Graphene Paste Electrode Modified with Sodium Dodecyl Sulfate Surfactant for the Determination of Dopamine, Ascorbic Acid and Uric Acid

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Abstract- Sodium dodecyl sulfate surfactant modified graphene paste electrode (SDSMGPE), prepared by electrochemical immobilization of the Sodium dodecyl sulfate surfactant (SDS) on a graphene paste electrode, was applied for simultaneous determination of dopamine (DA) in the existence of ascorbic acid (AA) and uric acid (UA) through cyclic voltammetry (CV) and differential voltammetry (DPV). The modified electrode shows strong electrocatalytic function for the oxidation of DA, AA and UA and three well-defined voltammetric peaks of about 167 mV, 12 mV and 303 mV by CV method. A linear response in the range of (1 × 10⁻⁵)-(1×10⁻³) M with a detection limit of 4.7×10⁻⁶ M and limit of quantification limit 15×10⁻⁶ M for DA was obtained. This SDSMGPE indicated a potent and persistent electron mediating behavior bring up by adequately separated oxidation peaks of DA, AA and UA. The bare graphene paste electrode (BGPE) and SDSMGPE were characterized using Energy-dispersive X-ray spectroscopy (EDX) and Field emission scanning electron microscopy (FESEM) were used to check the electrochemical efficiency of electrodes. The effects of graphene paste constitution, concentration, surfactant, pH, and scan rate were investigated. The modified electrode is highly stable and can be used to the determination of DA in injection samples. The proposed method is simple, fast, sensitive, selective, stable, reproducible and accurate.

Keywords- Graphene paste electrode, Cyclic voltammetry, SDS, Dopamine, Uric acid, Ascorbic acid
1. INTRODUCTION

Graphene have shown excellent affection towards scientific group [1-16]. It is a
2-dimensional sp²-hybridized carbon sheet hold many good physicochemical behavior like extremely high surface area, excellent electronic transport properties, high mechanical stiffness, and extraordinary thermal and electrical conductivity, scientists are curious in graphene recently, due to its appealing physical properties [1-6]. It also has been indicated to have outstanding commitment for numerous potential utilization, for example, sensors, nanoelectronics, batteries, supercapacitors, hydrogen storage and nanocomposites [1,7-10]. These supreme properties make it good candidate for electrochemistry applications specially in sensing [10-12]. It has also been recommended that graphene has the capacity to replace the other present materials used for the preparation of biosensors [13-16].

Dopamine (DA) is one of the important molecules of catecholamine’s which are in the mammalian central nervous system for signal transfer [17]. Abnormal levels of DA damages to neurological disorders such as Parkinson's disease, schizophrenia [17–19] and to HIV infection [18,20]. Uric acid (UA) is the primary final product of urine metabolism. Departing from the unusual levels of UA is indication of many diseases such as hyperuricaemia, gout and Lesch–Nyan disease [21]. Ascorbic acid (AA) it restrict scurvy and is known to take part in many biological reactions [22]. Therefore, simultaneous determination of DA, AA and UA is a complication of critical importance not only in the field of biomedical chemistry and neurochemistry but also for diagnostic and pathological research [23]. However, it is very hard to simultaneously determine DA, AA and UA directly at common (carbon and metal) electrodes, due to they undergo an overlapping oxidation potential and the electrode fouling takes place due to the adsorption of oxidation products [24-26]. Advancement of the sensitivity and selectivity of the working electrode towards DA has been becoming a long standing of researchers. To meet this work, different types of electrodes have been proposed to determine the content of DA by their selectivity and electrocatalytic activity. There are reports using modified carbon paste electrodes [27], modified glassy carbon electrodes [28], modified carbon nanotube paste electrodes [29], modified gold electrodes [30], graphene paste electrodes [31] modified electrodes could be successfully used to determine DA. All the modified electrodes, they have their application, draw back and limitations.

