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Fabrication of Modified SWNTs/Glassy Carbon Electrode for the Determination of Dopamine

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The SWNTs film was grown on the GC electrode by dropping a suspension of SWNTs in DMF on the GC electrode surface and then evaporating the solvent under an infrared heat lamp for 1 h, giving a modified SWNTs/GC electrode. Finally, the SWNTs/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 SWNTs/DMF film on the GC surface increased linearly with the amounts of SWNTs suspension over the range from 1 to 10 μL, and then increased slightly from 10 to 20 μL. SWNTs suspension of 10 μL was used for making the modified glassy carbon electrode. DPV technique was employed for the determination of dopamine. The drug samples containing dopamine obtained from Radvitee Hospital, Bangkok Thailand were tested as in the mentioned procedure.

Keywords Dopamine; glassy carbon electrode; modified electrode; single-wall carbon nanotube; voltammetry

Introduction

Carbon nanotubes (CNTs), consist of sheet of graphite rolled into cylinder. There are two groups of carbon nanotubes, multi-wall carbon nanotubes (MWNTs) and single-wall carbon nanotubes (SWNTs) [1]. Theoretical calculations have predicted that this material will behave either as a metal or semiconductor depending on its size and lattice helicity. SWNTs 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 [2]. The SWNTs can carry electrical current densities up to 109 G A/cm^2 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

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invertebrates [3]. 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 [4,5]. Differential pulse voltammetry (DPV) is a kind of electrochemical measurement [6]. It can be considered as a series of regular voltage pulses superimposed on a linearly changing voltage, in which the resulting current is measured between the ramped baseline voltage and the pulse voltage. A digital staircase voltage is commonly used as the ramped baseline. This technique processes following advantages as rapid response, low cost, low detection limit, excellent reproducibility and suitability for various sensing and detection. DPV has been employed to determine glanine, guanosine and adenine [7] and ascorbic acid in tablet dosage forms and some fruit juices [8]. There are several techniques for determination of dopamine such as chromatography [9], spectrometry [10] which are high cost and long analysis time.

In the present research, the SWNTs-DMF film coated glassy carbon electrode was fabricated for the determination of dopamine. The drug samples containing dopamine were obtained from Radvitee Hospital, Bangkok, Thailand.

Methods

The SWNTs 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 at 37°C for 24 h. A 1 mg of purified SWNTs was dispersed in 1 mL of N, N-dimethylformamide and ultrasonicated for 5 min, giving a black dispersion. The SWNTs film was grown on the GC electrode by dropping a suspension of SWNTs in DMF on the GC electrode surface and then evaporating the solvent under an infrared heat lamp for 1 h, giving a modified SWNTs/GC electrode. Finally, the SWNTs/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. SWNTs suspension of 1–20 μL was used for making the modified glassy carbon electrode. The DPV technique was employed for the determination of dopamine. 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. 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. The life time of the SWCNTs/GC 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%.

Results and Discussion

Figure 1 shows the cyclic voltammograms of 100 ppm dopamine at the SWNTs/GC electrode and bare GC in 0.1 M phosphate buffer pH 7.5 at the scan rate of 50 mV/s. The SWNTs/GC electrode showed better oxidation and reduction peak than bare

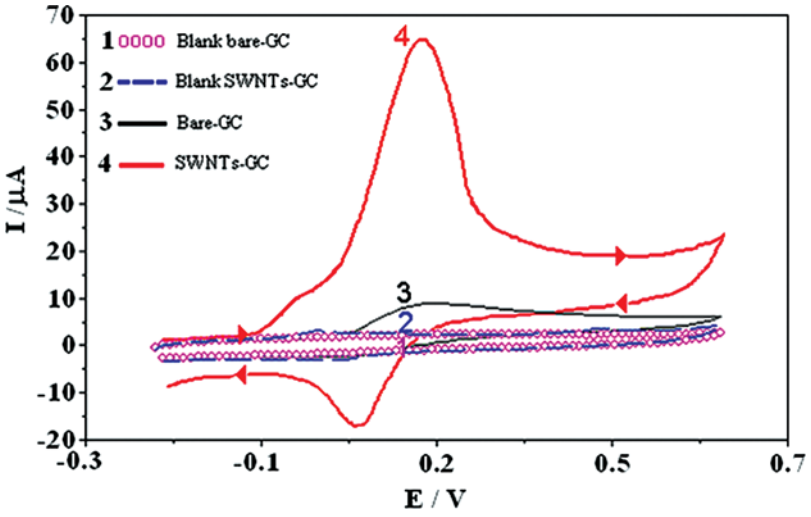

Figure 1. CV for 100 ppm dopamine at the SWNTs/GC (4), blank SWNTs/GC (2), bare-GC (3), and blank bare-GC (1) in 0.1 M phosphate buffer pH 7.5 with scan rate of 50 mV/s.

