Abstract—In this research, a glassy carbon electrode modified with single-wall carbon nanotubes for electrochemical determination of dopamine was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The oxidation and reduction potentials of dopamine using voltammetric technique were measured. The SWCNTs/GC 10 µL was used to test the linearity of anodic oxidation of dopamine by DPV. The peak current increased linearly with concentration of dopamine in the range of 2.5-25 ppm ($R^2=0.9766$). For the lifetime of the SWCNTs/GC, the cut-off criterion of the DPV was detected in the reduction of current by 50%. The lifetime of the SWCNTs-modified depended on the oxidation of dopamine because of fouling of the electrode surface due to the adsorption of oxidation products. 34 repetition cycles was obtained. The detection limit of the dopamine as obtained from the oxidation current in DPV was 0.021 ppm ($S/N=3$) with minimum current for the detection of dopamine of 0.033 µA. The reproducibility of electrocatalytical studies was better within 90% (10% RSD). The relative standard deviation (RSD) of 8.42% for 100 ppm dopamine (n=20) showed excellent reproducibility. Drug samples obtained from Radvitee hospital were tested as the mentioned procedure. The percentage recovery of dopamine in drug samples was 120.

Keywords-component; Single-wall carbon nanotube; Modified electrode; Dopamine; Glassy carbon electrode; voltammetry

I. INTRODUCTION

Carbon nanotubes (CNTs), consist of sheet of graphite rolled into cylinder. There are two groups of carbon nanotubes, multi-wall carbon nanotubes (MWCNTs) and single-wall carbon nanotubes (SWCNTs) [1-8]. The MWCNTs consist of several layers of graphite sheets rolled into cylinders with one cylinder inside another and SWCNTs consist of a single graphite sheet rolled seamlessly, defining a cylinder of 1-2 nm diameter. Theoretical calculations have predicted that this material will behave either as a metal or semiconductor depending on its size and lattice helicity. SWCNTs have low resistivity of 100-200 $\mu\Omega\cdot cm$ comparable with a high-quality carbon fiber with a resistivity of approximately 100 $\mu\Omega\cdot cm$ [9]. The SWCNTs can carry electrical current densities up to 109 G A/cm² and remain stable at high temperature in the chemical reaction.

Dopamine is a neurotransmitter occurring in a wide variety of animals, including both vertebrates and invertebrates [10-15]. Its main function as a hormone is to inhibit the release of prolactin from the anterior lobe of the pituitary. A loss of dopamine containing neurons may result in some serious diseases such as Parkinson. Therefore, the determination of the concentration of this neurochemical is important. Dopamine is easily oxidized therefore electrochemical methods are the ideal choice for the quantitative determination of dopamine [16-18]. This technique processes following advantages as rapid response, low cost, low detection limit, excellent reproducibility and suitability for various sensing and detection. There are several techniques for determination of dopamine such as chromatography [19], spectrometry [20-21] which are high cost and long analysis time.

In the present research, the electrochemical method for the determination of dopamine based on the SWCNTs-DMF film coated glassy carbon electrode has been proposed.
The SWCNTs was purified by dispersing in 6.0 M HCl for 20 h with stirring and ultrasonic agitation for 30 min., washing until the pH of solution approached to 7 and finally drying in an oven 37°C. A 1 mg of purified SWCNTs was dispersed in 1 mL of N,N-dimethylformamide and ultrasonicated for 5 min, giving a black dispersion. The glassy carbon (GC) electrode was carefully polished with emery paper and chamois leather containing Al₂O₃ slurry, and then ultrasonically cleaned in distilled water. The SWCNTs film was grown on the GC electrode by dropping a suspension of SWCNTs in DMF on the GC electrode surface and then evaporating the solvent under an infrared heat lamp for 1 hr, given a modified SWCNTs/GC electrode. Finally, the SWCNTs/GC was rinsed thoroughly with absolute ethanol and deionized water just before use. The optimum working electrode, pH, and buffer solution were glassy carbon electrode (GC), 0.1 M phosphate buffer pH 7.5, respectively. The thickness of the modified layer has great impact on the electrochemical properties of the SWCNTs/GC electrode. DPV technique was employed for the determination of dopamine. The SWCNTs/DMF film on the GC surface increased linearly with the amounts of SWCNTs suspension over the range from 1 to 10 µL, and then increased slightly from 10 to 20 µL. When the amount of SWCNTs suspension exceeded 20 µL, the SWCNTs film became thicker and blocked the mass transport and electron transfer, therefore SWCNTs of suspension 10 µL was used for making the modified glassy carbon electrode.

All experiments were carried out at room temperature under an atmosphere of nitrogen. A 0.1 M, pH 7.4 phosphate buffer was used as the supporting electrolyte for dopamine determination. Solution of dopamine was prepared daily using deionized water. The CV employed a scan rate of 50 mV/s. The quantitative electroanalytical studies are based on differential pulse voltammetry investigations to test the effect of concentration and electrode preparation.