Surfactant modified electrodes have lot of applications in the electroanalysis of biomolecules [32]. These surfactants are a kind of amphiphilic molecules, which are capable of altering the electrical properties of the electrode solution as in combine and the electrochemical process through adsorption at interfaces or aggregation into supramolecular structures [33]. Zhenget al. done the work Sodium dodecyl sulfate-modified carbon paste electrodes for selective determination of dopamine in the presence of ascorbic acid [34], the films indicated remarkably different structure, large surface area and good porosity specific. E. Colin-Orozcoet al. did electrochemical quantification of dopamine in the presence of
ascorbic acid and uric acid using a CPE modified with SDS micelles at pH 7 [35]. M. Espinoza-Castareda et al. have shown electrochemical study with surfactants [36]. Our research group has reported the determination of several analytes in the presence of surfactants [37–39]. The results shown that the electrochemical responses of biomolecules were highly enhanced. Surfactants also have potential applicability for suppressing electrode fouling from products of the electrochemical reaction [40].

In this paper, an electrochemical sensor was prepared with surfactant modified graphene paste electrode, and its properties were determined. Its selective and sensitive performance of DA was evaluated using electrochemical methods including CV, DPV, EDX and FESEM. The modified electrode shows high stability, sensitivity, selectivity, and antifouling. It has been favorably applied to analyzing injection samples of DA. The scheme of oxidations of DA, AA and UA is shown in Scheme 1.

![Scheme 1. The scheme of oxidations of DA, AA and UA](image)

2. EXPERIMENTAL

2.1. Reagents

Graphene powder (12 nm multilayer, 99.2% purity) was obtained from Graphene supermarket, graphene Laboratory.inc, Calverton, New York, USA. SDS, DA, AA, UA, Potassium ferrocyanide (K₄[Fe(CN)₆]), Potassium chloride (KCl), Silicone oil were obtained from Sigma Aldrich Malaysia. Stock solution of SDS, DA, AA, UA (25×10⁻³ M) and K₄[Fe(CN)₆] were in double distilled water, 0.1 M perchloric acid solution, double distilled water, 0.1 M sodium hydroxide solution and water respectively. Phosphate buffer solution
was prepared by mixing the suitable amount of 0.2 M monosodium phosphate and 0.2 M disodium phosphate.

2.2. Apparatus

CV and DPV were performed in a model EA-201 Chemilink system in a conventional three-electrode system. The working electrode was a GPE (graphene paste electrode), having cavity of 3 mm diameter. The counter electrode was a bright platinum wire with saturated calomel electrode (SCE) as reference electrode completing the circuit. All measurements were carried out at room temperature (25 °C).

2.3. Graphene paste electrode preparation

Initially, ratio 70:30% w/w graphene and silicone oil were mixed in a mortar until a homogeneous paste was obtained. Then, the paste was packed into the cavity of a homemade electrode and smoothed out on a weighing paper. A SDSMGPE were prepared by immobilizing 20 μL of SDS on the surface of the GPE for 5 min.

3. RESULTS AND DISCUSSION

3.1. Surface Morphology of BGPE and SDSMGPE

Fig. 1 shows the surface morphologies of BGPE and SDSMGPE characterized by FESEM. From the FESEM images, it can be seen, the surface of BGPE (Fig. 1a) was irregularly shaped flakes of graphene. However, the surface of SDSMGPE (Fig. 1b) was smoother, some agglomeration, covered by dense and compact film. The obvious differences on the surface morphologies confirmed that the GPE was coated by SDS.

![FESEM images of (a) BGPE (c) the SDSMGPE](image)

Fig. 1. FESEM images of (a) BGPE (c) the SDSMGPE
EDX was used to identify the elemental distribution of the electrodes. A typical EDX spectrum obtained from BGPE and SDSMGPE are also presented in figures. In Fig. 2a, BGPE shows presence of signals for carbon, silicon and oxygen with carbon weight percentage of 80.4% and oxygen weight percentage of 7.67%. Interestingly, SDSMGPE shows the presence of signals for C, O, Si, and S with weight percentage of 81.68, 8.30, 9.89 and 0.14% respectively. The presence of signals for S in the SDSMGPE clearly indicates that SDS molecules were connected with SDSMGPE.

