SIMULTANEOUS DETERMINATION OF DOPAMINE IN THE PRESENCE OF ASCORBIC ACID AND URIC ACID BY ELECTROCHEMICALLY OXIDIZED SCREEN PRINTED CARBON ELECTRODE

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ABSTRACT

This research reported the simple method to determine dopamine (DA) in the simultaneous presence of ascorbic acid (AA) and uric acid (UA). Three – electrode system manufactured by screen printing method was used due to its disposal and low cost. The screen printed carbon electrode (SPCE) was oxidized by electrochemical technique in acid medium. The capacity of oxidized electrode for selective detection of dopamine was confirmed in a sufficient amount of ascorbic acid and uric acid. The large separated peaks of DA from ascorbic acid and uric acid are observed. The peak separation between UA and DA, DA and AA was 110 mV and 160 mV, respectively. The bare SPCE cannot determine simultaneously AA and DA due to the overlap peaks of AA and DA around 0.2 V vs AgCl/Ag. This sensor also exhibited good sensitivity to DA with limit of detection 100 nM in phosphate buffer solution.

Keywords: dopamine, electrochemical sensor, electrochemical oxidization, SPCE.

1. INTRODUCTION

Dopamine (DA) is a simple organic compound but is an important neurotransmitter substance. DA plays a significant role in the function of the central mammalian brain [1], where the highest DA concentration is approximately 50 nmol/g in a region of the brain known as the “caudate nucleus” (approximately 50 μM if the caudate nucleus were considered as a homogeneous phase) [2]. And the very low concentration of DA in the “extracellular fluid” of the caudate nucleus provides a large challenge for detection of DA.

Monitoring and quantitative detection of DA have been a long-standing goal since the change in the level of DA has been proved to be a very effective route toward some diseases of brain such as Parkinson [3] with almost depletion of DA in synaptic cleft. Schizophrenia [4] with abnormal high concentration of DA in the brain, Huntington’s disease or depression. Electrochemical methods have been considered as one of the most potential approaches to this
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purpose because of their high sensitivity, simplicity and good electrochemical property of DA. However, the coexistence of ascorbic acid (AA), and uric acid (UA) with a concentration of 100–1000 times higher [2] than that of DA greatly renders electrochemical strategy very challenging for DA determination. Especially, AA is oxidized at almost same potential that of DA, thus at the normal solid electrode as glassy carbon (GC), gold, oxidation peaks of them is overlap and makes the fail in the detection of DA when simultaneous presence of AA. A number of studies have attempted to determine DA in the simultaneous presence of AA and UA. For example, organic redox mediators [5], nanoparticles [6, 7], polymers [8, 9], self-assembled monolayers [10, 11], carbon nanotubes [12, 13] and graphene [14, 15] have been employed in the modification of electrodes, mainly glassy carbon (GC) and carbon paste electrode (CPE). Although these modified electrodes have shown improved sensitivity and selectivity compared with the conventional electrode, the using of GC and CPE has the limitation of time-consuming for cleaning, polishing, and low reproducibility. In addition, the immobilized layers were prone to surface deactivation due to solvent evaporation, and they decay with time, resulting in nonuniform thickness and poor reproducibility [16]. It will be not suitable for practical use.

Screen printed carbon electrode (SPCE), disposable three-electrode system, have successfully prepared in our laboratory with the strong advantage of fabricating a large number of near identical electrodes at a low-cost [17]. However, the use of the SPPEs for simultaneous determination of AA, DA and UA has rarely been reported, since the unmodified SPCEs are unable to discriminate signals of AA, DA, and UA. Several works dealt with SPCE to improve selective detection of DA in the presence of AA and UA by coating the surface of SPCE with sulfonic acid–polyaniline nanoparticles [18], iridium oxide [19]. However, sensitivity and reproducibility of these electrodes are very poor, and the fabrication process is complex.

In this study, we use the simple and fast method to oxidize the surface of SPCE for determination of DA in the simultaneous presence of AA and UA. Cyclic voltammetry and differential pulse voltammetry (DPV) technique was used to investigate the electrochemical behaviors of DA, AA, and UA at oxidized SPCE. Based on the different electrocatalytic activities of the oxidized SPCE toward AA, DA, and UA, a sensitive and selective method for simultaneous determination of these three molecules was established and further used in real sample analysis.

2. EXPERIMENTAL

2.1. Reagents

Dopamine, L-Ascorbic acid, and uric acid were purchased from Sigma-Aldrich (Japan). NaH₂PO₄,2H₂O, Na₂HPO₄, NaCl, and KH₂PO₄ were purchased from Wako Pure Chemical Industries (Osaka, Japan). SCPE as a working electrode with area of 2.64 mm² was purchased from Biodevice Technology (Ishikawa, Japan). Other reagents were of analytical grade, and all solutions were prepared and diluted using ultra-pure water (18.2 MΩ.cm) from the Milli-Q system (Millipore, Billerica, MA, USA).

2.2. Instrument

Electrochemical measurements were performed on an ALS/CH Instruments electrochemical analyzer, model 730C (Austin, Texas, USA). A drop of 35 μL of the electrolyte solution was applied to the three electrodes of SPCE. All experiment was conducted at room temperature (25 °C).
2.3. Electrochemical oxidation of SPCE

SCPE were electrochemically oxidized using cyclic voltammetry in the potential range of 0 \( \pm \) 2.0 V vs. Ag/AgCl in an acid solution (H\(_2\)SO\(_4\), HClO\(_4\)) for 10 cycles with scan rate of 100 mV/s. The determination of DA was conducted in the phosphate buffer saline (PBS) 0.1M in the simultaneous presence of AA and UA by differential pulse voltammetry (DPV).

