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Single-Walled Carbon Nanotubes (SWCNTs), Ketjen Black (KB), and Gold Nanoparticles (AuNPs) Modified Glassy Carbon Electrode for Highly Selective Dopamine Sensing

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Modification of glassy carbon electrode (GCE) with single-walled carbon nanotubes (SWCNTs), Ketjen Black (KB), and gold nanoparticles (AuNPs) has been done. The modification was performed using drop coating method. Comparison performance between unmodified and modified GCE for detecting dopamine was carried out using cyclic voltammetry in 0.10 M acetate buffer solution (pH 4). It was performed in the potential range from – 0.80 V to 0.80 V with a scan rate of 100 mV/s at room temperature. The results showed that modified GCE could produce higher anodic peak currents than unmodified GCE. This indicates that the synergistic effect between SWCNTs, KB, and AuNPs has succeeded to improve the performance of GCE. The limit of detection (LOD) of modified GCE for dopamine solution was determined using a calibration curve which plots the concentration variation to the anodic peak current. The calculation of LOD was found to be 0.49 μM. Modified GCE showed good selectivity in dopamine without any interference signal from a solution of uric acid (UA), ascorbic acid (AA), glucose (Glu), and urea (U) in 0.10 M acetate buffer solution with pH 4. In this condition, only dopamine increases oxidation and reduction currents. The results indicated that modified GCE using SWCNTs, KB, and AuNPs can be used for highly selective dopamine sensing.

Keywords: SWCNTs, Glassy carbon electrode, Dopamine, Sensor, Ketjen Black, Gold nanoparticles.

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1. INTRODUCTION

In human body dopamine found in the brain's hypothalamus with critical function as a neurotransmitter and chemical messenger in the brain [1]. The deficiency of dopamine levels in the human body can cause serious effects such as Alzheimer, Schizophrenia, and Parkinson [1]. The great benefits of dopamine for humans have led to research on method development to analyze dopamine. Electrochemical sensors appear to be a potential alternative method that offers an advantage as fast sample response, inexpensive, low detection limits, and can be developed in a portable form [2]. Glassy Carbon Electrode (GCE) is a type of carbon-based electrode that is interesting to be improved [3]. GCE has the advantages of having excellent electrical properties, broad potential window, and relatively inert [4]. The performance of sensor can be improved by modify the surface of the sensor with other materials [5].

Numerous studies about the detection of dopamine have been done using various types of modified electrodes. The major problem is the presence of the other compounds signals during analysis, such as ascorbic acid, uric acid, urea, and glucose [6]. In the biological fluids, these compounds have concentrations up to 1000 times higher than the concentration of dopamine [1]. This condition causes the low selectivity of the electrode to dopamine. Some researchers have already used carbon-based and precious metal nanomaterials to increase the performance of glassy carbon electrodes as a dopamine sensor [7]. Types of carbon materials that can be used for modification of electrode are Single Wall Carbon Nanotubes (SWCNTs) [4] and Ketjen Black [4].

The advantages of SWCNTs as a material for electrode modification are good thermal conductivity, high surface area, and good electronic properties [7]. Ketjen Black is a type of carbon material that has the benefit of having high conductivity, a specific surface area and has a very porous structure that makes the surface area of ketjen black become very large and can absorb more analytes when used as a material for modification of electrochemical sensors [5]. Gold nanoparticles have great potential as a material for modification because of the biocompatibility in optical, electronic properties and their synthesis is relatively simple for electrochemical sensors. The gold nanoparticles material also has the potency to be used to increase the selectivity of electrochemical sensors [2].

In this work, modification of GCE using SWCNTs, KB, and AuNPs has been done to improve the selectivity and limit detection of the dopamine sensor.

2. MATERIALS AND EXPERIMENTS

2.1 Materials

Single-Walled Carbon Nanotube was synthesized in Saga University, Japan. Ketjen Black type EC 600 JD was purchased from LION Japan. Sodium cholate, uric acid, sodium acetate, sodium citrate dihydrate, sodium chloride and dopamine were purchased from Sigma Aldrich. Ascorbic acid, glucose, urea, disodium hydrogen phosphate, sodium dihydrogen phosphate, NaOH, glacial acetic acid was purchased from Merck. The gold wire (99.99 %) was purchased from Antam. The copper wire was bought from a local market.

