# Development of non-enzymatic screen-printed carbon electrode sensor for glucose using cyclic voltammetry

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## Abstract

Enzyme-based sensors frequently produce unsatisfactory results such as poor reproducibility and insufficient long-term stability due to the natural instability of enzymes, stringent experimental conditions, and complicated immobilization procedures. Thus, an electrochemical non enzymatic sensor was fabricated by deposition of the multi-walled carbon nanotube (MWCNT) with zinc oxide nanoparticles (ZnO NP) and also molecular imprinted polymer (MIP) on a screen-printed carbon electrode (SPCE). Then, the modified electrode (SPCE/MWCNT/ZnO/MIP) was formed on the surface area of the SPCE. This study wanted to demonstrate the glucose detection between molecular imprinted polymer (MIP) which contained glucose as template, o-phenylenediamine (oPD) and potassium persulfate as initiators in 0.1 M PBS at pH 7 and non-imprinted polymer (NIP) without addition of the template. The characterization and evaluation of various factor such as sensitivity, selectivity and limit of detection (LOD) were investigated through cyclic voltammetry (CV) and scanning electron microscopy (SEM) was used to look up onto the surface area of the modified electrode. The SPCE/MWCNT/ZnO/MIP eelectrode sensor showed a linear glucose concentration range from 0, 0.5, 1, 2 to 5 mM ($R^2 = 0.9709$). The sensitivity of the sensor was 0.3386 µA mM$^{-1}$ cm$^{-2}$ with low detection limit of 1.8l mM. The sensor showed good stability and reproducibility along with excellent anti-interference properties to ascorbic acid, lactic acid, tartaric acid, and acetic acid. Finally, the applicability of the as-prepared SPCE/MWCNT/ZnO/MIP electrode sensor was successfully studied for detection of glucose. The results obtained for our sensor confirm that it is a promising non-enzymatic glucose sensor to be used for practical purpose.

Keywords :
Non-enzymatic sensor, screen printed carbon electrode, molecular imprinted polymer (MIP), modified electrode (SPCE/MWCNT/ZnO/MIP), cyclic voltammetry

# 1 Introduction

Glucose biosensors have extraordinarily added to the observation of glucose levels in diabetic patients. Enzymatic electrochemical biosensors, for instance, offer great selectivity and affectability in any case, they additionally have disadvantages, for example, drawn-out immobilization steps, compelled operational conditions, and helpless dependability or reproducibility. To beat these inadequacies, chemical-free (non-enzymatic) glucose bio-sensing stages are being planned and created based on direct oxidation of glucose. A non-enzymatic sensor, in this manner, is an appropriate other option, utilizing nanostructured materials that offer protein-like action or nano-enzymes altered on the outside of the cathode. The nano-enzymes go about as electro-catalysts to produce electrical flow by straightforwardly oxidizing glucose on the outside of the terminal (Sridara et al., 2020).

In the course of recent many years, the advancement of exceptionally delicate and particular glucose sensors proposed for the discovery has pulled in a lot of consideration for research from such fields as the the food business, clinical analytic science and nature conservations.

When all is said in done, glucose sensors can be ordered into two sorts: enzymatic and non-enzymatic. With so many benefits as high affectability, quick reaction, and unwavering quality, enzymatic glucose sensors have involved more than 85 % of the sensor market. To address these issues, non-catalyst glucose sensors have been drawing in developing interest for their high steadiness, repeatability, and being liberated from compounds (Wei et al., 2021).

Several analysts were focusing on the development of glucose sensors based on electro-catalytic oxidation. Clark and Lyons were among the first to develop an enzymatic biosensor that catalyzes the conversion of -d-glucose to -gluconolactone, and this line of research was pursued by several experts. Regardless of their high affectability and selectivity, these sensors need dependability because of the deficiency of action of compound (Babu and Ramachandran, 2010). Although enzymatic-based test strips have dominated the glucose recognition market, protein's inherent shakiness due to its sensitivity to temperature and pH variations, as well as the need for gentle working/storage conditions, could

