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Application of Graphene/Tetraphenylboron-Dopamine Modified Graphite Electrode for Selective Determination of Dopamine

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A novel electrochemical sensor based on graphene and tetraphenylboron-dopamine electroactive material was developed for determination of dopamine which is correlative to some neurogenic disease. Graphene was synthesized by one-step liquid-phase exfoliation of graphite and the tetraphenylboron-dopamine was prepared by precipitation reaction on formation of ion association complex. The resultant electrode showed better performance in selectivity, sensitivity and narrow potential window comparing with bare graphite electrode and graphite electrode modified by tetraphenylboron-dopamine. In the presence of 1000-fold concentration interference of ascorbic acid and uric acid, the linear range for dopamine was successfully determined from 1×10^{-4} to 1×10^{-10} mol/L with a correlation coefficient of 0.9969. The detection limit was estimated to be 7.39×10^{-11} mol/L in 3 of signal to noise ratio (S/N = 3). According with successive measurements in 10 times, the relative standard deviation of all results for graphene/tetraphenylboron-dopamine /graphite electrode still kept in 1.83 %. Moreover, the graphene/tetraphenylboron-dopamine /graphite electrode could be stored for 30 days in 4 °C without sharply decrease of its electroactivity. All results clearly prove that this modified electrode is sensitive way for selective determination of dopamine.

Keywords: Graphene, Tetraphenylborate, Dopamine, Modified electrode.

INTRODUCTION

Dopamine, as one of the important neurotransmitters, plays a significant role in the function of human metabolism, cardiovascular, central nervous, renal and hormonal systems[1]. Deficiency of dopamine may cause some neurological diseases such as Schizophrenia, Huntington's disease and Parkinson's disease[2]. There are some methods for the requirements of dopamine determination, which include spectrophotometry[3,4], high performance liquid chromatography (HPLC)[5], flow injection chemiluminescence[6], spectrofluorimetry and capillary electrophoresis mass spectrometry[7]. Even though these methods exhibit high sensitivity, but require expensive instruments, long analysis times, troublesome and time-consuming pretreatment. Hence, a rapid, low-cost, sensitive and selective method is strongly required to satisfy real application for clinical diagnosis and pathological analysis.

Electrochemical measurements as a traditional analytical technique have been widely used in the determination of biological samples because of its intrinsic advantages such as portability, low-energy consumption and low-cost[8]. Therefore, the determination of dopamine based on its electrochemical activity in field of electrochemistry has attracted a dramatical interest[9-11]. However, the coexistence of ascorbic acid and uric acid with 100-1000 times of concentrations than that of dopamine interferes dopamine determination seriously, especially for overlapping oxidized potential at traditional bare electrodes. In order to overcome the difficulties of traditional dopamine determination, new techniques are needed to be developed.

In order to enhance the sensitivity and selectivity of the electrochemical sensors, a variety of materials have been employed to modify electrode. Graphene, a flat monolayer of carbon atoms tightly arranged in a two-dimensional (2D) honeycomb lattice, has been realized in 2004. It is the newest member of the carbon family that can be wrapped up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite. Advantages of electronic conductivity, high specific surface area and chemical stability provide a suitable microenvironment for biomolecules immobilization and facilitate electron transfer between immobilized biomolecules and electrode[12-19]. These promising properties together make graphene-based materials ideal candidates for the application in many areas including electrochemical sensing and biosensing[20-22].

Tetraphenylborate has been used in the formation of many sensors as a well-known ion exchanger[23,24]. Because of the interactions between the particles, tetraphenylborate ions with negative charges are able to exclude same negative ions but attract positive ions from the membrane[25]. In the present

research, dopamine was reacted with tetraphenylborate in the formation of a water insoluble ion association complex as an electrochemically active material used. The high lipophilicity of the complex suggests its suitable use in polyvinylchloride (PVC) matrix membrane sensors. To combine advantages of graphene and the electrochemical technique, a novel graphene/tetraphenylboron-dopamine modified graphite electrode own the excellent ability to determine dopamine in a rapid, selective, sensitive and low-cost way.