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Demineralized water was used for dilution and cleaning purpose.

2.2 Fabrication of Materials for GCE Modification

The manufacture of a mixture of carbon-based materials for GCE modification is carried out by preparing Single-Walled Carbon Nanotubes, Ketjen Black EC 600 JD, Sodium cholate, and demineralized water. All the ingredients were mixed in an ampoule and sonicated to form a thick solution which was a suspension of SWCNTs and ketjen black in demineralized water.

The synthesis of AuNPs was carried out by preparing gold and copper electrodes connected to a power supply with configuration the gold electrode connected to the positive pole and copper electrodes at the negative pole. Gold and copper electrodes were immersed in a beaker containing 400 ml boiling demineralized water while stirring with a magnetic stirrer. 10 ml of 0.40 M sodium citrate and 10 ml of 0.02 M NaCl were added. 50 V was applied to the electrolysis system to initiate the reaction. Heating was carried out for 45 min with constant stirring until the color of the solution changed from colorless to wine red. After that, heating was stopped, and the electrode was removed from the beaker. Then the result of colloidal gold was left for 5 h to reach room temperature.

2.3 Fabrication of SWCNTs, Ketjen Black (KB), and Gold Nanoparticles-Modified Glassy Carbon Electrodes

GCE was rinsed with demineralized water before being used and polished with alumina slurry for 3 min to have a smooth surface. The polished electrode was rinsed with demineralized water to remove the slurry. Then the process was continued with sonication in demineralized water and ethanol, respectively, for 20 min. The electrode was dried at room temperature and stored in a desiccator, ready for modification.

A 20 µl mixture of carbon-based material from section 2.2 was taken using a micropipette and dripped onto the surface of the GCE. GCE was transferred to a desiccator and left for 4 h. Next, 20 µl of gold nanoparticles were taken and dripped on the electrode surface, which previously had been modified with carbon-based material and stored in a desiccator for 12 h.

2.4 Signal Testing of Unmodified GCE and Modified GCE

The test solution was prepared by dissolving 90 µL of 0.10 M dopamine into 25 mL of 0.10 M acetate buffer solution (pH 4). Then dopamine was characterized by unmodified GCE and SWCNTs, KB, and AuNPs modified GCE. Measurements were carried out using the cyclic voltammetry method. The potential applied is in the ranges from – 0.80 V to 0.80 V with a scan rate 100 mV/s for 5 cycles with 3 repetitions.

3. RESULTS AND DISCUSSION

3.1 Performance of Unmodified GCE and Modified GCE Electrodes in Dopamine Solution

The voltammogram in Fig. 1 is the response of the GCE sensor without modification to the dopamine sample in 0.10 M acetate buffer solution with pH 4. The unmodified GCE response shows that a typical voltammogram is formed which is different from the blank with an anodic peak current value of 0.30 µA at a potential of 0.54 V.

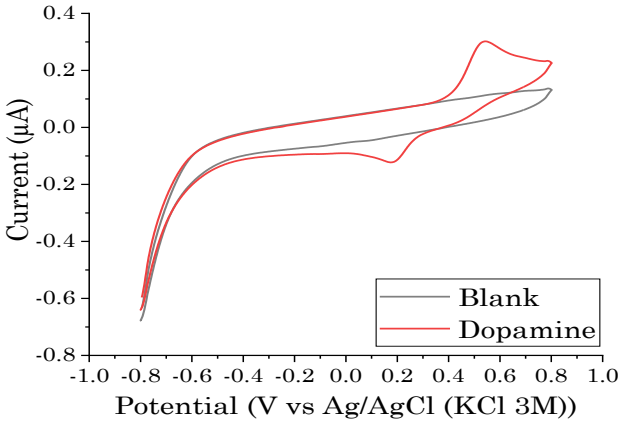

Fig. 1 – Voltammogram of 0.10 M acetate buffer solution; pH 4 (black) and dopamine solution in 0.10 M acetate buffer solution; pH 4 (red) on an unmodified GCE with a scan rate of 100 mV/s