use glucose detecting strips' realistic usability and detection execution. As a result, non-enzymatic glucose sensors are desperately needed to overcome some natural compound hindrances like pH- and temperature-dependent action, as well as a lack of chemical capacity in extreme climates (Dong et al., 2021). The manufactured senor likewise displayed a quick reaction time and acceptable outcomes for both securities just as reproducibility from different tests, consequently settling on it a decent material decision for glucose identification application (Leong et al., 2020). The presentation of detecting systems and working standards of metal oxides-based glucose sensors kicks off the metal oxide empowered non-enzymatic electrochemical glucose detecting (Dong et al., 2021). The development of a wide range of nano-materials has resulted in a plethora of unique and larger responsive glucose sensors (Wang et al., 2013). In addition to these metal oxides, the electrochemical properties of semiconductor metal oxides, particularly zinc oxide (ZnO), an n-type semiconductor, and carbon nanotubes (CNT) can be combined to improve performance in potential applications. ZnO nanomaterials with a high iso-electric point (IEP) of 9.521 and biocompatibility help immobilize low IEP biomolecules like glucose oxidase, hemoglobin, DNA, and cholesterol oxidase, making them excellent biosensors. ZnO nanomaterials in the presence of buffer solution enzymes and biomolecules favor the adsorption of negatively charged between enzyme/biomolecules and electrode at pH = 7. Besides, ZnO nanomaterials work well as mediators in enzymatic sensing applications (Ibrahim et al., 2016). In recent decade, there are a lot of interest in molecular recognition or unnatural receptors that use molecularly imprinting polymer (MIP) as a benefits synthetic polymeric material for building electrochemical sensors and it is the copolymerization of cross-link polymers with the functional monomers in custom-made in situ by the presence of the molecule's template. MIP has a few rewards, including large capacity and affinity recognition for the target molecule due to pre-designed recognition sites that are complementary in shape, size, and functional groups to the template molecule (Wu et al., 2019). The subsequent nanocomposites effectively showed a huge surface region and were shown through cyclic voltammetry (CV) electrochemical testing to have an improved electrocatalytic action. In addition, a screen-printed carbon electrode (SPCE) has been useful for glucose detection because of its flexible design and ability to be modified (Sridara et al., 2020). The use of screen-printed electrodes reduces the setup time for electrochemical measurements, necessitates less maintenance, and eliminates the need for large sample volumes. Screen-printed carbon electrodes (SPCE) with a three-electrode configuration are available from from DropSens. Aforementioned above, the objective of this study is to characterize and evaluate of various factor such as sensitivity, selectivity and limit of detection (LOD) were investigated through cyclic voltammetry (CV) and scanning electron microscopy (SEM) was used to look up onto the surface area of the modified electrode. The various electrodes are printed onto a ceramic substrate with a carbon W.E. and C.E., a pseudo-R.E., and silver electric contacts. Over these, an insulating layer is printed, leaving only a 50-microliter working area uncovered. A potential clarification for this outcome may be identified with the development of an exceptionally absconded structure with numerous synergist locales, shaped during doping (Onor et al., 2017). In addition, the nano-composites likewise show different valuable highlights, for cases, great selectivity, affectability, straight reach, and brilliant soundness (Leong et al., 2020).

# 2 Materials and methods

## 2.1 Reagent and solutions

D-(+)-Glucose was taken from Sigma-Aldrich and also it was prepared with distilled water (Babu and Ramachandran, 2010). O-phenylenediamine (OPD), phosphate buffered saline (PBS),

potassium persulfate (KPS), methanol and zinc oxide nano-powders (<100nm) were purchased from Sigma-Aldrich from Sekisui Diagnostics Ltd., Maidstone, UK (Madden et al., 2021) while for acetic acid (glacial) 100%, sulfuric acid 95-98% were obtained from Merck (Merck KGaA, Darmstadt, Germany) (Leitzen et al., 2021). L (+) Ascorbic acid and L (+) Tartaric aicd also were purchased form EMSURE® ACS,Reag. Ph Eur (Germany). Multi-walled carbon nanotube (MWCNT) was taken from Baytubes® C 150 (Leverkusen, Germany). Phosphate buffer solution (PBS, pH 7) was already prepared by mixing with distilled water. The standard solution of glucose from 0.5mM, 1mM, 2mM and 5mM were had diluted in 0.1M PBS in which at suitable pH7 as it need to be form in less concentration of glucose solution (Diouf et al., 2019).

