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Research Paper

Preparation and Application of Nickel Electroplating on Copper (Ni/EC) Electrode for Glucose Detection

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Abstract
An electrode of the nickel electroplating on copper (Ni/EC) has been prepared for a simple and low cost glucose sensor in human urine detection. The electrode was prepared by using pure copper (99.9%) with electroplating method in $NiSO_4$ solution. The electrochemical oxidation of Ni/EC electrode was investigated bys using cyclic voltammetry method. Material Ni/EC identification of morphology used Scanning Electron Magnetic (SEM) and Energy Dispersive X-Ray (EDX). The electrochemical reaction of glucose was analyzed by the cyclic voltammetry method in some electrolyte solutions. Calibration curved was constructed and a linear response for glucose concentration at range 0-0.004 M with R^2= 0.992, LOD and LOQ was determined 4.85x10^{-4} M, 1.6x10^{-3} respectively. The proposed electrode might open up a new possibility for the determination of glucose concentration in human urine. Its advantages are simple to prepare, low cost analyzing, and excellent results.

Keywords
Glucose, Electroplating, Human Urine

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1. INTRODUCTION

Diabetes is a condition in which blood glucose levels are higher than the normal range of 4.4-6.6 mM (Amatatongchai et al., 2017). It is caused by insulin production in the body's cell decrease. People with a high concentration of glucose are more prone to suffer renal, retinal and neural complications (Guo et al., 2015). Their blood glucose concentration must be controlled several times. Diabetes is one of the most serious problems for human society. Data WHO shows Indonesia has fourth ranks country with high diabetes mellitus cases and estimated will be increased in 2025 (Hakim and Riyanto, 2018). Therefore, sensitive, selective and accurate detection is very important. Some methods for the detection of glucose in products, food and urine sample have been interested. The application of enzyme-based to analysis glucose have been affected by temperature, pH, humidity and toxic chemicals. Unlike sensors using an enzyme, the non-enzymatic glucose sensors have advantages such as high stability, rapid response, high selectivity and accurate measurement (Xu et al., 2010).

Some of the electrodes have been developed for glucose analysis like glassy carbon (Raziq et al., 2017), gold (Xu et al., 2010), nickel sulfide (Kannan and Rout, 2015), Cu(Wu et al., 2010), Pb (Cui et al., 2007) and other hybrid materials. A nickel/carbon composite was used as an electrode for the nonenzymatic glucose sensor (Marini et al., 2018). Ni nanoparticle electrodes were investigated for the detection of glucose with a nonenzymatic sensor based on the formation of a high valent of Ni in high pH conditions (Yu et al., 2012).

2. MATERIALS AND METHODS

2.1 Materials and Apparatus

Glucose, KNO_3, NaOH, KOH, $NiSO_4$, $NiCl_2$, H_3BO_3, and other chemicals reagents were purchased from Merck (Darmstadt, Germany). The electrochemical studies were conducted at room temperature and carried out using cyclic voltammetry PGSTAT 100 N/250 mV (Metrohm Autolab). The counter and reference electrodes were made of Pt wire and Ag/AgCl (Metrohm Switzerland).

2.2 Preparation of Ni/EC Electrode

The Ni/EC electrode was prepared by the electrodeposition method in nickel ion solution as described by Riyanto and Rofida (2019). Briefly, the Cu metals wire (Aldrich Chemical) was formulated by length 0.5 cm and wide of 0.1 cm. Cu metals wire was immersed in a nickel ion solution with DC voltage. The nickel plating on copper was connected using conductive silver paint to silver cable. The electrode ready to use as a working electrode. The process of electrodeposition nickle on copper shown in Figure 1.

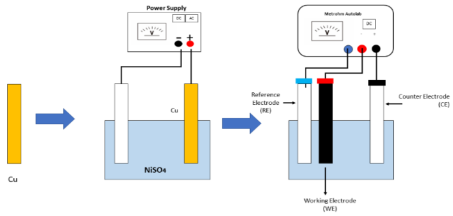

Figure 1. Schematic of Nickel Electroplating on Copper

2.3 Characterisation and Glucose Detection

The morphology of the electrodes was investigated using Scanning Electron Magnetic (SEM), while the element was determined by means of Energy Dispersive Spectrometry (EDS) to look surface of electrode. Glucose detection was performed by the cyclic voltammetry method. The cell electrochemical reaction was shown in Figure 2. Pt wire used as the counter electrode, Ni/EC as the working electrode and Ag/AgCl as the reference electrode. KOH, NaOH and KNO_3 solution were determined for good electrolyte in electrochemical detection of glucose.

