, catalyst and enzyme carriers, fuel cells, optical, tissue engineering and sensors [5]. It also used in many industries including instrumentation, sensors, automotive, energy, electronics, mechanical, and chemical industries.

Nanofibers can be created through a few techniques for instance template, self-assembly, phase separation, melt-blown and electrospinning [5]. However, the most favorable method to fabricate nanofibers is electrospinning process since it can be produced in a large scale [6]. Moreover, through this process, the diameter of fibers can be modified from nanometers up to microns. In addition, electrospinning process is popular as a quick and simple method in creating nanofibers.

Besides, in order to improve the biosensor performance, nanofibers were added with other materials such as Gold Nanoparticles (AuNPs), Graphene Oxide (GO) and Iron(III)Oxide nanoparticles (Fe_2O_3) to increase its conductivity. Gold nanoparticles have a special characteristics and have been widely used in many kind of applications such as food, environmental, pharmaceutical, chemistry and clinical diagnostics [7]. Researches have been conducted on gold nanoparticles for biosensors where it may enhance the electron transfer and own characteristics to improve biosensor performances.

Next, graphene is known as the most special material, a thin layer of pure carbon, one atom thick, conduct electricity better than silver, conduct heat better than diamond and it is stronger than steel. This uniqueness make many researchers are attracted to used graphene for biosensors. Generally, there are two derivatives of graphene which are graphene oxide (GO) and reduced graphene oxide (rGO). Graphene oxide is functionalized graphene with various oxygen-bearing groups such as C=O, C–O, and –OH, while reduced graphene oxide is formed from chemical reduction of graphene oxide. For this experiment, graphene oxide is being used.

Furthermore, Iron(III)Oxide nanoparticles also gain a huge interest in the applications of biosensor due to their superconductive nanoparticles, chemically stable, low toxicity and low cost for large-scale production. Furthermore, Iron(III)Oxide nanoparticles offer high conductivity and catalytic properties and suitable to enhance electron transfer.

Thus, electrospun nanofibers based on Poly (Acrylic Acid) and Polyacrylonitrile (PAA/PAN) polymer containing different types of

nanoparticles were used to study the electrochemical properties in order to find out which nanofibers able to give better performance of biosensor.

The objectives of this study were to determine the electrochemical properties of PAA/PAN based electrospun nanofibers containing Gold Nanoparticles (AuNPs), Graphene Oxide (GO) nanoparticles and Iron(III)Oxide nanoparticles (Fe_2O_3). Furthermore, this experiment was conducted to determine which nanofibers give better performance in Cyclic Voltammetry (CV) analysis.

II. METHODOLOGY

A. Materials

The materials used in conducting this experiment were electrospun nanofiber membranes which provided by the University of Edinburgh. Overall, there were four samples based on Poly (Acrylic Acid) (PAA) and Polyacrylonitrile (PAN) (PAA/PAN) polymer. The membrane with only PAA/PAN act as bare which not included with any other materials. The other three samples were mixed with different types of material which were Gold Nanoparticles (AuNPs) (PAA/PAN/AuNPs), Graphene Oxide (GO) nanoparticles (PAA/PAN/GO) and Iron(III)Oxide (Fe_2O_3) nanoparticles (PAA/PAN/Fe_2O_3). All of the chemicals used in this experiment were well prepared. Ferrocyanide ($K_4Fe(CN)_6$) was purchased from Sigma and Hydrogen Peroxide (H_2O_2) from HmbG® Chemicals. Potassium Chloride (KCl) Solution. Phosphate Buffer Solution (PBS) (0.1 M; pH 7.4) was prepared from powder form of PBS Fisher Bioreagents™. Other materials used were 0.1 % Glutaraldehyde Solution as cross-linking agent from Sigma-Aldrich, Distilled Water and PELCO® Conductive Carbon Glue from Agar Scientific. Screen-Printed Carbon Electrode (SPCE). Potentiostat Galvanostat by Autolab Nova was used for all Cyclic Voltammetry (CV) analysis.