## 2.2 Apparatus and measurements

All measurements were performed at room temperature and for the electrochemical measurements were used with a µSTAT 200 potentiostat (Dropsens, Oviedo, Spain) which was supported by Dropview software. The electrodes consist of Screen-printed electrodes (SPEs) which were consists of different type of the electrode and for this study, DRP C110 was approach to use as it can be simply do several methods in which either immersed or drop casting technique. The working electrode in diameter of 4 mm together with the counter electrodes were made from carbon materials (C, DRP C110) while the silver materials was chosen as reference electrodes. Usually, SPE was function for modification process towards the electrode (Ndiaye et al., 2016). Weighing balance, sonicators for the sonication process (20-23 kHz with a power of typically less than 100 W), stirrer for cleaning process for each step of running the sample, and 1000 micropipette for pipe the solution on the SPCE. As figure below show on how the electrode had been placed through the potentiostat.

## 2.3 Fabrication of SPCE/MWCNT/ZnO/MIP

This process of the fabrication towards the SPCE electrode was followed step by step to show how modified electrode was firmly obtained by coating of multi-walled carbon nanotube (MWCNT), zinc oxide nanoparticles (ZnO), molecular imprinted polymer (MIP) onto the surface area of screen-printed carbon nanotube (SPCE). Figure 3.1 show the fabrication of the modified electrode.

### 2.3.1 MWCNT and ZnO deposition

Before the modification towards the electrode, the SPCE was cleaned with 0.3 µm and 0.05 µm alumina powder and then was rinsed thoroughly with deionized water. Then the cleaned electrode was placed until it full dry (Shabnam et al., 2017). After SPCE had been dried, it will be coated first with MWCNT. 5 mg of the MWCNT will dispersed on 5 mL of DMF solution while for zinc oxide powder is taken about 5 mg to be dispersed also into 5 mL of DMF solution. After that, both of the mixture had been sonicated about 30 minutes at room temperature, 27°C and 360 W was fixed to get all the mixture dissolved well. This is because ultrasonication is the most often used technique for dispersion of nanoparticles. In this paper, DMF was used as the dispersant of MWCNTs (Baomin and Bo, 2020). Disintegration of strong van der Waals attraction towards the DMF molecules, which causes reducing the binding force between MWCNTs and disperse well by the methods of sonication.

Thus, this was the basic method for dispersion of the MWC-NTs. ZnO nanoparticles are important in the oxidation of glucose however, in non-enzymatic sensors, they do not directly react with glucose, but they do speed up the electron transfer from glucose to MWCNT. By adding ZnO nanoparticles, the electron transfer capacity and electro-catalytic performance of MWCNT towards the oxidation of glucose can be greatly improved. Then, 3.0 µL of the

dispersion mixture of MWCNT was put on the working electrode on the surface SPCE by using drop casting method and let it dried for a few hours. After that, the SPCE/MWCNT electrode was continue to coat ZnO mixture into the second layer on the surface of SPCE/MWCNT (Rezaei et al., 2014).

### 2.3.2  Electro polymerization

The glucose biosensor was developed from a SPCE that was functionalized with coating of the MWCNT, ZnO and the molecular imprinted polymer which were present of the MIP is responsibility to increase the electro-activity and sensitivity of the electrode in subsequent electrochemical for glucose sensing. Molecular self-assembly was achieved by mixing volume ratio (1:4) of 5 mM of glucose and 20 mM o-PD in 23 mL of 0.1 M PBS (pH=7.4) and left it for 5 hours to dry. It was a completely different way compared to the previous fabrication procedure, in which for electro polymerization of MIP towards the surface of WE, the electrode was totally immersed in the MIP mixture because I wanted all of the MIP layer to coat the whole surface of SPCE.

The MIP was obtained from a solution that contained o-phenylenediamine (o-PD) as the functional monomer, the template was glucose solution and a supporting electrolyte was PBS. Next, for a non-imprinted polymer (NIP) part was prepared with the same method but no adding of the template solution. Both modified electrodes for MIP and NIP were left at 27°C which was room temperature before proceed to analyze the sample (Diouf et al., 2019). As the figure below show the electrode was fully immersed into the solution.

