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# Modified screen-printed electrode using graphene ink for electrochemical sensor application

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**Abstract.** In lab-on-chip development, screen printed electrode (SPE) method is usually utilized as an electrochemical sensor. As a basic conductive material, carbon has several advantages compared to other conductive materials. SPE performance can be enhanced by using a nanomaterial due to its unique properties, such as its small size particle and large surface area that can accelerate the electron transfer on the surface of the electrode. Graphene as a carbon-based nanomaterial is an extraordinary material to work with because of its good electrical conductivity and large specific surface area. In this work, we developed a graphene paste from the water-based graphene ink with the addition of polyurethane binder material to realize a nanocarbon conductive paste, which insoluble in water and other electrolytes. Our graphene paste was deposited on the working electrode area of SPE and the performance was tested using cyclic voltammetry method. The result showed that the optimal ratio for the graphene carbon paste, polyurethane to graphene ink, was 1:15 %vol. With this ratio, the performance of the modified SPE could successfully be increased and it also showed a stable sensing performance by having a low error value, below 3%, for 7 times of repeated measurements.

## 1. Introduction

Electrochemical sensors become one of the many choices for testing an analyte. It has several advantages compared to other analytical methods, such as simple and require small amount of material and sample which are used in a wide sector: environmental, food and medicine, as well as in clinical laboratory [1-2]. Many point-of-care devices use electrochemical sensor principle. Simple electrochemical sensor can be developed using screen printing technique in the form of screen-printed electrode (SPE). SPE manufacturing based on thick film technology is cheap, easy and fast. Thus it is frequently being selected as a sensor platform with various methods of improving sensor performance [3]. SPE consists of layer-by-layer paste deposition on top of a solid substrate using screen or mesh, which will determine the geometry or the design of the sensor. This technology has several advantages such as flexible design, automation of the manufacturing process, high reproducibility and broad material choices [4].



SPE for electrochemical analysis generally consists of three-electrode configuration: working electrode (WE), counter electrode (CE) and reference electrode (RE). The most common product of SPE is based on carbon graphite material, thus called SPCE (Screen Printed Carbon Electrode). As a conductive material, carbon has several advantages compared to the other materials, such as cheaper, easy to modify and has inert properties [1]. On its manufacture, SPE will require two main ingredients, conductive ink and dielectric ink. The exploration of conductive ink is very important because it is used for the formation of conductive pathways in electrodes and as the material for WE [5].

Conductive ink, especially for WE, can be enhanced using a nanomaterial, and it is extensively being explored by the researchers [6]. The very small particle size and large surface area can help accelerate the rate of electron transfer and the catalytic reaction on the electrode surface [7]. Graphene as a fascinating carbon-based nanomaterial has extraordinary properties, such as large surface area and good electrical conductivity [8]. Graphene nanocomposites can be easily synthesized, and many researchers have applied organic graphene and inorganic composites to various devices, such as batteries, supercapacitors, biosensors, fuel cells, photovoltaics, transistors, and many more [9]. In this work, graphene material was used as a part of WE modification on SPE to enhance its performance.

Binders, as a mixture of conductive ink materials, are also important as protection for conductive ink to avoid unwanted chemical or mechanical damage that can result in a decrease in conductivity. Selection of suitable binder material can result in good flexibility properties on the film and can produce good adhesion between the conductive layer and the substrate. Polyurethane become one of promising materials for binder because the structure property (di-isocyanates and polyols) makes polyurethane suitable for any substrate [10]. Even polyurethane compatible for adhesion related to nanomaterials [10]. However, optimization of the conductive ink and binder is necessary because the use of the binder has to be as effective as possible, not too much that can cover the performance of the nanomaterial. Therefore, in this research, we will be carried out to study the effect of the polyurethane and graphene ratios in enhancing performance of the SPE.