B. SPCE Treatment

Firstly, SPCE was treated with 0.05 M of sulphuric acid (H_2SO_4) to improve the performance of the SPCE. $H2SO_4$ was dropped on the electrode of the SPCE and run the Cyclic Voltammetry (CV) analysis. SPCE pretreatment is an effective method to remove organic link-crossings from the carbon ink while also increasing surface roughness and functionality [8].

C. Electrochemical Measurement

Samples were glued on treated SPCE by using PELCO® Conductive Carbon Glue manufactured by Agar Scientific. The electrochemical properties of the samples were measured by Cyclic Voltammetry (CV) analysis. $K_4Fe(CN)_6$ and H_2O_2 solutions with different concentrations were prepared for concentration studies. For $K_4Fe(CN)_6$, the concentration used were 0, 0.2, 0.5, 1.0, 1.5 and 2.0 mM. The voltage used was between -0.4 to +0.8 V. While, scan rate was 0.1 V/s. For H_2O_2, the concentration used were 0, 2, 5, 10, 15 and 20 mM. The voltage used was between -0.2 to +1.2 V. While, scan rate was 0.1 V/s. The solution was dropped on top of the sensing area and CV analysis was recorded. For scan rate dependence study, for $K_4Fe(CN)_6$, the scan rate was varied by 0.02, 0.04, 0.06, 0.08, 0.10 and 0.20 V/s. The concentration used was 0.20 mM and the voltage applied was -0.4 to +0.8 V. Also for H_2O_2, scan rate was varied by 0.02, 0.04, 0.06, 0.08, 0.10 and 0.20 V/s. The concentration used was 5 mM and the voltage applied was -0.2 to +1.2 V.

III. RESULTS AND DISCUSSION

A. Concentration dependence study

The performance of the samples was evaluated by varying the concentrations of $K_4Fe(CN)_6$ and H_2O_2 solutions. The CV responses for samples PAA/PAN, PAA/PAN/AuNPs, PAA/PAN/GO and PAA/PAN/Fe_2O_3 with difference concentration of $K_4Fe(CN)_6$ as shown in Figure 1 (a), (b), (c) and (d), respectively and for H_2O_2 as shown in Figure 2 (a), (b), (c) and (d), respectively.

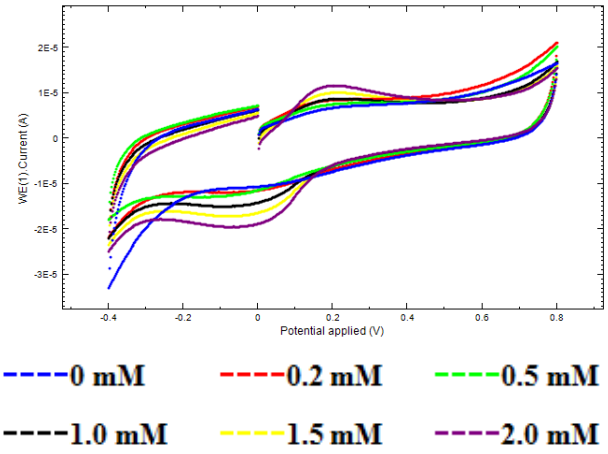


Figure 1(a): Sample PAA/PAN with difference concentration of $K_4Fe(CN)_6$ scan rate 0.1 V/s

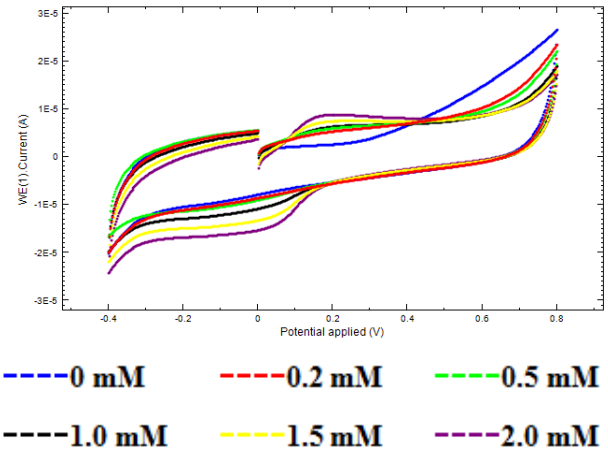


Figure 1(b): Sample AuNPs with difference concentration of $K_4Fe(CN)_6$ scan rate 0.1