### 2.3.3  Cleaning process

After electropolymerization process, cleaning step for modified electrode was done by stirring the electrode into the mixture of methanol: water (2:1) and left it for 5 min to stir. This step was important because to remove the template as clean as possible. Cleaning process must be done for every single step after use the modified electrode. As figure show how the cleaning process step done after every scanning through the cyclic voltammetry. In figure 3.4, the electrode was clean through stirring process. Characterization through SEM The scanning electron microscopy (SEM) were functioned to determine the surface area of the modified electrode of SPCE/MWCNT/ZnO/MIP throughout this study. Besides, topography and chemical composition of the electrode surface electrode also can be managed by scanning through this instrument. SEM was taken from JEOL model JSM-6390LV) combined with an energy dispersive spectrometer (JEOL model JED-2300) (Babu and Ramachandran, 2010). Because of the limitation of time, the only instruments can be available to detect was using SEM. Unfortunately, there were still had a disadvantage as it can only show the roughly surface of the electrode.

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## 2.5  Performance testing

For the performance of the modified electrode which were SPCE/MWCNT/ZnO/MIP, it would run through cyclic voltammetry technique. When running the modified electrode for each of the testing sample solution, there would be specific potential used, scan rate and how many cycles to run during the analysis. After all the sample solution was done, the modified electrode would be tested through the interferences solution which were ascorbic acid, acetic acid, tartaric acid and lactic acid. This performance wants to detect the efficiency of the non-enzymatic sensor throughout the appearances of the molecular imprinted polymer towards the screen-printed carbon electrode.

### 2.5.1  CV analytes

After coating with MWCNT/ZnO, the electro polymerization process had been continued which was immersed the mixture of the MIP solution and run the CV parameter at -0.5 V to 1.5 V, scan rates for 50 mV/s in 20 cycles. Then, the template molecules were removed from polymer by stirring in a mixture of methanol and distilled water at a ratio of 9:1 (V: V). This step would extract the template at the surface of the electrode and let the cavities with appearance of certain specificity of molecules of analytes towards the template molecules. Finally, the MIP sensor was washed with distilled water (Wu et al., 2019). During the fabrication part, 50 μL sample or standard solution were drop cast onto the modified electrodes (SPCE/MWCNT/ZnO/MIP) before running through the cyclic voltammetry measurements (Chaiyo et al., 2018). Cyclic voltammetry measurement was performed between 0 V and +1 V for the carbon electrodes (Ndiaye et al., 2016). The scan rate used was 100 mV/s in 3 cycles.

### 2.5.2  Interference test

Acetic acid, ascorbic acid, tartaric acid and lactic acid was chosen as interferences for glucose detection. Acetic acid with lactic acid were the in the form of liquid while the ascorbic acid and tartaric acid were in the form of solid substance. At first, both of the acetic acid and lactic acid must be diluted with phosphate buffer solution (0.1 M) in 23 mL of 1 mM concentration for each solution. Then, 0.405 g ascorbic acid and 0.375 g of tartaric acid were taken and also diluted in the 23 mL of phosphate buffer solution (0.1 M) to form 1 mM concentration solution. The parameter for scanning through CV were between potential of 0V until 1 V at 100 mV/s and run for 3 cycles. When running this interferences sample solution, the clean process was same goes with the modified electrode which was cleaned up by using methanol and water at ratio (2:1) to be make sure all the template cavities is clean for the next sample.

# 3  Results and discussion

## 3.1  Electropolymerization of molecular imprinted polymer

Electropolymerization process of the SPCE/MWCNT/ZnO by scanning the potential of the cyclic voltammetry technique between -0.5 to 1.5 V in a solution which content glucose o-phenylenediamine (o-PD) and potassium persulfate in the PBS pH7. The current diminishes gradually in the following scans approaching almost complete suppression, as it would expect to form the non-conducting polymer by covering the layer on the SPCE/MWCNT/ZnO surface electrode (Figure 1).

For both the NIP and MIP covered electrodes, 20 cycles of polymer deposition resulted that the defeat of the current showed on how thickness of the polymer coated had been created as seen in Figure 1. The creation of cavities onto the polymer film and then followed by removal of the target was specify that would be larger