![EDX spectrum of (a) the BGPE (b) the SDSMGPE](image)

**Fig. 2.** EDX spectrum of (a) the BGPE (b) the SDSMGPE

### 3.2. Optimization of experimental variables for electrocatalytic oxidations

The amount of SDS in the surface of the graphene paste has major role on the voltammetric response of the modified electrode. The effect of the modifier is to increase the peak currents enhanced as the content in the SDSMGPE increased. The modifier SDS was optimized as 20 µL in the SDSMGPE to get the good voltammograms, more than 20 µL of SDS caused a low reversibility as well as positive shift in the oxidation potential, increasing the capacitance background current and larger peak to peak separation. In cyclic voltammetric method parameters such as potential range, scan rate, pH must be optimized.

### 3.3. Stability and reproducibility of SDSMGPE

At present movement reproducibility and stability are important parameter to decide principle of a sensor. The proposed method for determining DA was tested in the PBS (pH 7.0) containing 0.6 mM DA by repetition for 10 cycles. The results indicated good reproducibility of the SDSMGPE with a relative standard deviation of 4% for DA. Later long-term stability of electrode was measured by keeping it in a dry place for a ten days, it shows the electrochemical performance of the SDSMGPE over the determination of DA shows almost
its initial activity, which indicated the good stability and reproducibility of the modified electrode.

3.4. Electrochemical behavior of DA at SDSMGPE

The advantage of the SDSMGPE for oxidation of DA was measured by cyclic voltammetry. The cyclic voltammetric responses of an SDSMGPE in 0.2 M PBS (pH 7.0), without and with DA are shown in Fig. 3. There are no peaks found only background current observed for a SDSMGPE without DA (curve a). However, after addition of 0.6 mM DA, a well-defined oxidation peak and reduction peak at 209 mV, 77 mV respectively (curve b). This result demonstrates the electrode response was proportional to the oxidation of an electroactive species produced.

![Fig. 3. A typical cyclic voltammograms of SDSMGPE with 0.6 mM DA in pH 7 PBS (curve b) without DA at pH 7 PBS blank (curve a)](image)

3.5. Electrochemical properties of the SDSMGPE in potassium ferrocyanide solution

The electrode performance of the SDSMGPE was investigated in $K_4[Fe(CN)_6]$ solution. Fig. 4 shows the electrochemical responses of the BGPE and SDSMGPE in 1 mM $K_4[Fe(CN)_6]$ and 1 M KCl solution (Potential range of -200 to 600 at the scan rate 100 mVs$^{-1}$). The solid line shows electrochemical response of BGPE having $E_{pa}$ 211 mV and $E_{pc}$ 140 mV with the $\Delta E_{pa}$=71 mV with less sensitivity and $i_{pa}/i_{pc}$ ratio is 1.32 $\mu$A. After modification of SDS, the electrode shows increasing cathodic and anodic peak current which was indicated in the figure (dashed line). The peak potential differences is 33 mV and the $i_{pa}/i_{pc}$ ratio is 1.09 $\mu$A indicates the electrode transfer kinetics. Both BGPE and SDSMGPE showed a quasi-reversible peaks, the current response at the SDSMGPE was much larger than that at the BGPE, indicating the SDS was able to enhance charge-transfer capability of the electrode.
**3.6. Electrochemical response of DA on the SDSMGPE**