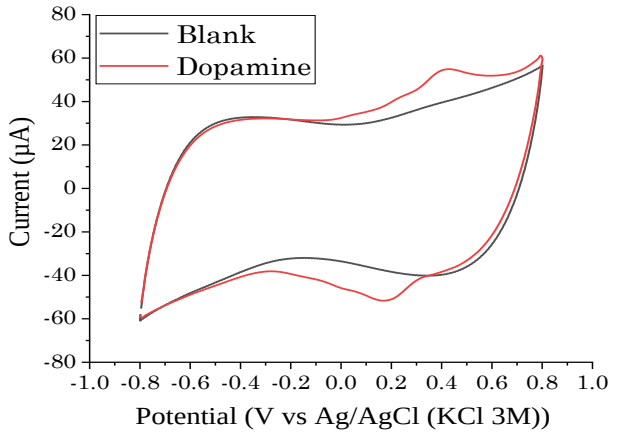

Fig. 2 –Voltammogram for 0.10 M acetate buffer solution; pH 4 (black) and dopamine solution in 0.10 M acetate buffer solution; pH 4 (red) on SWCNTs, KB, and AuNPs modified GCE with a scan rate of 100 mV/s

Fig. 2 shows a dopamine voltammogram with SWCNTs, KB, and AuNPs modified GCE sensors. The anodic peak current appears at a potential of 0.41 V with a value of 54.54 µA. The electrode is said to be sensitive to dopamine solution because it shows an oxidation and reduction peak, while these peaks cannot be found in the voltammogram of blank solution [8].

Fig. 2 shows that anodic current dopamine using the modified electrode has a higher current than the unmodified electrode (Fig. 1). It is caused by a synergistic effect of the mixed modified material added to the surface of the glassy carbon. The KB can absorb many analytes due to its porosity [9]. The AuNPs can improve the affinity of the sensor. The SWCNTs have an ultra-sensitive characteristic in sensing [2]. Refer to the individual property of each material added, and then the electrode can improve its performance more than the unmodified electrode.

3.2 Selectivity Study

The results of measuring dopamine, uric acid (UA), urea (U), glucose (Glu), and ascorbic acid (AA) are shown in Fig. 3. The result shows that the measurement of the dopamine sample produces a distinctive voltammogram than the blank solution. The dopamine sample produced one anodic peak and one cathodic peak current. The voltammogram produced by uric acid, urea, glucose, and ascorbic acid showed the same response as the blank with neither anodic nor cathodic peak currents displayed. These results indicate that SWCNTs, KB, and AuNPs modified GCE sensors are only selective for dopamine in 0.10 M acetate buffer solution with pH 4.

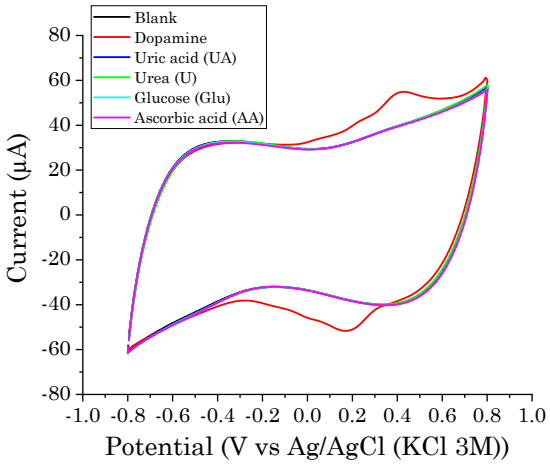

Fig. 3 – Voltammogram of interference study

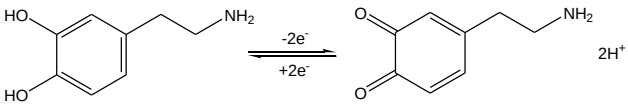

Fig. 4 – Redox reaction mechanism from dopamine to dopamine-o-quinone

Fig. 4 explained about redox reaction of dopamine and dopamine-o-quinone. When the potential applied was between – 0.80 to 0.80 V, dopamine is oxidized to dopamine-o-quinone by releasing two electrons to produce a current which is detected by the instrument as the oxidation peak. Scanning back from 0.80 to – 0.80 V dopamine o quinone reduced to dopamine by gaining two electrons and detected by the instrument as the reduction peak [8].