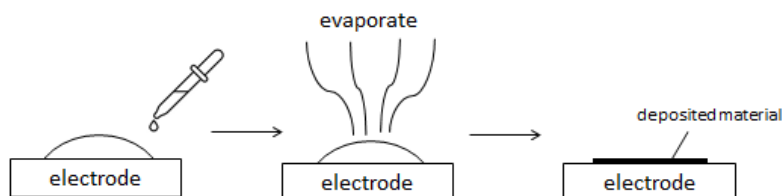
## 2. Experimental

### 2.1. Materials

Polyurethane Biocolours® BioThane Topcoat PU from bioindustries (Indonesia). Graphene Conductive Ink from UGENT TECH SDN BHD (Malaysia). Ethanol (C<sub>2</sub>H<sub>6</sub>O) and Acetone (C<sub>3</sub>H<sub>6</sub>O) from Sakura Medical Store (Indonesia). Aquades Aqua Pro Injection from IKAPHARMINDO PUTRAMAS (Indonesia). Ferrocyanide (Fe(CN)<sub>6</sub><sup>3/4</sup>) from Sigma Aldrich (Singapore). METROHM's Dropsens (DS 110) commercial SPE will be used for the electrochemical testing.

### 2.2. Device fabrication

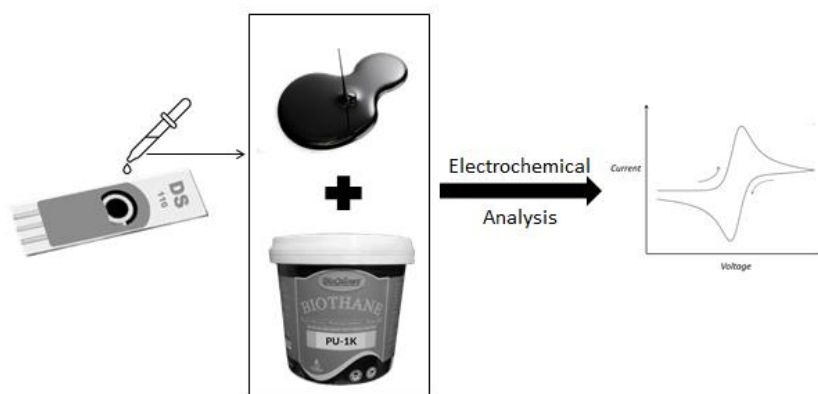
On this paper, graphene paste will be made using commercial graphene ink added with Polyurethane. The mixing of the paste was done using spatula and magnetic stirrer for 2-3 minutes until homogeneous. Polyurethane and graphene composition will be tested using several different ratios of polyurethane to graphene from 1:5 to 1:20 (%vol). 4  $\mu$ L of paste was deposited on WE with drop-casting method and dried for 30 mins at room temperature (**Figure 1**).



**Figure 1.** Material deposition scheme using drop-casting method on the working electrode surface.

### 2.3. Electrochemical testing

The general overview of the electrochemical testing method is illustrated in **Figure 2**. For electrochemical testing, we selected cyclic voltammetry (CV) with ferrocyanide ( $\text{Fe}(\text{CN})_6^{3/4}$ ) as a reagent. Using CV method, electroactive information, such as reduction, oxidation, and the rate of electrochemical reactions from analytes qualitatively and quantitatively can be obtained. 10 mM ferrocyanide solution was mixed with 10 mM Phosphate Buffered Saline (PBS). PBS is an electrolyte that has similar properties with body fluid (pH  $\sim 7.4$ ). The mixing of the sample was conducted by magnetic stirring process for 5 minutes at 250 rpm speed. We used a commercial potentiostat CorrTest for electrochemical analysis of our prepared device. CV testing is done with a potential range of  $-0.4$  V to  $0.8$  V for 3 cycles and scan rate  $50$  mV/s.

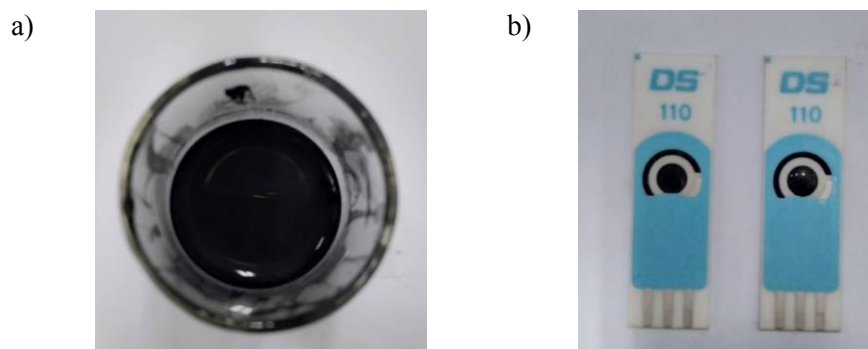


**Figure 2.** Electrochemical testing scheme. After working electrode of SPE being modified with graphene ink and polyurethane, the electrochemical analysis is performed.