Fig. 5 shows the cyclic voltammograms recorded in pH 7.0 PBS consisting of 0.6 mM DA at the BGPE and the SDSMGPE at 100 mVs$^{-1}$. At BGPE exhibited a pair of poor redox peaks at anodic peak potential $E_{pa}$ and the cathodic peak potential $E_{pc}$ 138 mV and 86 mV respectively, the difference between the anodic peak potential $E_{pa}$ and the cathodic peak potential $E_{pc}$, was approximately 52 mV (Fig. 5a), while at the SDSMGPE, the anodic peak potential and the cathodic peak potential shifted negatively and positively respectively with great enhancement of reversibility, well-defined, anodic and cathodic peaks with $E_{pa}$ and $E_{pc}$ of 209 and 77 mV, respectively. The peak potential difference, $\Delta E_p=(E_{pa}-E_{pc})$ of 132 mV, was higher than the value of 59/n mV expected for a reversible system [49,50], suggesting that the redox couple of SDSMGPE has a quasi-reversible nature. These results indicated that the SDSMGPE showed an obvious electrocatalytic response toward DA. The reason may be that SDS could improve the electrochemical activity and redox reversibility of DA by increasing the rate of electron transfer and mass transport between the electrode and DA because of its better physical and chemical properties such as good conductivity, huge specific surface area, and great biocompatibility.

Fig. 5b shows the cyclic voltammetry for DA (0.6 mM) was carried out at different scan rates. Results indicated that there is a linear relationship between the peak currents and the scan rate ($v$) in the range of 100-250 mV/s using SDSMGPE at pH 7. It is clear that both the redox peak currents are enhanced with increasing of the scan rate. Both the oxidation and reduction peak currents were increased with the increase of scan rate, and peak currents linearly proportional to the scan rate (Fig. 5c).
Fig. 5. (a) Cyclic voltammograms of 0.6 mM DA in pH 7 PBS at (a) BGPE (solid line), (b) SDSMGPE (dashed line); (b) Cyclic voltammograms of 0.6 mM DA at the SDSMGPE in pH 7 PBS at various scan rates. From: 100-250 mV/s; (c) Plot of the anodic peak current of DA as a function of the scan rate; (d) Cyclic voltammograms obtained at the SDSMGPE in 0.2 M PBS in pH values, 6-8 containing 1 mM DA; (e) Plot of anodic peak current vs. pH (6.0–8.0) of 1 mM DA at the SDSMGPE; (f) Plot of E_{pa} vs. pH for DA.

In addition, with increasing scan rate, the oxidation peak potential (E_{p}) shifts to more positive values and the peak current increases linearly with the scan rate and dependence of peak current on scan rate can be stated by below equation.
\[ i_p(\Delta A) = 95.078 \nu + 1.378 \]

Where \( \nu \) is scan rate in \( \text{mVs}^{-1} \) having correlation coefficient 0.9927. These results show that the electron transfer reaction is controlled by the diffusion of DA at SDSMGPE, which is more supportive for quantitative determination.

The effect of pH on the electrochemical response of the SDSMGPE towards the 1 mM DA over the pH range 6 to 8.0 in 0.2 M PBS solution was illustrated in Fig. 5d. The peak current of dopamine is increased with the increase of pH, and the peak current of dopamine reached the highest value when the pH of PBS is 7.0, (Fig. 5e) therefore, all voltammetric determinations were done in pH 7.0 as the supporting electrolyte. It was found that the peak potential for peak Ia shifted to more negative potentials with increasing pH indicates that protons take part in the electrode reaction. The change of peak potential with pH was linear and abide by the following equation: \( E_p \text{ (mV)} = 650.2 - 58.6 \text{ pH} \) \( (r^2=0.9853) \). The graph has a slope of 59.64 mV/pH, (from Fig. 5f) this behavior was obeyed the Nernst equation for equal number of electron and proton transfer reaction [41].

3.7. Calibration plot and limit of detection for DA

Cyclic voltammetry (CV) is a sensitive electrochemical technique that can be applied to analytic measurements; this method was used to determine the linear range and detection limit of DA. The CV of DA at SDSMGPE in concentration range of \( 1\times10^{-5} \text{–}1\times10^{-3} \text{ M} \) in PBS (pH 7) was recorded. The variation of catalytic peak current versus DA concentration represent two calibration curve corresponding to two concentration range.