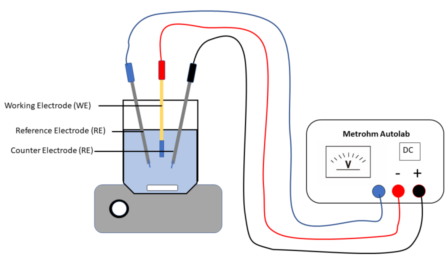

Figure 2. Electrochemical Cell

3. RESULTS AND DISCUSSION

3.1 Characterization of Ni/EC

The preparation of Ni/EC electrode was illustrated as Figure 1. Ni was deposited on copper by taking electrochemical deposition method. The morphology of these electrode was examined using SEM. Ni/EC electrode shows smooth morphology (Figure 3).

Figure 3a the morphology of the Ni/EC surface can be seen that there is a layer on the surface of Cu metal which is doped with Ni metal with a magnification of 5 times (Figure 3a) and 5000 times (Figure 3b) used SEM. Figure 3c, can be seen that the results of Ni deposited onto Cu metal material have been successful with a percent weight (%WA) of Ni deposited onto Cu of 91.46% of the EDX results. More than Ni metal has been successfully doped in Cu. This metal pile binds Cu in a coordinated interaction between Ni and Cu.

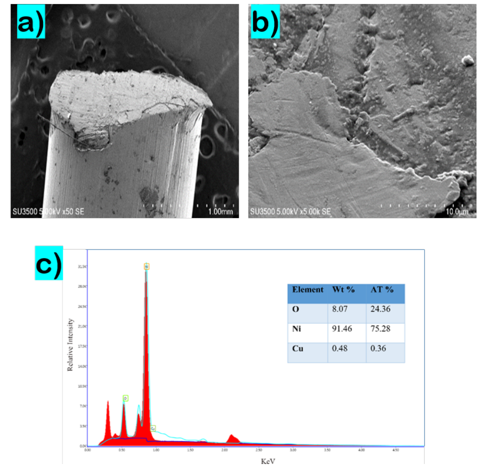

Figure 3. Morphology Scanning Electron Magnetic (SEM) of Material Ni/EC Surface with Magnification 5 Times (a), 5000 Times (b) and Result of Energy Dispersive X-Ray (EDX) from SEM Data Surface Electrode Ni/EC (c)

3.2 Determination of Electrolyte and Electrocatalytic Oxidation of Glucose

The CVs in KOH 0.1 M solution in the absence and presence of glucose are shown in Figure 4a. Its show the CVs in the absence of glucose from +0.0 to +2.0, there is no increase peak current of CV in the presence of glucose. Figure 4b shows a cyclic voltammogram from potential +1,0 V to -1,0 V in KNO_3 0.1 M solution in the absence and presence of glucose. The cathodic and anodic peak was not confirmed in KNO_3 solution. The CVs of the Ni/EC electrode in alkaline solution in the presence and absence of glucose are presented in (Figure 4c). The cyclic voltammogram of Ni/EC in 0.1 M NaOH solution showed nonsymmetrical wave, between anodic and cathodic peak with potential at about +5.78 V and +3.44 V versus reference electrode. The electrochemical reaction of Ni(III)/(II) in the alkaline solution may be described as following (Zhao et al., 2007).

$$Ni + 2OH^- - e^- \longrightarrow NiO(OH). \text{ Or}$$
$$Ni(OH)_2 + OH^- - e^- \longrightarrow NiO(OH) + H_2O$$

When Ni(0) is oxidized to Ni(II) at a potential smaller than -600 mV, NiO and $Ni(OH)_2$ are formed (Luo et al., 1996).

$$Ni + 2OH^- - e^- \longrightarrow NiO + H_2O$$
$$Ni + 2OH^- - e^- \longrightarrow Ni(OH)_2$$

Based on previous research, carbohydrates can be oxidized at strong basic (Das et al., 2006). As shown in Figure 4c, the nickel ion on the electrode's surface works as a catalyst for the oxidation of glucose. The potential reduction and oxidation peak about 358 mV, 654 mV, respectively. Glucose is quickly