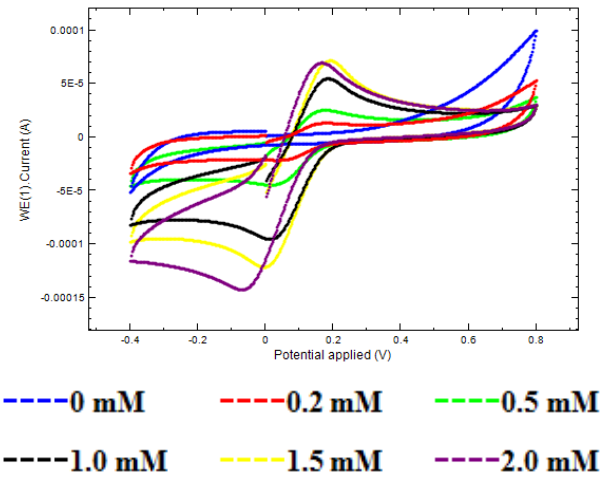


Figure 1(c): Sample GO with difference concentration of $K_4Fe(CN)_6$ scan rate 0.1 V/s

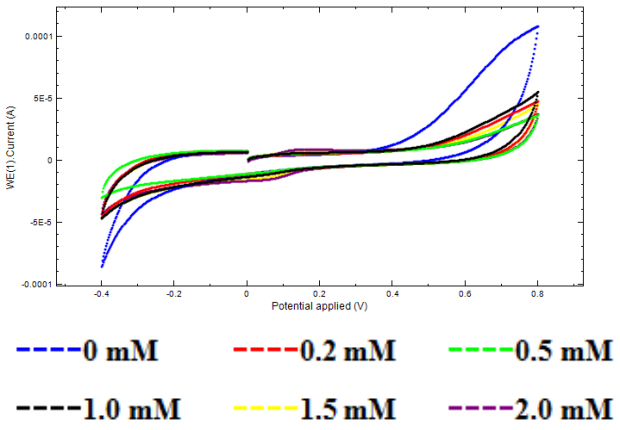


Figure 1(d): Sample Fe_2O_3 with difference concentration of $K_4Fe(CN)_6$ scan rate 0.1

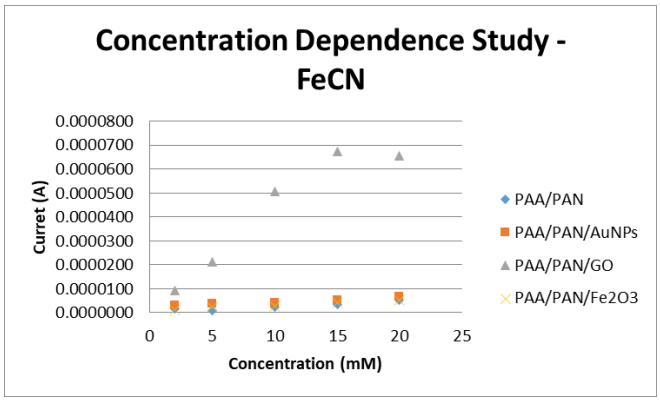


Figure 1(e): Concentration dependence study of $K_4Fe(CN)_6$

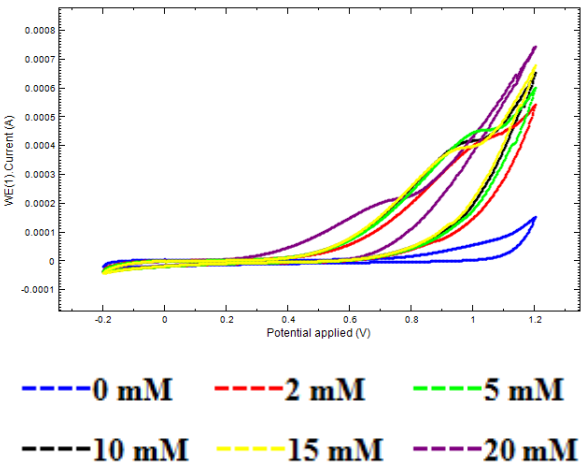


Figure 2(a): Sample PAA/PAN with difference concentration of H_2O_2 scan rate 0.1