![Fig. 6. Calibration plot for the determination of DA at the SDSMGPE in pH 7 PBS with the scan rate 100 mV/s](image)

The first calibration equation is \( i_{pa}(A) = 8.47\times10^{-5} + 0.10907 \text{ C} \) [41] with regression coefficient of \( r^2 = 0.99158 \) for the concentration range of \( 1\times10^{-5} \text{–}1\times10^{-4} \text{ M} \). The second calibration equation is \( i_{pa}(A) = 9.544\times10^{-5} + 0.0604 \text{ C} \) with regression coefficient of \( r^2 = 0.99303 \).
for the concentration range of $1.5 \times 10^{-4} - 1 \times 10^{-3}$ M (Fig. 6). The detection limit (according to $DL=3 \cdot sb/m$ where $sb$ is the standard division of the blank response and $m$ is the slope of the calibration plot) was obtained as $4.7 \times 10^{-6}$ M using the calibration equation of first linear segment and limit of quantification obtained as $15 \times 10^{-6}$ M. Table 1 shows the linear range and detection limit for DA at SDSMGPE in comparison with some sensors of other research groups Refs [42-46] while the proposed sensor easier than other sensors.

**Table 1.** The comparison of SDSGPE with some modified electrodes for the determination of DA at different modified electrodes

<table>
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<tr>
<th>Electrode</th>
<th>Linear range (µM)</th>
<th>Detection limit (µM)</th>
<th>Ref.</th>
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<td>0.5–60</td>
<td>0.5</td>
<td>[42]</td>
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<tr>
<td>4-Amino butyric acid/glassy carbon electrode</td>
<td>5.0–100</td>
<td>1.0</td>
<td>[43]</td>
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<tr>
<td>Palladium nanoparticles/carbon nanofibers</td>
<td>0.5–160</td>
<td>0.2</td>
<td>[44]</td>
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<tr>
<td>Chitosan–graphene/GCE</td>
<td>1.0–24</td>
<td>2.0</td>
<td>[45]</td>
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<tr>
<td>Graphene flower/carbon fiber electrode</td>
<td>3.9–371.5</td>
<td>3.9</td>
<td>[46]</td>
</tr>
<tr>
<td>Multiwalled carbon nanotube/modified carbon ceramic electrode</td>
<td>0.5–100</td>
<td>0.31</td>
<td>[47]</td>
</tr>
<tr>
<td>para-Phenylenediamine/glassy carbon electrode</td>
<td>10–1250</td>
<td>1.0</td>
<td>[48]</td>
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<td>This work</td>
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**3.8. Electrochemical Response of AA at SDSMGPE**

The redox nature of AA, PBS/pH 7 at BGPE and SDSMGPE is shown in Fig. 7a. Broad anodic peak appeared at 85 mV at BGPE and SDSMGPE exhibited effective electrocatalysis toward AA, resulting that the peak current increased as well as the peak potential shifted to 22 mV.

The relationship between the currents of oxidation peak of AA and scan rates were obtained by changing scan rate from 100-500 mV/s shown in Fig. 7b. The current of oxidation peak of AA obtained at SDSMGPE was linearly neither related to scan rates, which indicated the oxidation process of AA at SDSMGPE is not only controlled by diffusion but also involved a surface process with a correlation coefficient $r^2 0.99654$ (Fig. 7c).
Fig. 7. (a) Cyclic voltammograms obtained for the oxidation of 1 mM AA at SDSMGPE (solid line) and BGPE (dashed line); (b) Cyclic voltammograms of 1 mM AA at the SDSMGPE in pH 7 PBS at various scan rates. From: 100-500 mV/s; (c) Plot of the anodic peak current of AA as a function of the scan rate.