## 3. Results and Discussion

### 3.1. Modification of the working electrode

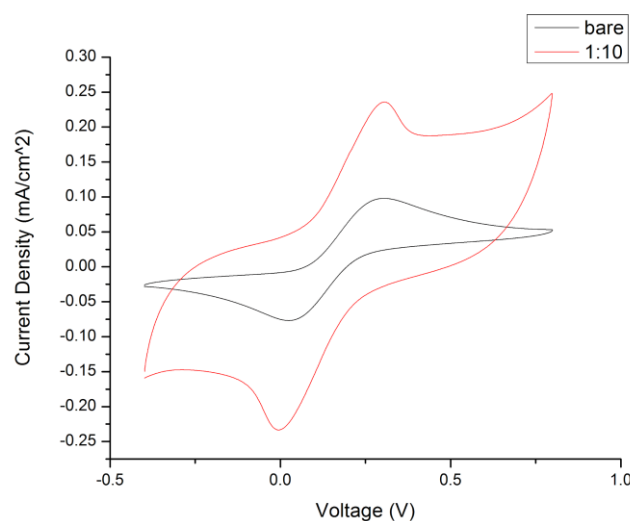
The results of graphene/polyurethane (GP-PU) paste are shown in **Figure 3(a)**. Modification was made using drop-casting method. The volume of suspension to be dropped must be suitable so that the suspension only covers the working electrode. The counter electrode and reference electrode parts must not be exposed to additional material.  $4 \mu\text{L}$  is the ideal volume to cover the working electrode. The suspension was left to dry for about 30 minutes at room temperature. The difference of the SPE before and after graphene paste modification on, WE are shown in **Figure 3(b)**. After the suspension dries on the surface of the working electrode, a CV test with a  $10$  mM ferrocyanide solution was performed to check its electrochemical performance.



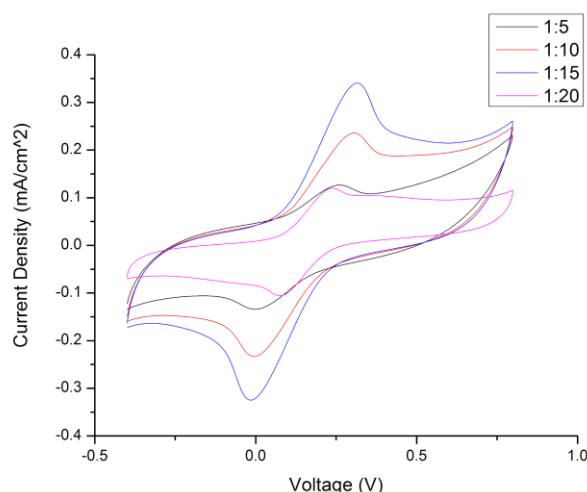
**Figure 3.** (a) Graphene paste obtained from mixing graphene ink with polyurethane (GP-PU). (b) bare SPCE and SPCE that have been modified with GP-PU paste.

### 3.2. Comparative testing of SPCE with and without modification of GP-PU paste

Cyclic voltammetry was selected to study the electrochemical properties of the SPCE. **Figure 4** displayed a CV diagram of the bare SPE and SPE/GP-PU (polyurethane to graphene ratio was 1:10) electrode in 0.01 M ferrocyanide at the scan rate of  $50 \text{ mVs}^{-1}$ . A couple of redox peaks corresponding to the reduction and oxidation of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  were observed for indicating a reversible electron transfer process [11]. Both anodic and cathodic peak currents were increased after SPE being modified. Oxidation value (anodic peak) increased ( $I_p$ ) from  $0.1004 \text{ mA/cm}^2$  (without modification) to  $0.165 \text{ mA/cm}^2$  (with modification) meanwhile the reduction value (cathodic peak) increased from  $0.098 \text{ mA/cm}^2$  to  $0.16897 \text{ mA/cm}^2$ . This is consistent with the theory that the presence of nanomaterials will increase the conductivity of electrodes by increasing the effective surface area of the electrodes that represent with the increase of oxidation and reduction values [7].