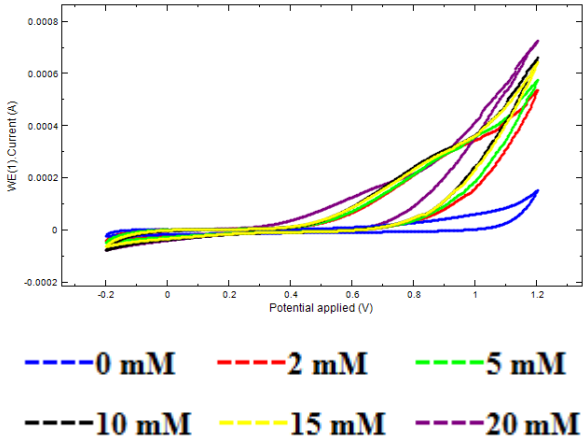


Figure 2(b): Sample AuNPs with difference concentration of H_2O_2 scan rate 0.1

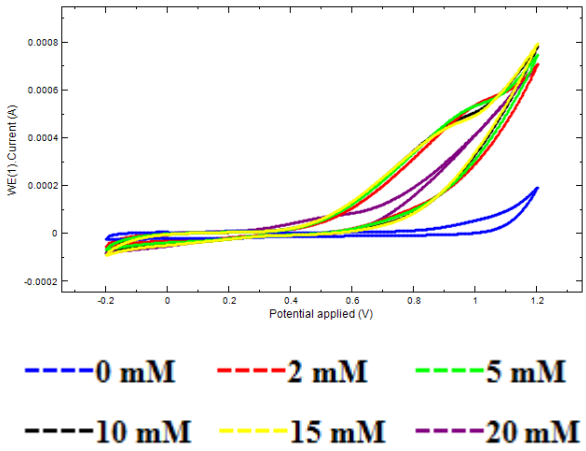


Figure 2(c): Sample GO with difference concetration of H_2O_2 scan rate 0.1

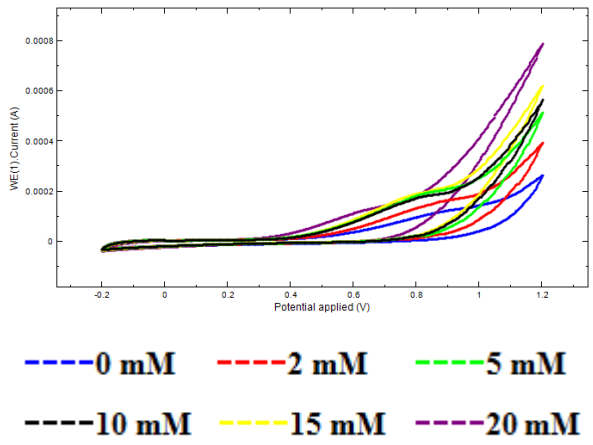


Figure 2(d): Sample Fe_2O_3 with difference concentration of H_2O_2 scan rate 0.1