for the peaks of the glucose in the CVs after incubation of the MIP-covered electrode in 0.1 M PBS pH 7. It was discovered that the lower current was noticed because the MIP solution mixture must adhere to the electrode SPCE's surface area. Moreover, the dense films were formed after 20 scans, and thus it was time for the template removal process, in which the cavities for the glucose had to be removed in order to test the sample solution quickly. As a result, we can examine how much glucose can be connected to the empty spaces left by the MIP section of the electrode.
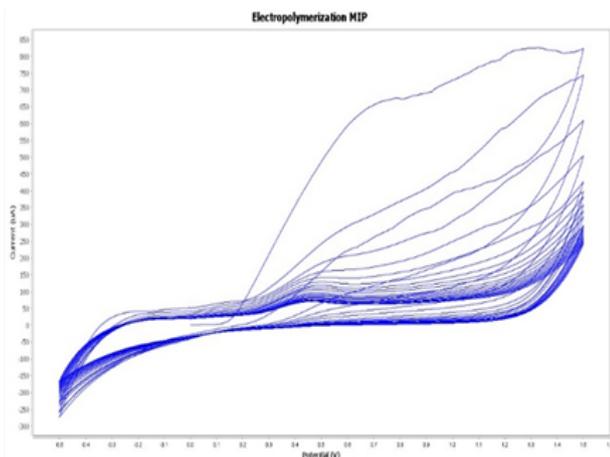


**Figure 1** Cyclic voltammogram showing the electropolymerization of MIP that run for 20 cycles onto SPCE/MWCNT/ZnO. The scan rates were selected at 50 mV/s and run through potential from -0.5 V until 1.5 V

As a result, for the MIP preparation, a set number of 20 cycle scans was used throughout the investigation. The decreasing of the current showed the MIP was electrotro-polymerized on the SPCE/MWCNT/ZnO electrode. 1f shows the CV for electro polymerization of MIP in the presence of o-PD, glucose and potassium persulfate on the SPCE/MWCNT/ZnO. During the first cycle, this CV shows a large peak oxidation at 0.2 V, which gradually declines during successive cycles. The absence of a clear decrease peak in the CV shows that the polymerization process was an irreversible. The oPD is mixed with glucose solution in PBS as a supporting electrolyte and then enhance the formation of MIP onto the electrode whereas oPD would go through electro polymerization reaction with no addition of glucose was called non-imprinted polymer (NIP) sensor. Both MIP and NIP were suddenly had similarly experience oPD deposition on the modified electrode and based on the reading CV graph could identified the differences between them. After that, polymerization will be followed by the extraction of template molecules. By breaking down the glucose molecules attached in the MIP, the cavities had been generated for a redox reaction of sample solution to land up at the electrode's surface. Thus, an extracting solution was applied. Diffusion restrictions induced by mass transfer of the analytes circulate into the bulk solution through the membrane, it would attempt the process of nonlinear.

For removing glucose from the MIP matrix, various solutions were investigated, including toluene and methanol, with the optimal ratio of methanol/water (2:1) being utilized as a cleaning step. Because of the constancy of the interactions between the sorbent bed and the analyte during elution, methanol is considered the optimum solvent for both washing and elution. When washed with methanol, the leftover solvent that is not water miscible is removed, and the sorbent is then washed with distilled water to prepare it to take the aqueous sample. Methanol is employed because it is miscible with both the early wash solvent and the water, and it serves as a transition between the two. These solutions either removed glucose from the MIP matrix or fully damaged the oPD matrix.

## 3.2 Surface characterization of modified SPCE via SEM

The surface of modified electrode of SPCE/MWCNT/ZnO/MIP was characterized through the scanning electron microscopy (SEM) as seen in Figure 2. As the result, the coating on the surface area of MWCNT and ZnO were looked fill up closely the whole onto the surface but when it comes to the to the MIP part by process of electro-polymerization, the deposition on the electrode were small enough.
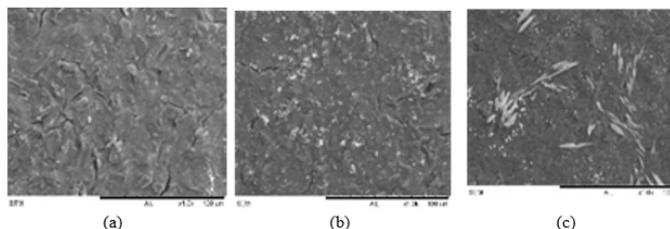


**Figure 2** Morphology modiefied SPCE: (a) multi-walled carbon nanotube (MWCNT), (b) MWCNT/ZnO (white sport appeared for zinc oxide), (c) MWCNT/ZnO/MIP (parallel shape of MIP appeared).

