Response of SWCNTs/KPG5-modified carbon electrode on dopamine, uric acid and ascorbic acid

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Abstract. SWCNTs/KPG5-modified carbon electrode as electrochemical sensor have been successfully fabricated. The sensor was prepared by dropping the modification material, i.e. SWCTs and KPG5 in the surface of carbon electrode. The performance of the sensor was investigated in medical samples such as dopamine, uric acid, and ascorbic acid. The concentration of all tested samples was 10 mM. The electrochemical experiments were analysed using cyclic voltammetry method from -0.8 until +0.8 V with scan rate of 50 mV/s at acidic condition (pH 4) in room temperature. The best response of SWCNTs/KPG5-modified carbon electrode was obtained during dopamine measurement. No response detected from uric acid and ascorbic acid. The result was proved that SWCNTs and KPG5 have a good potential as modified material for selective electrochemical sensor in determination of medical samples.

1. Introduction
The detection and quantification of electrochemical active compounds such as blood and urine are important to diagnose and monitor several diseases [1]. Dopamine (DA) is one of the important component in human body [2,3]. This component includes in the catecholamine group and plays an important role in the function of central nervous, renal, hormonal and cardiovascular systems and normal level in blood is very low (from 0.01 to 1 µmol.L⁻¹) [3–6]. The deficiency of this component causes brain disorders such as Alzheimer, Parkinson’s disease or schizophrenia [2,7,8]. Ascorbic Acid (AA) also called vitamin C, is a vital component in human diet. High concentrations of ascorbic acid, i.e. 34-85 µmol.L⁻¹ and 570-3400 µmol.L⁻¹, can be found in human plasma and urine, respectively. Uric Acid (UA) and other oxipurines are the major catabolize of purines breakdown (guanine and adenine), being an important physiological component that is associated to symptoms of some diseases, most notably gout, hyperuricemia and Lesch–Nyhan syndrome. Its normal concentration in the blood is in range of 120-450 mol.L⁻¹ and in urine about 2 mmol.L⁻¹ [1]. This reason makes researchers compete to develop a fast method for determining dopamine, uric acid and ascorbic acid levels in the human body. Recently, the considerable efforts were made in determining those samples by electrochemical biosensor.

Basically, the electrochemical biosensor comes from coupling the ligand-receptor binding reaction to the transducer signal [6–10]. One of the first electrochemical study of DA was reported by Ralph Adams and his team at University of Kansas in 1967 [8]. They was found that the oxidation mechanism of DA depending on the pH conditioning. Sensor for determined of DA, AA, UA has been reported, modified electrode with multi-walled carbon nanotubes and single-walled carbon nanotubes doped to glassy and carbon paste electrode. The performance of the sensor were not maximum, while needed the sensor with high performance, low cost, simply, and fast. Developing of selective and sensitive electrochemical biosensor for DA, AA, UA detection is still challenging task. To overcome this challenge, modification of electrodes by several materials have been reported [1,9–12]. New
nanomaterial, i.e. carbon nanotubes was shown good performance for DA, UA and AA detection as described in previous studies [1,5,8,9,13–17].

Single-walled carbon nanotubes (SWCNTs) belongs to carbon materials that is attached any attention. This material have advantages as sensors compared to other materials. High electrical conductivity, high surface area, chemical stability and significant mechanical strength are unique characteristics [18–21]. Because of its unique characteristic, the electron transfer reaction between other materials and molecules can work well. The SWCNTs has combined particles to form nodular aggregates [22,23]. During the dispersion process, the aggregate does not break up and there is a spread process consisting of the breakdown of large agglomerates. Suspense that occurs in carbon particles shows the conductivity of conductive networks that have graphite structure on the surface [13,24]. Performance of SWCNTs can be improved by the addition of a binder. The binder must have high mechanical strength, good chemical resistance and good thermal stability and resistance.

In the present work, we modify the carbon electrode by SWCNTs and KPG5. The adding of modification materials aim to improve the performance of the electrode as electrochemical sensor. All modification materials was dropped in the surface of carbon electrode. The performance of the sensor was investigated in medical samples such as dopamine, uric acid and ascorbic acid. All measurement was analyzed using cyclic voltammetry method at acidic condition (pH 4) in room temperature.

2. Experiments

2.1. Chemical and Materials
Dopamine (C$_8$H$_{11}$NO$_2$, 98%) and uric acid (C$_5$H$_4$N$_4$O$_3$, 99%) were bought from Sigma-Aldrich Co. (St. Louis, MO, USA). L(+)-Ascorbic acid (C$_6$H$_8$O$_6$) was purchased from Merck KGaA (Darmstadt, Germany). All chemicals were used without any purification. The solution of acetate buffer (pH 4) was prepared from a cetate acid (CH$_3$COOH, Merck, Germany) and sodium acetate (CH$_3$COONa, Merck, Germany). KPG5 as binder was supplied from Saga University, Japan. Carbon disk electrode was obtained from eDAQ with dimensions of 3 mm diameter x 65 mm long and 1 mm diameter of carbon disk. Demineralized water was used for chemical preparation and cleaning.

2.2. Instrumentation
Electrochemical measurement were using a potentiostat from eDAQ (potentiostat E161 and e-corder 410, equipped with e-chem software version 2.1.13) and an electrochemical analyzer (model 700B, equipped with ALS/CHI700B software).

2.3. Preparation of SWCNTs
SWCNTs was prepared at Department of Chemistry and Applied Chemistry, Graduate School of Science and Engineering, Saga University, Japan. SWCNTs was synthesized by CVD method as from our previous work [18,19].