GC electrode. pH of the solution had the effect on the performance of the SWNTs/GC electrode. Figure 2 shows the oxidation peak currents and peak potentials of 100 ppm dopamine in the phosphate buffer solution in the pH range of 5.5–8.5. The peak current increased with increasing pH but the peak potential conversely decreased. The highest oxidation peak currents of dopamine occurred at pH 8.0 phosphate buffer at the SWCNTs/GC electrode but the precipitation of dopamine

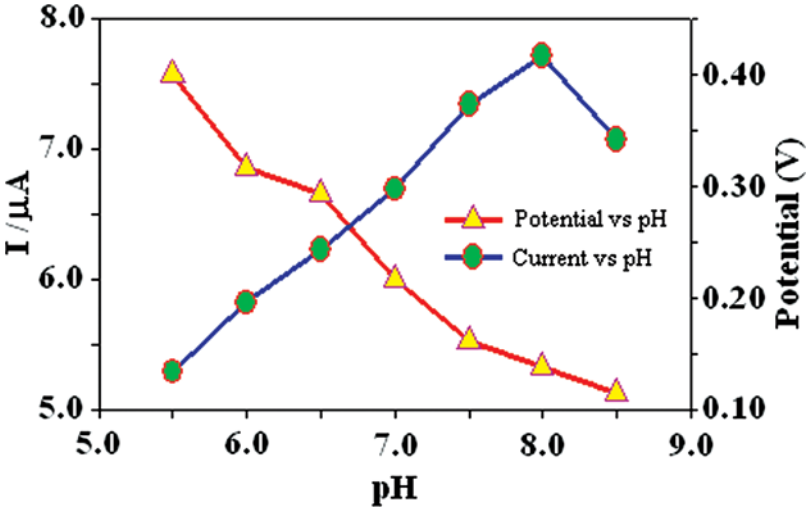

Figure 2. Oxidation peak currents and peak potentials of 100 ppm dopamine in the phosphate buffer solution of pH 5.5–8.5.

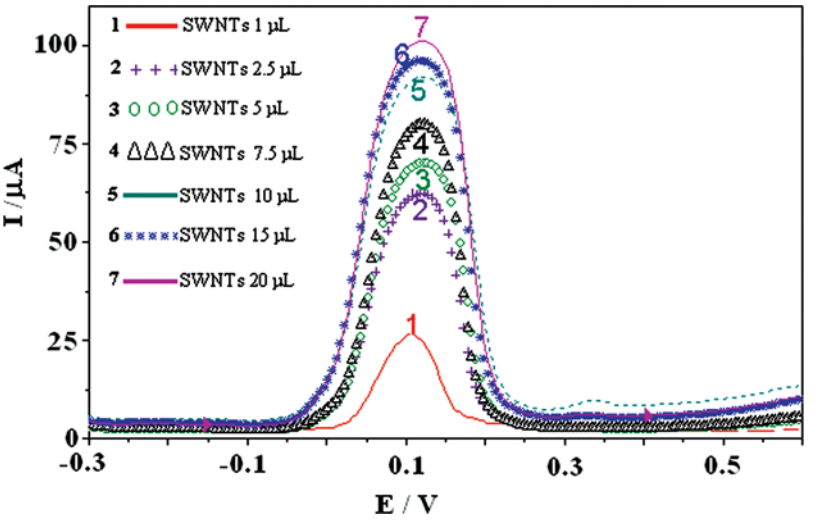

Figure 3. DPV at the SWNTs/GC electrode for 100 ppm dopamine in the presence of different amounts of SWNTs (1) 1 μL, (2) 2.5 μL, (3) 5 μL, (4) 7.5 μL, (5) 10 μL, (6) 15 μL, and (7) 20 μL in 0.1 M phosphate buffer of pH 7.5.

occurred in the pH range of 8.0–8.5, therefore the optimum phosphate buffer of pH 7.5 was used in all experiment.

The thickness of the modified layer has great impact on the electrochemical properties of the SWNTs/GC electrode. The DPV of dopamine 100 ppm with different amount of SWNTs were shown in Figure 3. The SWNTs film on the GC surface enhanced the oxidation peak current of dopamine. The oxidation peak current of dopamine increase linearly with the amounts of SWNTs suspension over the range from 1 to 10 μL, and then increased slightly from 10 to 20 μL. When the amount of SWNTs suspension exceeded 20 μL, the SWNTs film became thicker and blocked the mass transport and electron transfer, therefore SWNTs suspension of 10 μL was used for fabrication of the modified glassy carbon electrode.