Fig. 1 shows CVs of 100 ppm dopamine in 0.1 M phosphate buffer pH 7.5 with scan rate of 50 mV/s at different SWCNTs-modified electrodes, namely (1) SWCNTs/Graphite electrode, (2) SWCNTs/Pt electrode, (3) SWCNTs/Au electrode and (4) SWCNTs/GC electrode. The electrochemical behaviors of SWCNTs-modified glassy carbon electrode showed better peak current of dopamine therefore it was chosen for the electrochemical study of dopamine.

The cyclic voltammograms of 100 ppm dopamine at the SWCNTs/GC electrode and bare GC in 0.1 M phosphate buffer pH 7.5 with scan rate of 50 mV/s showed better oxidation and reduction peak than bare GC electrode (Fig. 2). The peak currents at this modified electrode increase linearly with the square root of the scan rate in the range of 10-100 mV/s, which shows the electrode reaction is diffusion-controled process.

Fig. 2 CVs for 100 ppm dopamine at the SWCNTs/GC (4), blank SWCNTs/GC (2), bare-GC (3) and blank bare-GC (1) in 0.1 M phosphate buffer pH 7.5 with scan rate 50 mV/s.

The peak currents of SWCNTs/GC electrode increased linearly with the square root of the scan rate in the range of 10-100 mV/s, which showed the electrode reaction was diffusion-control process. The oxidation peak currents and peak potentials of 100 ppm dopamine in the phosphate buffer solution pH 5.5-8.5 were investigated. The peak current increased with increasing pH but the peak potential conversely decreased. The highest oxidation peak current of dopamine was in pH 8.0 phosphate buffer (Fig. 3) at the SWCNTs/GC electrode. The optimum phosphate buffer pH 7.5 was used in all experiment because dopamine precipitated out in the pH range of 8.0-8.5.
The thickness of the modified layer has great impact on the electrochemical properties of the SWCNTs/GC electrode. The DPV of dopamine 100 ppm with different amount of SWNTs were shown in Figs. 4-5. The SWCNTs film on the GC surface enhanced the oxidation peak current of dopamine. The oxidation peak current of dopamine increase linearly with the amounts of SWCNTs suspension over the range from 1 to 10 µL, and then increased slightly from 10 to 20 µL. When the amount of SWCNTs suspension exceeded 20 µL, the SWCNTs film became thicker and blocked the mass transport and electron transfer, so SWCNTs suspension of 10 µL was used for fabrication of the modified glassy carbon electrode.

The SWCNTs/GC 10 µL was used to test the linearity of anodic oxidation of dopamine. The concentrations ranging between 1-400 ppm of the analyte were investigated by DPV. The results of these experiments are shown in Figs. 6-7. The calibration curve for dopamine in 0.1 M phosphate buffer pH 7.5 shows the DPV voltammograms of dopamine at the SWCNTs-modified electrode at various concentrations. The peak current increased linearly with concentration of dopamine in range from 2.5-25 ppm ($R^2=0.9766$).
The peak current increased linearly with concentration of dopamine in the range from 2.5-25 ppm.

The lifetime of the SWCNTs/GC (Fig. 8) was tested as in the mentioned procedure. The electrode was dried and subsequently exposed to the standard analyte again. The cut-off criterion of the differential pulse voltammetry (DPV) was detected in the reduction of current by 50%.

The lifetime of the SWCNTs-modified depended on oxidation of dopamine because of fouling of the electrode surface due to the adsorption of oxidation products. 34 repetition cycles was obtained. The detection limit of the dopamine as obtained from the oxidation current in DPV was 0.021 ppm (S/N=3) with minimum current for the detection of dopamine as 0.033 µA. The reproducibility of electrocatalytical studies was better within 90% (10% RSD). The relative standard deviation (RSD) of 8.42% for 100 ppm dopamine (n=20) show excellent reproducibility.

The drug samples obtained from Radvitee hospital were tested as in the mentioned procedure. The percentage recovery of dopamine in drug sample was 120.

### IV. CONCLUSIONS

In this research, a glassy carbon electrode modified with single-wall carbon nanotubes for electrochemical determination of dopamine was studied by cyclic voltammetry and differential pulse voltammetry. A pair of well-redox waves was obtained. The electrochemical behavior of oxidation of dopamine at the SWCNTs-modified electrode was a diffusion-controlled process. The peak currents of differential pulse voltammetry (DVP) increased with the concentrations of dopamine in the range from 2.5-25 ppm ($R^2=0.9766$), the detection limit was 0.021 ppm (S/N=3), minimum current to detection dopamine was 0.033 µA and reproducibility (n=20) was 8.42.

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### REFERENCES