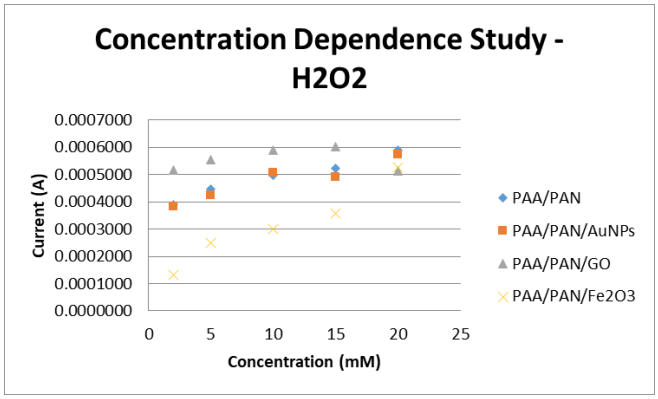


Figure 2(e): Concentration dependence study of H_2O_2

The detection performance of biosensor is evaluated from the CV responses in different concentration of $K_4Fe(CN)_6$ and H_2O_2 shown in the above Figure 1 and Figure 2. Figure 1(e) and Figure 2(e) showed the performance of the samples based on concentration dependence study of $K_4Fe(CN)_6$ and H_2O_2, respectively. From the obtained data, it showed that sample PAA/PAN/GO able to detect the highest current make it as the most better performance of biosensing compared to other samples PAA/PAN, PAA/PAN/AuNPs and PAA/PAN/Fe_2O_3. The other view regarding the study of concentration dependence study of $K_4Fe(CN)_6$, as the concentration increases, the oxidation peak increases. However, only sample of nanofiber with GO (Figure 1(c)) following the expected pattern while the other samples can detect the current but not accordingly to the concentration. There may be some errors during conducting the analysis and the problem may come from the contamination from the surrounding along conducting the experiment. As for concentration dependence study of H_2O_2, all sample showed a good result as the concentration increases, the oxidation peak increases.

B. Scan rate dependence study

The scan rate dependence study was performed to 2.0 mM of $K_4Fe(CN)_6$ and 0.5 mM of H_2O_2 for each sample. $K_4Fe(CN)_6$ and H_2O_2 solutions were measured at different scan rates of 0.02, 0.04, 0.06, 0.08, 0.10 and 0.20 V/s. CV responses for each sample PAA/PAN, PAA/PAN/AuNPs, PAA/PAN/GO and PAA/PAN/Fe_2O_3 with $K_4Fe(CN)_6$ were demonstrated in Figure 3 (a), (b), (c) and (d), respectively. CV responses for each sample PAA/PAN, PAA/PAN/AuNPs, PAA/PAN/GO and PAA/PAN/Fe_2O_3 with H_2O_2 were demonstrated in Figure 4 (a), (b), (c) and (d), respectively.

