Single-Walled Carbon Nanotubes-Modified Gold Electrode for Dopamine Detection

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Modification of gold electrode using single-walled carbon nanotubes (SWCNTs) has been done. The synthesis of SWCNTs on the gold electrode surfaces was carried out using chemical vapor deposition (CVD) method. The performance of the electrodes as a sensor was characterized using dopamine (DA) solution at pH 4 by cyclic voltammetry. A change in electrode capacitance was found before and after DA detection. The detection limit and sensitivity of the electrodes are 0.79 µM and 3.414 µA mm−2 µM−1, respectively. No interference signal was found from ascorbic acid (AA) during DA measurement.

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Dopamine Detection

Electrochemistry is an analytical method that had been applied as a biosensor.6 This method is commonly used because it is relatively fast, simple and low-cost.10 Biosensors selectivity and sensitivity improvements can be conducted by modifying the electrodes using a specific material.9 Most of the modified electrodes are platinum, silver and gold.9 The modified electrodes have been reported as a dopamine (DA) biosensor, i.e. gold nanoparticles electrode,1 calixarene modified GCE,2 nanoporous Au-Ag alloy electrodes,3 and carbon nanomaterial electrodes.2

Several scientists already used carbon nanotubes (CNTs) with various materials combinations to detect DA.8–12 In this research, we used single-walled carbon nanotubes (SWCNTs) modified gold electrode as working electrodes for DA detection. SWCNTs is one of the most preferred materials that is used as a biosensor because of its dimensional character.12 This material was made in our laboratory by a CVD method which is relatively different with available catalyst in the Market.14 The type of the catalyst used in the SWCNTs synthesis influenced the activity performance of the catalyst itself.12 In our previous research, we modified gold electrodes using gold nanoparticles that have detection limit of 2 µM.1 The performance of the SWCNTs modified gold electrode in this research will be compared with the previous work.

Experimental

Synthesis of single-walled carbon nanotubes (SWCNTs).—Gold electrodes were modified with SWCNTs by CVD method as from our previous work.14,16 The results obtained from Field-emission scanning microscopy (FE-SEM) and Transmission electron microscopy (TEM) indicated that SWCNTs were bundled with each other, resulting in tubes with diameters of 5–20 nm. The SWCNTs intensity ratio obtained from Raman Spectroscopy at G-band and D-band at ca.1590 cm−1 and 1350 cm−1 respectively, was ca. 20 when a wavelength of 514.5 nm was used. The D-band was very weak, which indicated that the SWCNTs contained high level crystallinity with few defects. The radial breathing mode obtained from SWCNTs provided information on the SWCNTs diameter distribution. The estimated diameter distribution was 0.9–1.6 nm, which matches with the results obtained from TEM measurement.16,18 The Brunauer–Emmet–Teller (BET) specific surface area of the SWCNTs was measured using an adsorption analyzer (Quantachrome Instruments, NOVA2200e) and liquid N2 (77 K). From the results, we estimated that the BET specific surface area for the SWCNTs in this research is 110 cm2, which is equivalent to an apparent surface area of 1 cm2. This estimated value corresponds to the value in the previous report.16 All characterization were based on the report written by Williams and Eklund.17

Electrochemical measurements.—Electrochemical measurements were carried out using a potentiotstat from eDAQ (potentiostat E161 and e-corder 410, which is equipped with e-chem software vs 2.0.1). The measurements were performed using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). All measurements were carried out using three-electrode cell system. This system uses platinum as counter electrode (CE), Ag/AgCl (KCI 3 M) as reference electrode (RE), and SWCNTs modified gold electrode as working electrode (WE), except stated otherwise. The potential was swept from 0.0 to 0.6 V vs. Ag/AgCl (KCI 3 M), with 20 seconds of rest time before being measured and scan rate of 100 mVs. The DPV technique, scan rate, pulse amplitude, step potential, and pulse width obtained each were 50 mVs, 25 mV, 5 mV and 50 ms, respectively. Stock solutions were made by dissolving DA in 0.2 M acetate buffer solutions. Concentrations of DA used to obtain the calibration curve were 0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 µM. Limit of detection (LOD) and sensitivity of DA were determined from the linear equation of the calibration curve. The calibration curve was plotted from the anodic peak current at the maximum potential.

Electrochemical impedance spectroscopy (EIS) was monitored by Autolab PGSTAT128N. Impedance data was measured at the frequency range of 100 kHz to 0.1 Hz using signal amplitude of 0.1 V. Data and equivalent electrical circuit analysis were performed with Nova 1.11 software. SWCNTs characteristics before and after DA measurement were compared.

Results and Discussion

Characterization of single-walled carbon nanotubes (SWCNTs) electrodes in dopamine solution.—Data obtained from electrochemical measurement was used to analyze the performance.
of SWCNTs on the examined DA solution. Figure 1 shows the cyclic voltammogram from 0.2 mM acetate buffer solution with (B) and without DA (A). The electrode oxidizes and reduces DA at potential +0.479 V \( (i_{pa} = 408.803 \mu A) \) and +0.240 V \( (i_{pc} = -412.917 \mu A) \) respectively. It shows that the electrode can be used for DA detection.