**Figure 4.** Cyclic voltammogram of SPCE with and without modification with GP-PU paste.



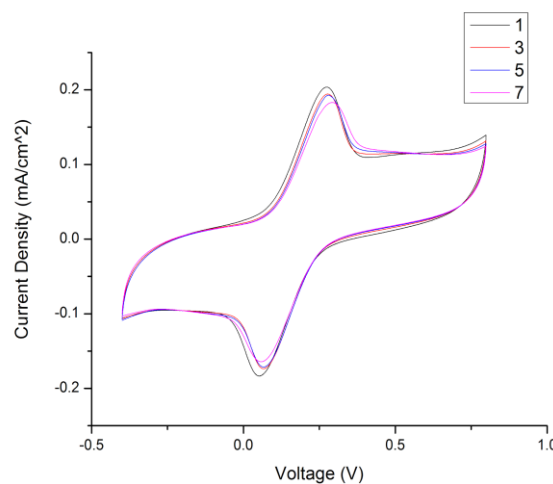
**Figure 5.** Cyclic voltammogram of SPE with various polyurethane-graphene ink ratio from 1:5 to 1:20 (%vol).

To find the optimum polyurethane to graphene paste ratio, various variations were carried out, below and above 1:10 ratio. Based on the graphs in **Figure 5**, the optimum ratio is 1:15 %vol. The

sensor performance increased as graphene ratio added that means the graphene ink still work well even with the addition of polyurethane. However above 1:15 %vol ratio, the performance decreased. This is due to polyurethane binder could not keep up with the amount of graphene ink, thus the performance reduced to original commercial water-based graphene ink properties, which is soluble in water and electrolyte solutions. Also, in 1:15 %vol ratio the adhesion of the graphene pastes to the substrate still maintains when immersed in the electrolyte solution or distilled water. Therefore, the next test was conducted using modified graphene paste on binder with 1:15 %vol ratio.

### 3.3. Stability testing

Repeated measurement tests were used to determine the error percentage of a measurement. This CV measurement was performed 7 times using a 10 mM ferrocyanide solution in PBS to see the stability performance of modified SPCE, as shown in **Figure 6**.



**Figure 6.** Cyclic voltammogram of repeated measurement in the same modified SPE.

Current peak measurement was not change much until 7 repeated measurements. At the 8th measurement above, the relative error is large (above 10%) which indicates the limitations of repeated measurements when using this sensor. The percent value of measurement error is obtained from the calculation of the absolute value of the relative error of each measurement of concentration then averaged. The relative error calculation formula is shown in the **Equation 1**.

$$|Relative\ Error| = \left| \frac{measured\ value - reference\ current}{reference\ current} \right| \times 100\% \quad (1)$$

The absolute percentage value of relative error in the repeated measurements is shown in **Table 1** with average error 2.39% in 7 measurements. This shows that modified electrode with GP-PU paste has a good stability until 7 measurements.

**Table 1.** Stability of the measurement.

Measurement	Current Density (mA/cm <sup>2</sup> )	Relative Error (%)
1	0.164	-
3	0.162	1.35
5	0.161	1.56
7	0.157	4.25

#### 4. Conclusion

Polyurethane as a binder could interact well with the conductive carbon material (graphene ink) and produced a good adhesion to the substrate when the graphene ink-polyurethane was deposited on the electrode using the drop-casting method. The electrochemical analysis showed that the graphene ink-polyurethane improved the electroactive surface area of the electrode and mediated the electron transfer between electrode and electrolyte with the optimum ratio of polyurethane to graphene ink paste was 1:15 %vol. The nanomaterial graphene can lead to the promotion of the electron transfer rate and enhancement the redox currents, which led to a higher sensitivity of the output signal. It also had a good stability with an average error of the measurement was 2.39% for 7 times of repeated measurements.

#### Acknowledgment

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