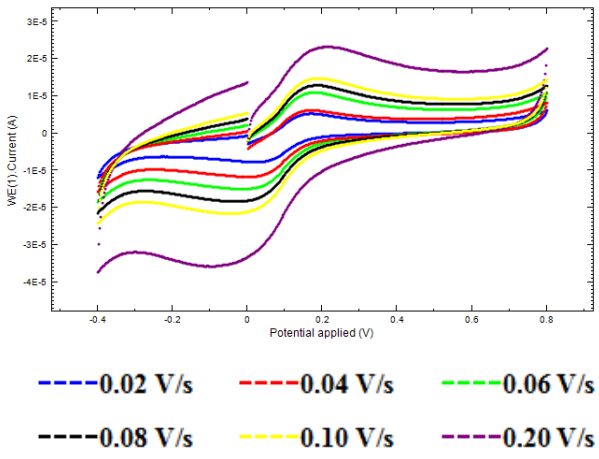


Figure 3(a): Sample PAA/PAN 2.0 mM of $K_4Fe(CN)_6$ with difference scan rate

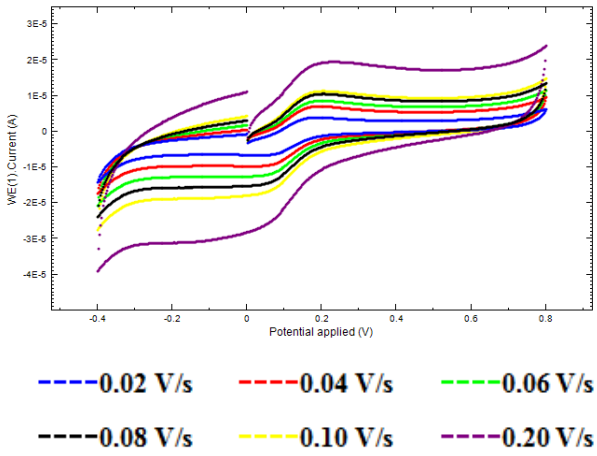


Figure 3(b): Sample AuNPs 2.0 mM of $K_4Fe(CN)_6$ with difference scan rate

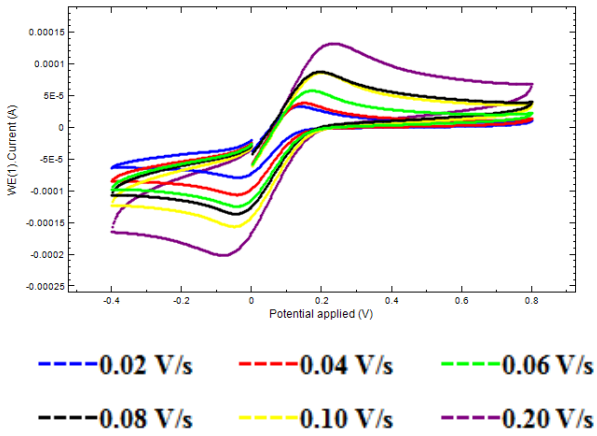


Figure 3(c): Sample GO 2.0 mM of $K_4Fe(CN)_6$ with difference scan rate

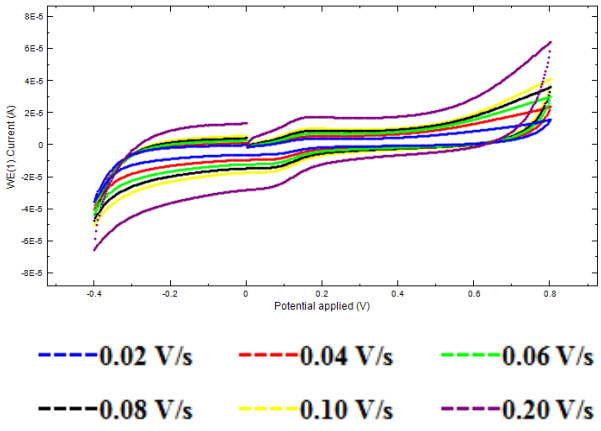