Performance of SWCNTs modified gold electrode before and after used to determine DA was also studied using EIS. In this analysis, we can determine the characteristics of the materials. It was discovered that there was a difference between the electrodes from before (Figure 2A) and after (Figure 2B) DA measurement. It can be seen from the Nyquist plot of the electrode before measurement of DA was dominated by the characteristic of linear line approach at 45° angle in the high-medium frequency region. This pattern is attributed from the porous or rough electrode surface, which contributes to the rise of the constant phase element in the high frequency region. In addition, from the figure an almost straight line on the low frequency region is also seen. And simultaneously there is an underlying semicircle at the high-medium frequency region (Figure 2B) after the DA measurement. This occurrence can be explained by the pseudo capacitance that associated with the surface-bound functional groups. Impedance parameters, i.e. Rs (solution resistance), Rct (charge transfer resistance) and CPE (constant phase element) were simulated using an equivalent circuit, which are shown in Figure 2. The CPE1 at Figure 2A and B represent the interfacial capacitance and CPE2 in Figure 2B indicates the pseudo capacitance from the surface of the functional groups. Capacitance \( C \) as a function of frequency can be evaluated by following equation:

\[
C = \frac{1}{2\pi f Z''},
\]

where \( f \) is frequency and \( Z'' \) represents the imaginer of \( Z \).

Figure 3 shows that capacitance tends to increase when the frequency decreases for SWCNTs, both before and after the DA measurement. This also can be seen that SWCNTs capacitance after DA measurement is higher than the initial value before DA measurement. This is because the DA oxidation product attaches on the surface of the SWCNTs modified gold electrode. Based on the EIS result, the performance of the electrode after DA measurement can be restored by cleaning process. The cleaning process was performed by applying cyclic voltammetry in 0.2 M of acetate buffer at pH 4 for 30 cycles with sweep rate of 100 mV/s. The results show that the DA oxidation product which attached on the surface of the electrode can be removed. Hence the performance of the electrode can be restored to their original state. The electrode still produce good performance after being cleaned for 20 times.

DA-o-Quinone was the oxidizing product from DA. The possible mechanism of reversible reaction of DA and the interaction between the SWCNTs modified gold electrodes with DA are presented in

![Nyquist plots and equivalent circuit of SWCNTs modified gold electrode before (A) and after (B) DA measurement.](image-url)
Figure 3. Capacitance of SWCNTs modified gold electrode before (A) and after (B) DA measurement.

Figure 4. The free electrons from the oxygen atoms of hydroxyl groups on DA bond temporarily with the electrode. This in turn causes the oxygen atoms to become unstable and hence releasing hydrogen atoms, thus forming an oxidation product (DA-o-Quinone).

**Calibration curve for dopamine detection using SWCNTs electrodes.**—Calibration curve was obtained from electrochemical measurement using various concentrations of DA solutions. The measurement was conducted using DPV with potential sweep of 0.200 V to 0.500 V and scan rate of 50 mV/s. The DA voltammogram at various concentrations is shown on Figure 5A. The anodic current increased as DA concentration increases. Calibration curve was obtained using an ipa value at potential of 0.350 V (Figure 5B). The linear regression equation and its correlation coefficient ($R^2$) are $ip_a (\mu A) = 86.25026 + 1.22965c (\mu molL^{-1})$ and 0.9967 respectively. This calibration curve was used to determine the LOD and the sensitivity of the SWCNTs modified gold electrode on the DA solution. The LOD of the electrode for the DA measurement was found at 0.79 $\mu$M. Sensitivity of the electrode was calculated from the linear regression equation in Figure 5B, which was 3.414 $\mu$A mm$^{-2}$ $\mu$M$^{-1}$. This justifies that our SWCNTs modified gold electrode is better than the electrode in our previous research and other studies as shown in Table I.

**Selectivity of SWCNTs electrode.**—Ascorbic acid (AA) is a major interfering compound in DA detection. This compound is usually oxidized at a similar potential with DA. The electrochemical measurement on the AA solution was conducted so that the selectivity of the SWCNTs modified gold electrode can be analyzed. Figure 6 shows the cyclic voltammogram (5 cycles) of 1 mM AA solution obtained using the same electrode. The oxidation peak was formed only on the first cycle at 0.146 V. Furthermore, no peaks were formed on the potential range of 0.000–0.550 V during the latter cycles (2–5). Even
The first five cyclic voltammogram of SWCNTs modified gold electrode shows a good performance as a sensor for DA detection. This proves that the particular electrodes being researched are selective toward the DA with the presence of ascorbic acid, dopamine, uric acid and folic acid based on activated graphene/MWCNT nanocomposite loaded Au nanoclusters. Sens. Actuators B Chem., 221, 659 (2015).

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