Table 1 shows some research regarding modified GCE electrodes as a dopamine sensor and the types of interference. Most studies show a common problem for detecting dopamine that they suffer from interference. In our work, we show that we can overcome this problem. This research is only selective for dopamine without interference from uric acid, ascorbic acid, urea, and glucose.

Table 1 – Interference comparation with another research

Modification material	Interference Type				Ref.
	UA	AA	U	Glu	
Mp-GR/GCE	X	X	–	–	[10]
PG/GCE	X	–	–	–	[11]
CTAB/rGO/ZnS/ GCE	X	X	–	–	[12]
Capsaicin Oxidized/MWCNT/GCE	X	X	–	–	[6]
SWCNTs/KB/AuNPs/GCE	X	X	X	X	This work

3.3 Limit of Detection (LOD) from SWCNTs, KB, and AuNPs Modified GCE to Dopamine

The test solution was prepared by dissolving dopamine in 0.1 M acetate buffer solution at pH 4 in concentrations of 0, 12, 14, 16, and 18 μM. The voltammogram obtained (Fig. 5) is then made a calibration curve between the concentration and the peak current of the anode (Fig. 6) and then the detection limit is determined. The potential applied is between – 0.80 V to 0.80 V for 5 cyclic with 5 repetitions.

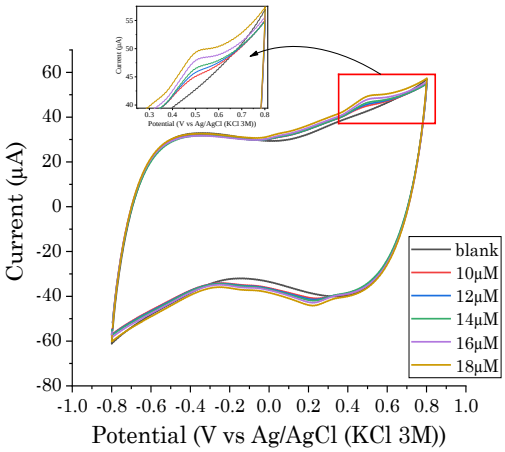

Fig. 5 – Voltammogram of dopamine measurement results with various concentrations, i.e., 0 μM (Blank), 10 μM, 12 μM, 14 μM, 16 μM, 18 μM in 0.10 M acetate buffer solution (pH 4). Measurement was done using scan rate of 100 mV/s

Furthermore, through the linear curve in Fig. 6 obtained a linear regression equation:

$$y = 0.4577x + 40.4770 \quad (1)$$

with R^2 value is 0.9897. The R^2 value obtained in this study is still acceptable because the acceptable linear correlation value or R^2 in chemical research is greater than 0.80 and less than 1.00 [13]. It can be said that the dopamine concentration is directly proportional to

the anodic peak current produced.

The linear regression equation (equation (1)) that obtained from the calibration curve between the dopamine concentration and peak anodic current in Fig. 6 were used to determine the detection limit of dopamine samples using modified GCE sensors with acetate buffer solution pH 4.

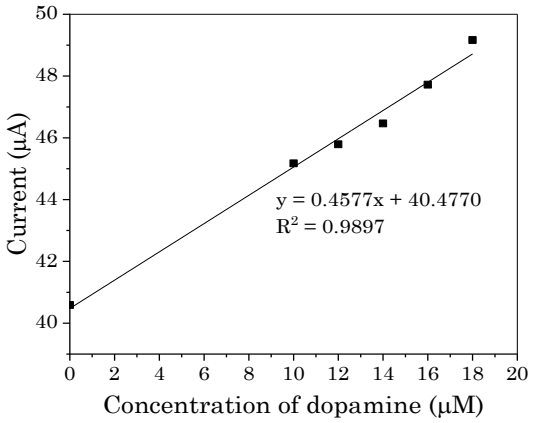

Fig. 6 – Plot of dopamine concentration vs. anodic peak current of the modified GCE sensor