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## 3.3 Electrochemical characterization of MIP glucose sensor

The development of non-enzymatic sensor through bare SPCE, NIP and MIP were had calibrated for glucose sensing. The concentrations of the glucose had been conducted (0 mM, 0.5 mM, 1 mM, 2 mM and 5 mM) in phosphate buffer solution (PBS) and then run the sample analytes during CV by scanning over the potential range from 0 V to 1 V (Figure 3). In the Figure 3, there were a small peak appeared during the scanning, the peak for the oxidation of detection of glucose concentration had totally shown started from potential of 0.2 V and the current read at almost 76 µA. Following that, cyclic voltammetry was utilized to assess the electrode's electro-activity before and after various stages of production and electropolymerization.
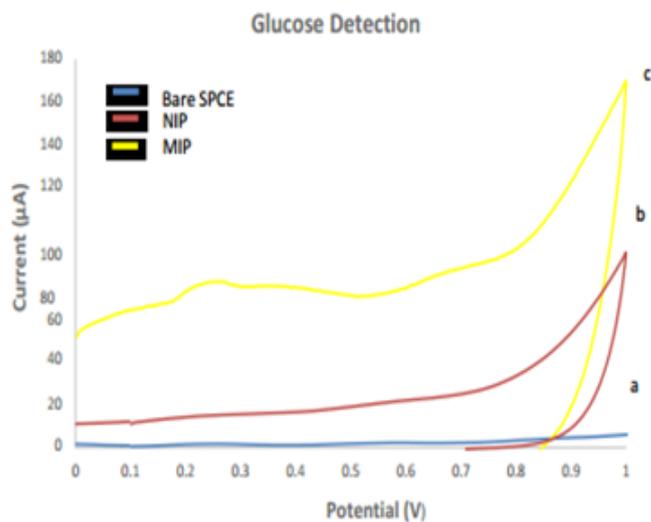


**Figure 4** Cyclic voltammograms for SPCE/MWCNT/ZnO/MIP a) Bare SPCE, b) NIP and c) MIP

Figure 3 showed that cyclic voltammograms for SPCE/MWCNT/ZnO/MIP recorded between 0 and 1 V during run the sample of 1 mM of glucose concentration (0.1 M PBS pH7). a) Bare SPCE, b) NIP and c) MIP. The scan rate was at 100 mV/s and 3 cycles. The working electrode and counter electrode used was carbon while silver/silver chloride (Ag/AgCl) was used as reference electrode. Following that, cyclic voltammetry was utilized to assess the electrode's electro-activity before and after various stages of production and electropolymerization. It should be observed that following functionalization with MWCNT and ZnO drop coatings, the bare electrode would not be giving any changes towards the oxidation current. In fact, when the electrode's numerous layers electrochemically behave similarly to bulk carbon, there will the small different in changes of current for bare SPCE surface. The electro-deposition of MWCNT/ZnO/MIP on the electrode, on the other hand, boosts the current from 85 to 160 μA, implying that the modified electrode greatly increases the electrode's electro-reactive nature. The electrochemical deposition of MWCNT/ZnO/MIP on SPCEs was considerably more efficient than the NIP electrode, which had no template (Glucose). In addition, the rationale for including MWCNT and ZnO onto the SPCE where both materials enabled electrochemical glucose monitoring after addition with the MIP, whereas the bare SPCE was layered by the MIP, it would cause a lacked value of sensitivity for glucose sensing. Finally, because this polymer is called as non-conducting, electropolymerization of the o-PD electrode results by increasing oxidation current.

The functional monomer o-phenylenediamine was used to build extremely selective cavities for the template molecule. In reality, the equilibrium between the monomer and the template dictates that the functional monomers be added in excess of the number of moles of the template in order to favor the formation of the complex, with template: functional monomer ratios commonly ranging from 1:4 to 1:8. As a result, there were a variety of template-functional monomer complex combinations, resulting in a heterogeneous binding site distribution in the final MIP with a range of closeness to constants. When glucose was extracted from MIP, holes were produced that were the same shape and size as glucose molecules. These pores allow the glucose sample solution to interact with the SPCE/MWCNT/ZnO/MIP electrode surface, resulting in a greater current. Because the full surface of the electrode is not really reached to the glucose cavities, the current peak shown at 0.2 V of potential is small. Because the poly (o-PD) film covered the surface of the modified electrode in the absence of glucose, the peak current for the NIP peak in Figure 3 declined dramatically from the curve. Because no imprinted cavities were created after the NIP electrode, the decrease in current was small as shown on the curve. These CV characteristics was almost identical to those of past review based on MIP sensors in which the electrode surface has been redesign with metal that in form of nanoparticles to improve electrode sensitivity and selectivity, and hence the resulting electrochemical biosensor.