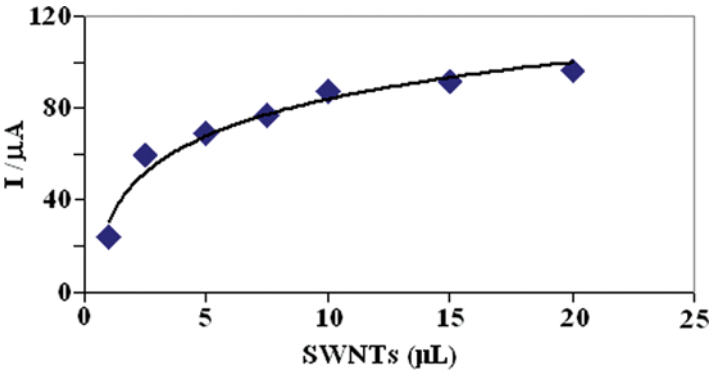

Figure 4. Effect of the amounts of SWNTs on the oxidation peak current of 100 ppm dopamine by DPV.

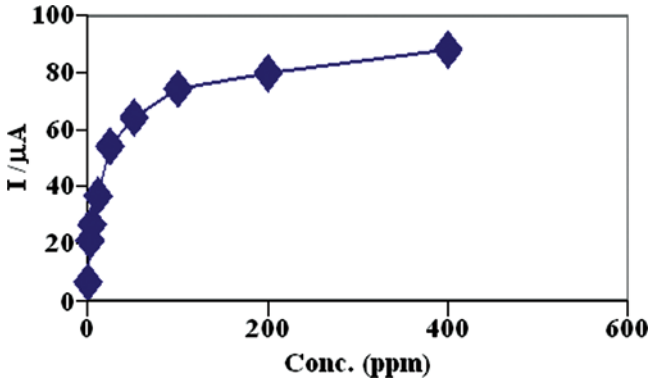

Figure 5. DPV voltammograms of dopamine at the SWNTs-modified electrode at concentrations 1–400 ppm of dopamine in 0.1 M phosphate buffer pH 7.5.

The SWNTs/GC 10 µL was used to test the linearity of anodic oxidation of dopamine using 1–400 ppm of dopamine in 0.1 M phosphate buffer pH 7.5. The results of these experiments are shown in Figures 4–6. Figure 4 shows the effect of the amounts of SWNTs on the oxidation peak current of 100 ppm dopamine by DPV. The peak current increased with increasing dopamine concentration. The linearity occurred in the range of 5–20 µL of dopamine. Figure 5 shows DPV voltammograms of dopamine at the SWNTs-modified electrode at concentrations between 1–400 ppm. The calibration curve for dopamine in 0.1 M phosphate buffer pH 7.5 is shown in Figure 6. The peak current increased linearly with concentration of dopamine in range from 2.5–25 ppm ($R^2 = 0.9766$).

Figure 7 shows the life time of the SWCNTs/GC of 100 ppm dopamine in .01 M phosphate buffer pH 7.5, in which 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%

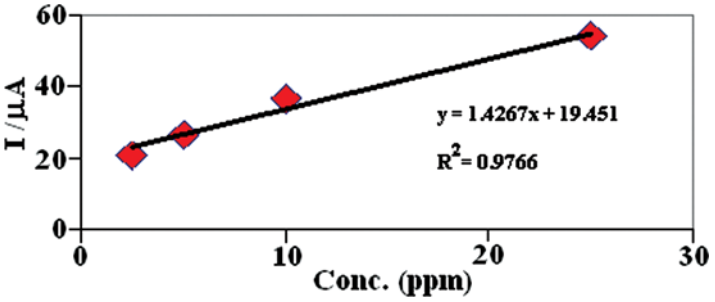

Figure 6. Calibration curve for dopamine in 0.1 M phosphate buffer pH 7.5 with concentration of dopamine in the range of 2.5–25 ppm.

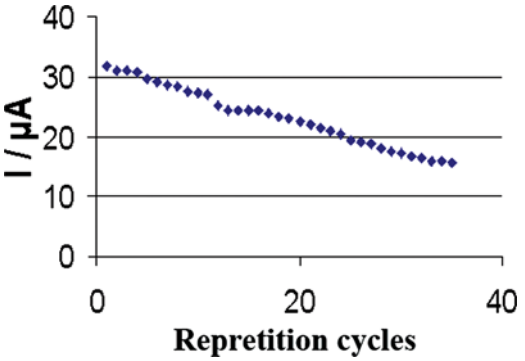

Figure 7. The life time of the SWNTs/GC of 100 ppm dopamine in .01 M phosphate buffer pH 7.5.

(10% RSD). The relative standard deviation (RSD) of 8.42% for 100 ppm dopamine (n = 20) showed excellent reproducibility. The drug samples containing dopamine obtained from Radvitee Hospital were tested as in the mentioned procedure. The percentage recovery of dopamine in the drug samples was 120.

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