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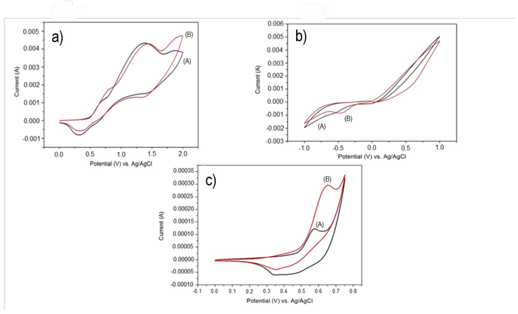

Figure 4. CVs of Ni/EC Electrode in Absense (A) and Presence (B) of Glucose 0.001 M in (a) KOH 0.1 M solution, (b) KNO_3 0.1 M solution and (c) NaOH 0.1 M Solution. Scan Rate 100 mVs^{-1}

oxidized to gluconolactone and increasing anodic peak when the addition of glucose (Figure 4c).

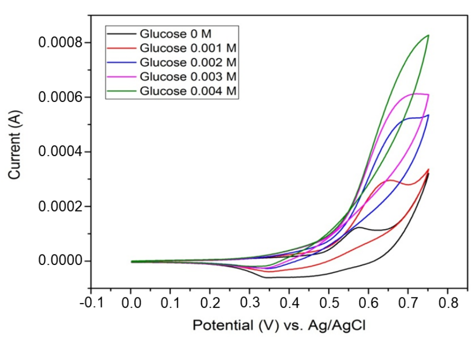

Figure 5. CVs of Ni/EC Electrodes in NaOH 0.1 M at Different Glucose Concentrations Scan Rate of 100 mVs^{-1}

The effect of different glucose concentrations on Ni/EC was investigated. The results (Figure 5) showed that the peak currents were gradually increased by increasing glucose concentrations. As can be seen, glucose may be oxidized in an alkaline solution, and the nickel ion functions as a catalyst in this reaction.

The cyclic voltammetry method was used to evaluate the electrocatalytic oxidation of Ni/EC electrodes in NaOH 0.1 M solution. Figure 5 indicates that when glucose was added to the NaOH solution, the anodic peak increased and the potential switched to a more positive state, whereas the cathodic peak declined without any further potential changes. It indicates that the oxidation of glucose was an irreversible electrochemical process. Mechanisms reaction described by (Cai et al., 2017; Yu et al., 2012) oxidation of glucose in the surface of the electrode (Figure 6):

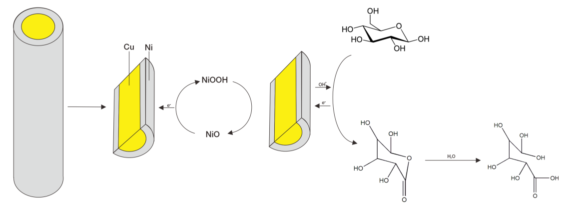

Figure 6. Reaction Possible of Glucose in Surface Ni/EC Electrode

$$Ni(OH)_2 + OH^- \longrightarrow NiO(OH) + e^-$$
$$NiO(OH) + glucose \longrightarrow Ni(OH)_2 + glucolactone$$

The calibration curves of glucose were obtained by cyclic voltammetry results (Figure 7). It shows the calibration curve of glucose with a current peak for the Ni/EC electrode. The CV determined for glucose with the different concentrations that were linear at range 0-0.004 M. The calibration curve was created with a Ni/EC electrode with the correlation (R^2) is 0.992 and a linear regression is y= 0.133x+0.000276. The linear regression equation can be used to determine glucose concentration in a sample of human urine.

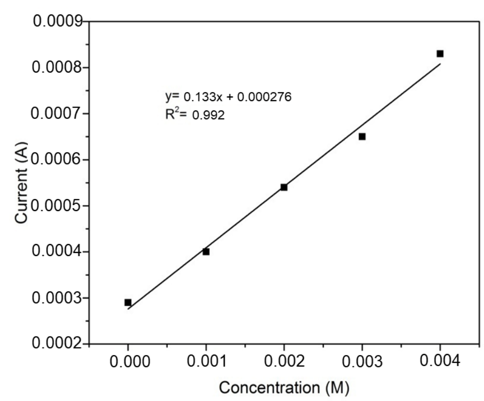

Figure 7. The Corresponding Calibration Curve of Ni/EC Electrode

Figure 8 shows the CVs of Ni/EC electrode with various scan rates in 0.1 M NaOH containing 0.001 M of glucose. The results show that the cathodic and anodic peak current increases linearly with the increasing scan rate in the range of 10-100 mV/s, the R^2 of 0.995 and 0.990 for the anodic and cathodic peak. It indicates the electrochemical reaction is controlled on the surface of the electrode.