3. RESULTS AND DISCUSSION

3.1. Electrochemical properties of DA, AA, and UA at bare and oxidized SPCE

Cyclic voltamograms were conducted on electrochemically oxidized SPCE in 10 \( \mu \)M DA (Figure 1) showed a ten times increase in background current than that on bare SPCE. This is an indicator of more electrochemical active surface area resulting from electrochemical oxidation of electrode surface. Likewise, current intensity response for DA on oxidized SPCE illustrated an approximately 10 times higher than that on bare SPCE. The oxidation potential of DA kept unchanged on oxidized SPCE compared with that on bare SPCE (around 140 mV vs. AgCl/Ag). Our observation result is similar that obtained on electrochemical pretreatment of carbon nanotubes (CNT) modified glassy carbon electrode by Musameh et al. [20] and [16]. According to them electrochemical oxidation of CNT, similar as our SPCE using carbon material, would lead to cleavage and expose many new edge plane sides that are favorable interaction and prone to catecholamine electrochemistry.

The oxidation potential of DA is negative than that of AA (ascorbic acid) on bare SPCE in PBS solution. This result is consistent with previous results on carbon paste electrode [21, 22] and leads homogeneous catalyst oxidation of AA following equation.

\[
\text{DA} + 2e^- + 2H^+ \rightarrow \text{DOQ}
\]

\[
\text{DOQ} + \text{AA} \xrightarrow{k_r} \text{DA} + \text{DHA}
\]

DOQ and DHA represent the oxidized forms of DA and AA.
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Figure 2. CVs curve of Bare SPCE (blue) and Oxidized SCPE (red) in 50 mM PBS pH 7.4 containing 1 mM AA, scan rate 100 mV/s.

The CV curves of AA oxidation at bare SPCE and Oxidized SPCE are shown in Figure 2. There was a large negative shift of AA oxidation potential peak from ~220 mV (vs. AgCl/Ag) on bare SPCE to ~50 mV on oxidized SPCE. This could be explained by the repulsion of ascorbate ion AA\(^-\) (AA with pK\(_a\) = 4.1 is negative charge at pH 7.4) from the negative surface expected to be on the oxidized SPCE after the electrochemical oxidation [22]. According to Alwarappan et al. the negative charge present on the surface of the electrochemically oxidized SPCE tends to act like a layer that is specific toward repulsing anion species at physiological pH. As a result of this electrostatic repulsion anion species are difficult to reach electrode surface to a greater extent to undergo an enhanced redox reaction [16].

Figure 3. CV curves of Bare SPCE (blue) and Oxidized SCPE (red) in 50 mM PBS, pH 7.4 containing simultaneous 1 mM AA, 10 \(\mu\)M DA, scan rate 100 mV/s.

The CV curves of AA and DA simultaneous oxidation at bare SPCE and Oxidized SPCE are shown on Figure 3, respectively. On the bare SPCE only one peak was obtained. It meant that bare SPCE could not distinguish the oxidation of AA and DA. Whereas two peak shoulders were observed at Oxidized SPCE. This means that Oxidized SPCE can be used for the discrimination of DA in the presence of AA.
On the Figure 4 shows the CV curves of oxidized SPCE in the PBS containing 1 mM AA, 0.01 mM DA and 0.025 mM UA. These curves clearly illustrate the peaks at different potential position. That mean that the oxidized is able to distinguish DA in the presence of AA and UA.

3.2. Effects of pH

![Figure 5](image)

Figure 5. a) DPV curves illustrates oxidation potential of DA (10 μM) on oxidized SPCE in 0.1 M PBS solution at different pH values; b) Plot shows linearly dependence DA oxidation potential on pH in range of 4.0 – 8.0; c) DA oxidation current intensity relates to pH values.

The effect of pH values of the supporting solution on the electrochemical behavior of oxidized SPCE was also studied (see Figure 5a). Higher pH value made anodic peak potential
shift negatively. The plot of peak potential versus pH value showed linearity, $R^2 = 0.9987$, in the pH value range of 4.0–8.0 with a slope of $-62.2 \text{ mV/pH}^{-1}$ (Figure 5b). Higher pH value made decreasing in oxidation current intensity (Figure 5c).

3.3. DPV detection of DA in the presence of AA and UA

![Figure 6. Differential pulse voltammograms of Oxidized SPCE 50 mM PBS, pH 7.4 containing simultaneous 1 mM AA, 35 μM UA, and different concentration of DA.](image)

DPV curves for detection of DA in the simultaneous presence of AA and UA are shown on Figure 6. The concentration of AA and UA was kept constant of 1mM and 0.035 mM respectively, in that time the concentration of DA was increase from 1.0 to 50.0 μM. The current intensity of DA peak increases when the concentration of DA increases. These DPV curves illustrate that the presence of AA and UA has no effect in the detection of DA on oxidized SPCE. The inset of figure 6 shows the plot of current intensity vs logarithm of DA concentration. This plot induces the linear relationship of the $i$ (μA) vs. log $C$ of DA (from 1 ÷ 50 μM) with confident constant $R^2 = 0.9903$. Limit of detection (LOD) defined as $3\sigma$ of the described method for DA was 100 nM in the simultaneous presence of AA and UA.

4. CONCLUSION

The simple method for selective and sensitive detection of DA in the simultaneous presence of AA and UA was developed successfully. Large peak separations between DA, AA and UA allow the detection and determination of DA, AA, and UA simultaneously at Oxidized SPCE by using cyclic voltammetry or Differential pulse voltammetry. The rate of oxidation of DA at electrode surface was improved on oxidized SPCE compared with bare SPCE.

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