**Table 1** Comparison between my studies research with the other study of enzymatic and non-enzymatic glucose sensor

| Study of Experiment | Sensitivity ($\mu A \ cm^{-2} \ mM^{-1}$) | Limit of Detection | Correlation Coefficient | Selectivity |
|---|---|---|---|---|
| SPCE/MWCNT/ZnO/MIP (This work) | 0.3386 | 1.8 mM | 0.97 | Acetic acid, tartaric acid, ascorbic acid, lactic acid |
| Pd Cu/SPCE (Non-enzymatic) | 396.7 | 0.7 μM | 0.99 | Ascorbic acid, glucose, uric acid |
| Pt /CeO2-ZrO2 NP (Enzymatic) | 138.9 | 1.8 μM | 0.99 | Uric acid and glucose |
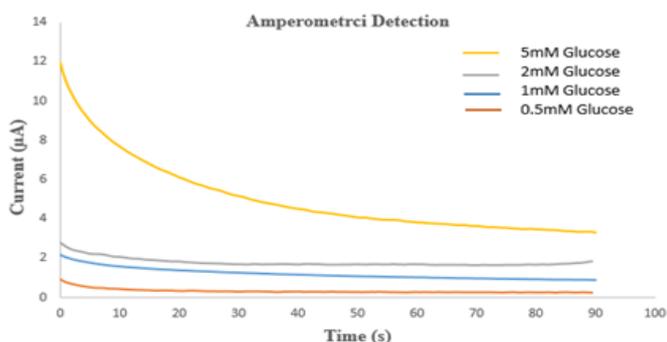
**Figure 5** Amperometric detection curve for concentration of glucose from 5 mM, 2 mM, 1 mM and 0.5 mM selected potential at 0.2 V

**Figure 6** Calibration curve from the glucose concentration of 0mM, 0.5 mM, 1 mM, 2 mM and 5 mM based on selected potential that showed a peak at 0.2 V. The correlation for $R^2$ was obtained at 0.9709 value during the scanning

The glucose calibration plot was based on the amperometric detections curve's planned peak oxidation (Figure 4). For the SPCE/MWCNT/ZnO functionalized with the MIP, a linear line between concentrations with the oxidation current was seen across. However, the bare SPCE combined with the MIP, it had showed no interaction in oxidation current even the glucose concentration had been rising up. Furthermore, for the SPCE/MWCNT/ZnO functionalized with the MIP, the correlation coefficient ($R^2$) had been calculated and it was found to be 0.97, and the detection limit was determined to be 1.8l mM as seen in Figure 5. However, it did not reach minimum value $R^2$ which was 0.995 that causes this linearity were not acceptable. Thus, from this result come out with sensitivity of 0.3386 μA cm$^{-2}$ mM$^{-1}$. Based on the comparison at Table 1, the value of the LOD with the sensitivity could be more improve compare to the previous study.

Due to alkaline nature of the buffer media, oxidation peak current indicate there are increasing of electron moved from glucose molecules dissolve in aqueous PBS to the electrode. This current response was increase in contrast to the reduce in current response that would be looked ahead to glucose (non-electroactive analytes) that selectively tied up to the MIP cavities and turn aside the electrochemical from diffusing into the cavities of imprinted, resulting in a fall down in current response as concentration become larger. As a result, the increment in transferring the electron from MIP attached glucose molecules to the SPCE/MWCNT/ZnO electrode causes created MIP biosensor is better than the expected dropping signal response from distribution of the glucose to the electrode surface.