A comparison of the performance of Ni/EC with other glucose sensors shown in Table 1. It can be noted that all of the them have differences limit of detection with other modified material. As-prepared Ni/EC electrode offered lower detection limit than gold glyconanoparticle. GC/MWCNT/NiOOH and Se-MCM-41 mesoporous have detection limit $4.3x10^{-3}$,

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Table 1. Comparison of Determination Glucose with Some Published Work

Electrode/Material	Method	LOD (M)	Reference
Gold glyconanoparticle	Colorimetric bioassay	$2.01x10^{-3}$	(Lim et al., 2013)
(GC/MWCNT/NiOOH)	Cyclic voltammetry	$4.3x10^{-4}$	(de Sá et al., 2014)
Se-MCM-41 Mesoporous Composite	Amperometric	$1x10^{-4}$	(Yusan et al., 2018)
Ni/EC	Cyclic voltammetry	$4.85x10^{-4}$	This work

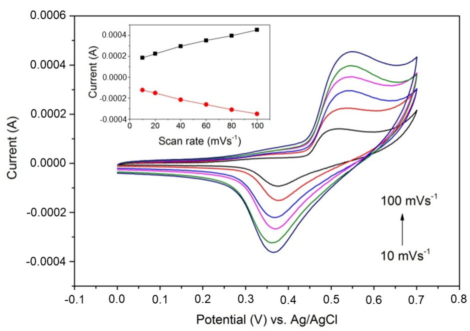

Figure 8. Cyclic Voltammogram of Various Scan Rate (10-100 mVs^{-1}) in 0.001 M Glucose

Table 2. Validation Method of Purpose Electrode

No.	Parameters	Value
1	Linierity	0.992
2	LOD (M)	$4.85x10^{-4}$ M
3	LOQ (M)	$1.6x10^{-3}$ M
4	Precision (%)	3.85
5	Recovery (%)	90.2-105.26

$1x10^{-4}$ respectively. However, their methods were complicated and the material used in the fabrication were more expensive. The advantages of the proposed electrode are simple and low-cost preparation. The proposed electrode is suitable for the determination of glucose concentration in the urine sample. Table 2 shows the parameters of the validation method in glucose analysis with cyclic voltammetry. This method was very useful and promised for glucose determination in human urine sample.

Table 3. Application for Real Sample

Sample	Glucose Added (M)	Glucose Founded (M)	Recovery (%)
A	-	0.0012	-
	0.002	0.0031	93.99
	0.003	0.0039	90.22
B	-	0.0014	-
	0.002	0.0035	105.26
	0.003	0.0043	95.24

3.3 Application for Real Samples

The proposed electrode was used to detect glucose in urine samples from humans. The current peak was measured after 5 mL of human urine samples were added to 5 mL NaOH 0.1 M solution. The recovery of Ni/EC electrode was analyzed using spiking method in pure glucose solution containing human urine sample. The results (Table 3) show recoveries of the sensor about 90.2-105.26%, which indicates the electrode great potential to determine glucose concentration in human urine samples.

4. CONCLUSIONS

In summary, Ni/EC electrode material has been prepared to investigated for glucose detection. The material Ni has been doped by electroplating in Cu Metal. Ni/EC has been successfully and investigation surface by SEM-EDX. SEM data on to surface Ni/EC electrode formed layer and EDX data showed 91.46% (weight atom) doped in Cu metal surface. All detection for glucose with electrochemical reaction. 0.1 M NaOH it is good electrolyte for reaction glucose in surface electrode Ni/EC to electrochemical reaction. Calibration curved was constructed and a linear response for glucose concentration at range 0-0.004 M with R^2= 0.992, LOD and LOQ was determined $4.85x10^{-4}$ M, $1.6x10^{-3}$ respectively.

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