Table 2 – Measurement data of blank solution using modified GCE sensors SWCNTs, KB, and AuNPs

Blank current signal on measurement (μA)					Average (μA)	S_b
1	2	3	4	5		
40.59	40.61	40.51	40.59	40.59	40.59	0.04

Table 2 is the current measurement data for 0.10 M acetate buffer solution (pH 4). The detection limit value is then determined by entering the average current signal value in the following equation:

$$I_{pa} = I_{pa} + (3S_b), \quad (2)$$

where I_{pa} is peak current detection limit and S_b is standard deviation of blank. The value obtained from equation 2 is entered in the linear regression equation 1 as the y value. The x value obtained from the calculation is the detection limit value of the sensor against the analyte. Through calculations, the detection limit of the modified GCE using SWCNTs, KB, and AuNPs for dopamine samples dissolved in 0.10 M acetate buffer solution (pH 4) was 0.49 μM.

Table 3 – Research on dopamine detection limits with modified GCE

Modification of Electrode	LOD (μM)	Ref.
Mp-GR/GCE	1.50	[10]
PG/GCE	2.00	[11]
CTAB/rGO/ZnS/GCE	0.50	[12]
Capsaicin Oxidized/MWCNT/GCE	1.78	[6]
SWCNT/KB/AuNPs/GCE	0.49	This work

Table 3 presents data on studies that have been conducted on the use of modified GCE for dopamine detection. Referring to the data, this research has the smallest detection limit compared to the other research. It indicates that GCE modification with SWCNT, KB, and AuNPs can improve the performance of glassy carbon electrodes.

4. CONCLUSIONS

Modification of GCE with SWCNTs, KB, and AuNPs has been successfully carried out. The modified GCE using SWCNTs, KB, and AuNPs have better detection limits to detect dopamine than the modified GCE study with other materials. The detection limit was 0.49 μM. The best selectivity was obtained when the measurement was performed in pH 4 acetate buffer solution. No current appears in the voltammogram from uric acid, ascorbic acid, urea, and glucose in anodic and cathodic peaks indicating that the interference was successfully removed.

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Модифікований одностінними вуглецевими нанотрубками (SWCNTs), Ketjen Black (KB) і наночастинками золота (AuNPs) скловуглецевий електрод для високоселективного визначення дофаміну

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Виконано модифікацію скловуглецевого електроду (GCE) одностінними вуглецевими нанотрубками (SWCNTs), Ketjen Black (KB) та наночастинками золота (AuNPs). Модифікацію проводили методом крапельного нанесення покриття. Порівняння показників немодифікованого і модифікованого GCE для виявлення дофаміну проводили з використанням циклічної вольтамперометрії в 0,10 М ацетатному буферному розчині (pH 4). Воно проводилося в діапазоні потенціалів від – 0,80 В до 0,80 В зі швидкістю сканування 100 мВ/с при кімнатній температурі. Результати показали, що модифікований GCE може генерувати вищі анодні пікові струми, ніж немодифікований GCE. Це вказує на те, що завдяки синергічному ефекту між SWCNTs, KB та AuNPs вдалося покращити показники GCE. Межа виявлення (LOD) модифікованого GCE для розчину дофаміну була визначена за допомогою кривої калібрування, яка відображає зміну концентрації від анодного пікового струму. Було знайдено, що розрахунок LOD становить 0,49 мкМ. Модифікований GCE показав хорошу селективність щодо дофаміну без будь-якого інтерференційного сигналу від розчину сечової кислоти, аскорбінової кислоти, глюкози і сечовини в 0,10 М ацетатному буферному розчині з pH 4. У цьому стані тільки дофамін посилює окислювальні та відновні струми. Результати показали, що модифікований GCE з використанням SWCNTs, KB, та AuNPs можна використовувати для високоселективного визначення дофаміну.

Ключові слова: SWCNTs, Скловуглецевий електрод (GCE), Дофамін, Датчик, Ketjen Black (KB), Наночастинки золота.