## 3.4 Interferences testing of MIP glucose

The sensor's sensitivity to acetic acid, ascorbic acid, tartaric acid, and lactic acid was used to assess the MIP's glucose selectivity. Ascorbic acid and tartaric acid have molecular weights that were similar to glucose. Thus, these solutions were suitable as used as interferences for this study. It was important that depend on the molecular structure of the pores left on the surface area of modified electrode by the target species to function, evaluating the selectivity of modified electrode is a critical step in validating the sensor's potential efficacy in sample detection. The MIP was subjected to varied concentrations of these interfering species, ranging from 1 mM to 10 mM for each solution. During experiments with the modified electrode, all interfering species show no change in current response (Figure 7).
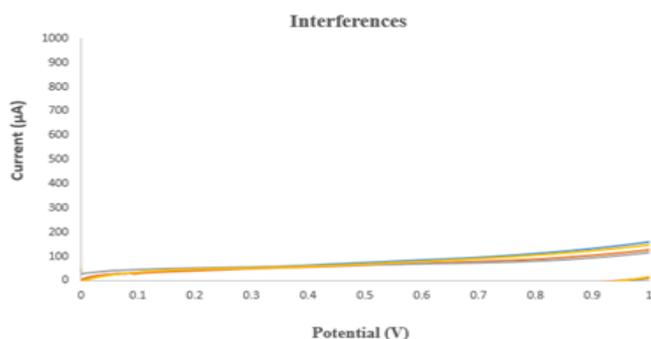


**Figure 7** Cyclic voltammetry between the interferences involved for selectivity towards the glucose which run from potential of -0.5 V until 1 V. The scan rates was at 100 mV/s at 3 cycles on modified electrode of SPCE/MWCNT/ZnO/MIP

The existence of cavities inside the MIP had thoroughly selective to glucose binding was demonstrated by these findings. Glucose which was stick to these holes through weak hydrogen bonds and also Van der Waals interactions should be highlighted. These species' adsorption into MIP cavities, roughly would prevents the Van der Waals interactions or formation of hydrogen bond with the cavity. Acetic acid, ascorbic acid, tartaric acid, and lactic acid had no effect on the analytical peak current, according to interference experiments. This result showing that the selectivity efficacy of the developed sensor towards the glucose.

## 4 Future recommendation

Many obstacles lie ahead for the human body in terms of utilizing for these sensors. Most of the non-enzymatic glucose sensors (based on metal oxide electrodes) have been constrained by their insufficient range of the glucose detection, deficient long-term of the stability, and poor biocompatibility when contrast to enzyme-based biosensors. For the upcoming project, researchers hope to detect minuscule quantities of glucose in various physiological fluids and develop sensors that may be implanted for constant level monitoring of the glucose. All of these needs stimulate more thorough research and development of next creation of the non-enzymatic glucose sensors. Besides, there are a few recommendations could be improvised these studies.

First, for the next project on the non-enzymatic sensor for glucose detection by approaching the molecular imprinted polymer (MIP), the concentration of the analytes used should be increase compare to my studies. Second, the specifically used the Autolab Metrohm voltammetry instruments which mean that there will more method can be used for example cathodic stripping voltammetry or anodic stripping voltammetry. This will be more preference to run the analysis better and can play with the different type of the electrode used. Thus, the application for the non- enzymatic glucose sensors needs the co-efforts of researchers global.

We would keep do a lot of progressive to even more advanced developments of non-enzymatic glucose sensors.

## 5 Conclusions

A non-enzymatic sensor biosensor was created by coating a SPCE with multi-walled carbon nanotube (MWCNT), electrochemically deposited also with zinc oxide (ZnO) and finally layered by molecular imprinted polymer (MIP) which was consists glucose, o-phenylenediamine and potassium persulfate in the 0.1 M phosphate buffer solution at pH 7. The combination of the monomer and template solution was utilized for MIP producing. The characterization of SEM prescribed that the coating on the surface area of MWCNT and ZnO were looked fill up closely the whole onto the surface. Non-enzymatic glucose sensor also had good sensitivity to glucose ($0.3386 \ \mu A \ cm^{-2} \ mM^{-1}$) and with a low detection limit (1.81 mM). The selectivity for the glucose sensor was tested with similar molecular which were ascorbic acid, acetic acid, tartaric acid and lactic acid. In the nutshell, the sensitivity, selectivity, and quick approach of the modified electrode based on the non-enzymatic sensor make it is well-suited for bio-sensing at many works scope in applications such as medical and also production in drug delivery. By electro polymerization of MIP by including the components of oPD could be bear on for a wider diversity of the other targeted species such as neurotransmitters, proteins, and chemical compounds. Hence, the development of the non-enzymatic sensor in biosensor serves as a low production in cost services of biosensor for variety of diagnostic and analyte monitoring applications had been improvise including for the use of protein transportation of the protein, bacteria detection bacteria in food and agriculture utilization.

## Declaration of competing interest

The authors declare no known competing interests that could have influenced the work reported in this paper.

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