Figure 3(d): Sample Fe_2O_3 2.0 mM of$K_4Fe(CN)_6$ with difference scan rate

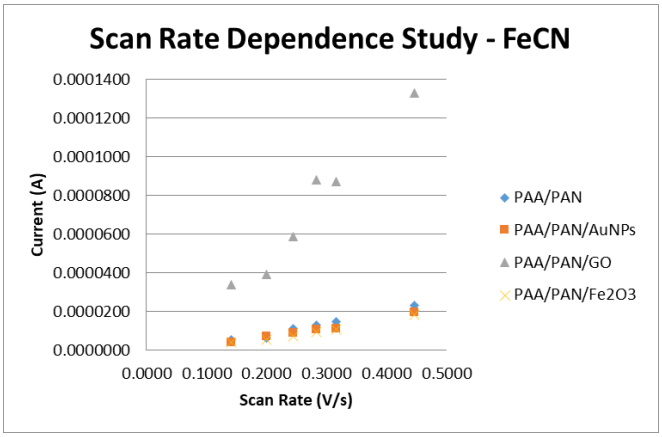


Figure 3(e): Scan rate dependence study of $K_4Fe(CN)_6$

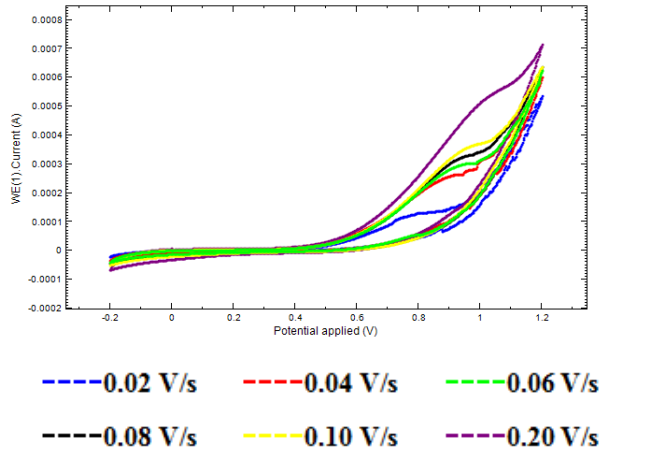


Figure 4(a): Sample PAA/PAN 5 mM of H_2O_2 with difference scan rate

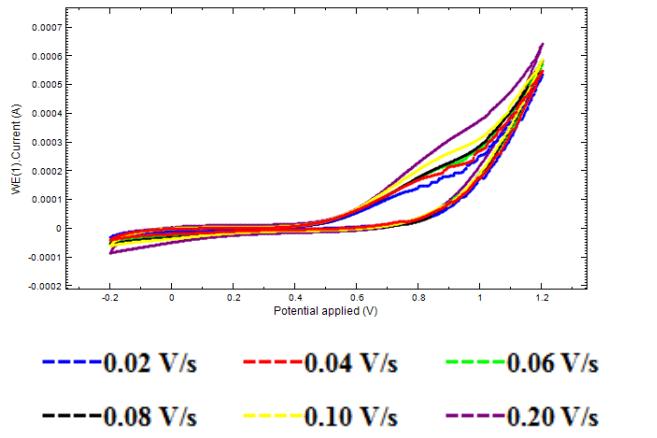
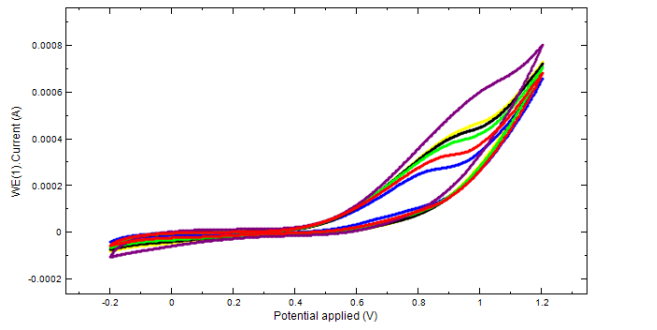