2.4. Fabrication of SWCNTs/KPG5-modified carbon electrode
The modified carbon electrode was prepared by adding of SWCNTs and KPG5. All modification materials with composition 1:1 were mixed until homogeneous under sonication condition. The mixed material was attached to the surface of the carbon electrode by dropping method. The modified electrode was dried at 50°C for 3 hours. Furthermore, the modified electrode was cooled at room temperature prior to use.

2.5. Performance of SWCNTs/KPG5-modified carbon electrode
Electrochemical experiments were observed using the cyclic voltammetry method as our previous work [4,5]. All experiments were carried out using three-electrode cell system. The system uses platinum wire as counter electrode (CE), Ag/AgCl (KCl 3 M) as reference electrode (RE), and the modified carbon electrode as working electrode (WE). The potential was swept from -0.8 to 0.8 V vs. Ag/AgCl (KCl 3
M), with 20 seconds of rest time before being measured and scan rate of 50 mV/s. A 10 mM samples were prepared by dissolving dopamine, urea acid and ascorbic acid, each in acetate buffer solution (pH 4).

3. Result and Discussion

Performance of sensor based on SWCNTs/KPG5-modified carbon electrode

The performance of sensor based on SWCNTs/KPG5-modified carbon electrode against DA, UA and AA were shown in Figure 1, 2, and 3, respectively. The modified electrode shows different response for DA, UA and AA. DA was observed two oxidation peaks and two reduction peaks (Figure 1). Potential of dopamine oxidation was appeared at -0.152 V (Ipa = 2.928 µA) and +0.261 V (Ipa = 1.066 µA), while the potential reduction was 0.057 V (Ipc = -2.193 µA) and -0.442 V (Ipc = -5.344 µA). The cycles shows that the sensor surface fouling effect by the presence of DA. Both oxidation and the formation of reduction peaks during measurement prove that the sensor can be used to detect DA. Dopamine has good electrochemical activity and easily oxidized because two electrons undergo an irreversible reaction process by transferring two protons [25]. Dopamine is weakly basic with a pKb value of 8.87, thus affecting the dopamine equilibrium reaction [8]. The optimum peak current occurs at pH 4 because in this acid pH dopamine is protonated so that the dopamine oxidation reaction can occur perfectly. Protonation occurs in the amine group (-NH₂ to -NH₃⁺) in dopamine [4,5,25].

Figure 1. Response of electrochemical sensor based on SWCNTs/KPG5-modified carbon electrode in acetate buffer, pH 4 (A) and 10mM dopamine in acetate buffer, pH 4 (B).

Different response from electrochemical sensor based on SWCNTs/KPG5-modified carbon electrode was found during UA and AA measurement at pH 4. Oxidation and reduction reaction of UA was disappeared (Figure 2). Whereas, the modified sensor give one oxidation peak without formed a reduction peak during AA testing (Figure 3). The response of the sensor on UA and AA were also observed irreversible. The irreversible behavior of the sensor can be caused by several changes in the multilayer structure, desorption and loss of material in oxidation adsorption or reduction of both samples which cannot be reversed on the sensor surface. So that in Figure 2 there is no reduction and oxidation peaks which show that there is no adsorption of UA particles on the sensor surface. The peak current that occurs is smaller than the solvent used. It is clear that the electrochemical reaction of this species to the sensor cannot be changed, indicating that the electron transfer kinetic is slow in this compound. Another possible thing in this species is the distribution of molecules in the solvent that is not maximum
attached to the sensor so that fouling occurs on the sensor surface. This observation is supported by results that have been reported that UA cannot be oxidized and completely reduced at pH 4 [21].

Figure 2. Response of electrochemical sensor based on SWCNTs/KPG5-modified carbon electrode in acetate buffer, pH 4 (A) and 10mM uric acid in acetate buffer, pH 4 (B).

Increasing of oxidation current peak was occurred in the electroactive area of the sensor against AA which increased significantly. The oxidation potential of AA was observed at +0.254 V with \( I_{pa} = 8.158 \) µA. The oxidation peak means there is interactions between species with sensor surfaces. This interaction not produce perfect electrocatalytic activity. The distribution of AA species occurs maximally with the electrode surface at range pH from 4.5 to 8. The AA signal shifted to more cathodic potentials as the pH increases. The current peak for AA oxidation increased and shifted to more positive potentials with increase in pH [26].

Figure 3. Response of electrochemical sensor based on SWCNTs/KPG5-modified carbon electrode in acetate buffer, pH 4 (A) and 10mM ascorbic acid in acetate buffer, pH 4 (B).

According to the response from the electrochemical sensor based on SWCNTs/KPG5-modified carbon electrode, it can be seen that the measurement of dopamine give anodic and cathodic peaks. The SWCNTs used in sensor fabrication are carbon materials that can function as catalysts in measurement activities [5]. So that the electron transfer between the sensor and tested molecules can work well. The use of binders in sensor fabrication also adds the power of the sensor to bind molecules to dopamine. Selection of the right binder can improve sensor performance. In this study, we shows that KPG5 has a good potential for binder because it can improve the response of the sensor.
4. Conclusion
The performance of SWCNTs/KPG5-modified carbon electrode was successfully studied for medical samples. The modified electrode gives the best response during DA measurement at pH 4 in room temperature. DA was oxidised at potential of -0.152 V and +0.261 V, while the potential reduction of DA was observed at 0.057 V and -0.442 V. This response not interfered by the presence of UA and AA.

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