3.9. Electro catalytic oxidation of UA

The SDSMGPE can singly determine UA. Fig. 8a illustrates the CVs of UA at the bare and SDSMGPE in phosphate buffer (pH 7). As can be seen from figure, at the bare electrode (dashed line), the CV exhibited a broad peak at a higher potential about 270 mV with poor current response for UA oxidation. In contrast, at the SDSMGPE (solid line), the oxidation potential to 288 mV and an increase in peak current were observed, which indicated that the SDSMGPE possessed a strong electrocatalytic activity for the oxidation of UA. Fig. 8b shows the CVs of the SDSMGPE at various scan rates obtained in 0.2 M phosphate buffer (pH 7) containing 1 mM UA. The peak current was proportional to the scan rate in the range of 100-400 mV/s with a correlation coefficient of 0.99342(Fig. 8c). In addition, the anodic potentials shifted positively with the increase of scan rate.
3.10. Voltammetric Resolution of AA, DA and UA

Ascorbic acid (AA) coexists with DA and UA in the extracellular fluid of the central nervous systems. We can use the anodic peak potential for DA detection to eliminate the interference of AA and UA.

Thus, a sensitive determination of DA in the presence of AA, UA is of great importance in DA measurements. The interference from AA, UA has been studied in 0.2 M PBS at pH 7.0. The cyclic voltammograms of the mixture of DA, UA and AA at BGPE and the SDSMGPE are given in Fig. 9a. At BGPE (dashed line) two voltammetric peaks at 176 mV and 291 mV was observed. However, at SDSMGPE, three well-defined voltammetric peaks were obtained. The anodic peaks were appeared at about 12, 167 and 303 mV for AA, DA and UA, respectively. This shows that SDSMGPE could easily separate the oxidation peak potentials of AA, UA and DA.

Fig. 8. (a) Cyclic voltammograms obtained for the oxidation of 1 mM UA at SDSMGPE (solid line) and BGPE (dashed line); (b) Cyclic voltammograms of 1 mM UA at the SDSMGPE in pH 7 PBS at various scan rates. From: 100-400 mV/s; (c) Plot of the anodic peak current of UA as a function of the scan rate.
Fig. 9b shows differential pulse voltammograms obtained in the presence $2 \times 10^{-3}$ M AA solution, $0.2 \times 10^{-3}$ M DA solution and $1.8 \times 10^{-3}$ M UA of at the SDSMGPE. The peaks were appeared at about 43, 119 and 246 mV for AA, DA and UA, respectively.

![Differential pulse voltammograms](image)

**Fig. 9.** (a) CVs of mixture of 0.2 mM DA, 2 mM AA and 0.8 mM UA in 0.2 M PBS of pH 7. At SDSMGPE; (b) DPVs of mixture of 0.2 mM DA, 2 mM AA and 1.8 mM UA in 0.2 M PBS of pH 7. At SDSMGPE; (c) Different concentration of UA (1.4-2 mM) vs Current (DPV recordings in the presence of 0.2 mM DA and 2 mM AA)

Differential pulse voltammograms (DPV) of the mixture of AA, UA and DA is also shown in Fig. 9c. Peak current of increasing concentration of UA was not influenced by coexisted AA and DA. This behaviour reveals that SDSMGPE could enable the determination of UA in the presence of AA and DA.

### 3.11. Analytical Application

Using the proposed methods described above, the injection of DA hydrochloride was analyzed. The average determination result of DA in the injection was 10 mg mL$^{-1}$, which was quite corresponding to the value specified on the injection (10.00 mg mL$^{-1}$). Different standard concentrations of DA were added to the diluted DA injection and the recovery was
between 102.8 and 103.4% for 5 measurements. A good recovery obtained with the present system indicates the reliability of the method for application to monitoring of DA.

4. CONCLUSION

The carbon and other type of paste electrodes can be widely used in the determination of drugs, biomolecule and other organic species because of its easy preparation and simple modification. In experimental conditions GPE has a wider potential window and its residual currents are lower than those of the glassy carbon electrodes or metallic electrodes. The GPE modified with SDS was considerably stable. This electrode is simple, easy to prepare and renew its surface. The redox behaviour of SDS incorporated in the graphene paste was different from that observed in non-aqueous solutions. The problem of separating the oxidation peaks of DA, UA and AA was resolved by using the CV and DPV. The latter methodology proved to be powerful for simultaneous quantification of DA, especially considering the similarity of voltammetric response of the analytes. Furthermore, the immobilization simplicity in a conductive matrix opens up the possibility of using SDS in electrocatalysis of other species.

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