Figure 4(b): Sample AuNPs 5 mM of H_2O_2 with difference scan rate



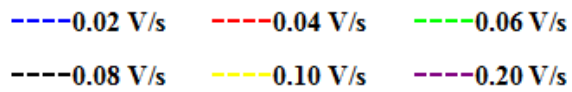


Figure 4(c): Sample GO 5 mM of H_2O_2 with difference scan rate

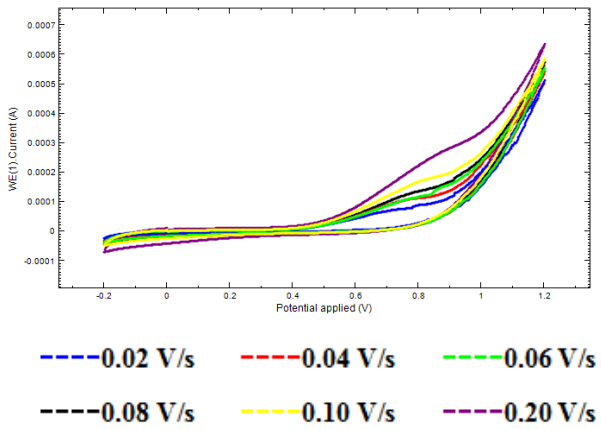


Figure 4(d): Sample Fe_2O_3 5 mM of H_2O_2 with difference scan rate

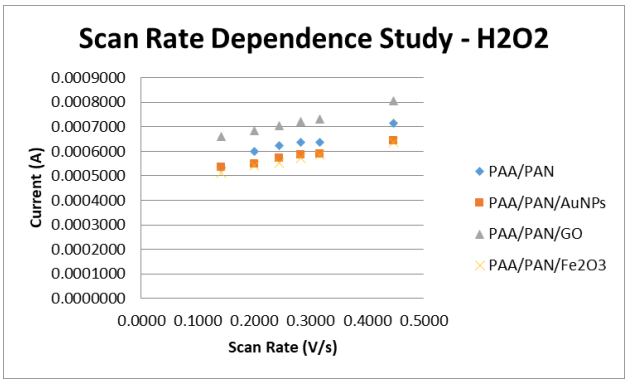


Figure 4(e): Scan rate dependence study of H_2O_2

From Figure 3 and Figure 4, it shown that the current responses for $K_4Fe(CN)_6$ is dependent on the scan rate. Thus, the redox reaction of $K_4Fe(CN)_6$ are relatively slow and limited by the scan rate. In contrast, the current responses for H_2O_2 varies slowly with the scan rate. This shown that the oxidation of H_2O_2 is quite fast so that similar reaction rate is obtained at different scan rate. To further investigate, Figure 3(e) and Figure 4(e) shown the scan rate dependence study both for $K_4Fe(CN)_6$ and H_2O_2, respectively. It showed that, PAA/PAN/GO have the highest peak and proven as the best biosensing performance among other samples followed by PAA/PAN, PAA/PAN/AuNPs and PAA/PAN/Fe_2O_3, respectively. This is due to the graphene oxide based that have better conductivity compared to PAA/PAN, PAA/PAN/AuNPs and PAA/PAN/Fe_2O_3.

IV. Conclusion

In this study, PAA/PAN/GO is proven as the best biosensing performance of electrochemical properties in detecting the ferrocyanide ($K_4Fe(CN)_6$) and hydrogen peroxide (H_2O_2). The concentration dependence study showed that PAA/PAN/GO able to detect the highest current compared to others. This concluded graphene oxide has better conductivity compare to gold nanoparticle and iron oxide. As for scan rate dependence study showed that PAA/PAN/GO have better current responses while detecting the analytes. As suggestion for future research, Screen-Printed Carbon Electrode (SPCE) treatment is highly recommended to be conducted first to ensure the good reading of the result. Furthermore, for the Screen-Printed Electrode (SPE),

instead of using carbon electrode, it could be better to replace it with gold electrode since it can improve the conductivity.

ACKNOWLEDGMENT

Firstly, thank you Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM) Shah Alam for having me as a student and give me an opportunity to study Chemical Engineering courses. Next, thank you to my supportive supervisor, Dr. Tan Huey Ling for her endless support and guidance until I am able to complete my final year project successfully. Furthermore, thank you to University of Edinburgh for providing good samples for this research and I hope that this research able to give values to the community in the future. Other than that, I would like to thank both my parent, mom and dad for always supporting me with their advices and wise words that keep me moving forward. Last but not least, thank you to all my friends who are involving in completing this final year project directly or indirectly. For me, your kindness and support was really helpful and wonderful. Thank you so much everyone and I am really appreciating every single help from all of you.

References

[1] D. Grieshaber, R. MacKenzie, J. Vörös, and E. Reimhult, "Electrochemical Biosensors - Sensor Principles and Architectures," 2008.

[2] S. Malhotra, A. Verma, N. Tyagi, and V. Kumar, "Biosensors: Principes, Types and Applications," vol. 3, no. 2, 2017.

[3] M. M. Rahman, A. J. Ahammad, J. H. Jin, S. J. Ahn, and J. J. Lee, "A comprehensive review of glucose biosensors based on nanostructured metal-oxides," *Sensors (Basel)*, vol. 10, no. 5, pp. 4855-86, 2010.

[4] J. Fang, X. Wang, and T. Lin, "Functional Applications of Electrospun Nanofibers," 2011.

[5] J. Fang, H. Niu, T. Lin, and X. Wang, "Applications of electrospun nanofibers," *Science Bulletin*, vol. 53, no. 15, pp. 2265-2286, 2008.

[6] H. Karakaş, "Electrospinning of nanofibers and their applications," *MDT 'Electrospinning'*.

[7] M. Vidotti, R. F. Carvalhal, R. K. Mendes, D. C. M. Ferreira, and L. T. Kubota, "Biosensors Based on Gold Nanostructures," *J. Braz. Chem. Soc.*, vol. 22, no. 1, 3-20, 2011.

[8] P. Research, "Screen-Printed Electrode Information," *Pine Research Instrumentation*, p. 10, 2016.