EXPERIMENTAL

Dopamine hydrochloride was purchased from Sigma-Aldrich (Germany), (+)-sodium L-ascorbate and uric acid was obtained from Sigma-Aldrich (China). Graphite was obtained from Tianjin Chemical Reagent Factory (China). Tetraphenylboron sodium, tetrahydrofuran, N,N-dimethyl formamide and dibutyl phthalate were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Polyvinylchloride powder was obtained from Sandong haihua Co., Ltd (China). All the reagents used in this study were of analytical grade. All electrochemical measurements were performed by a CHI650D workstation (Chen Hua, Shanghai). A graphene/tetraphenylboron-dopamine modified graphite electrode, a platinum wire and an Ag/AgCl electrode were used to complete the three-electrode system.

Synthesis of graphene: The graphite with a concentration of 0.1 mg/mL was dispersed in 25 mL N,N-dimethyl formamide solution by sonicating for 30 min. Then the resultant dispersion was centrifuged for 90 min at 500 rpm[26].

Preparation of tetraphenylboron-dopamine electrochemically active material: 0.1 mol/L Dopamine hydrochloride solution was added to 0.1 mol/L tetraphenylboron sodium solution in the equal volume. Flocculent white precipitates quickly generated. Then the precipitates were filtered with the No. 3 sand core funnel and washed with distilled water. The clean precipitates were stored in a desiccator until constant weight obtained.

Preparation of graphene/tetraphenylboron-dopamine/graphite electrode: A mixture containing 1.5 mL graphene suspension, 20 mg tetraphenylboron-dopamine with 0.3 mL dibutyl phthalate, 100 mg PVC and 3 mL tetrahydrofuran was prepared and shaken vigorously. Then the polished graphite electrode was dipped into the mixture mentioned above. A graphene/tetraphenylboron-dopamine/graphite electrode fabricated for a working electrode was gotten when the mixture coated on the graphite electrode tightly.

RESULTS AND DISCUSSION

The SEM images graphene (a), graphene/tetraphenylboron-dopamine complexes (b) and graphene/tetraphenylboron-dopamine/graphite electrode (c) are shown in Fig. 1. From Fig. 1a showed that graphene nanosheets are as thin as transparent paper. It means that these nanosheets were exfoliated successfully from graphite. Fig. 1b shows that graphene nanosheets were packed with tetraphenylboron-dopamine evenly. It can also be proven that graphene/tetraphenylboron-dopamine complexes are uniformly wrapped in the surface of graphite electrode (Fig. 1c).

Electrochemical response of dopamine at the graphene/tetraphenylboron-dopamine/graphite electrode: For studying advantages of graphene/tetraphenylboron-dopamine/graphite electrode, the cyclic voltammograms (CVs) was used to determine the performance of the bare graphite electrode, tetraphenylboron-dopamine/graphite electrode and graphene/tetraphenylboron-dopamine/graphite electrode, respectively. As shown in Fig. 2, the oxidation peak current of dopamine on the surface of graphene/tetraphenylboron-dopamine/graphite electrode is 378.9 uA, which is the largest peak current because of the great conductivity. To compare with other tested electrodes, the smaller ΔE_p of graphene/tetraphenylboron-dopamine/graphite electrode is 137 mV means better reversibility.

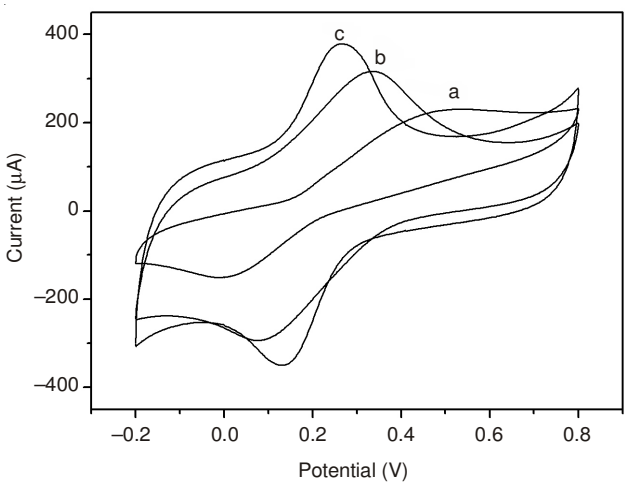

Fig. 2. Cyclic voltammograms of bare graphite electrode (a), tetraphenylboron-dopamine/graphite electrode (b), graphene/tetraphenylboron-dopamine/graphite electrode (c) in 0.1 mol/L phosphate buffer (pH 7) containing 1×10^{-4} mol/L dopamine. Scan rate: 100 mV s^{-1}

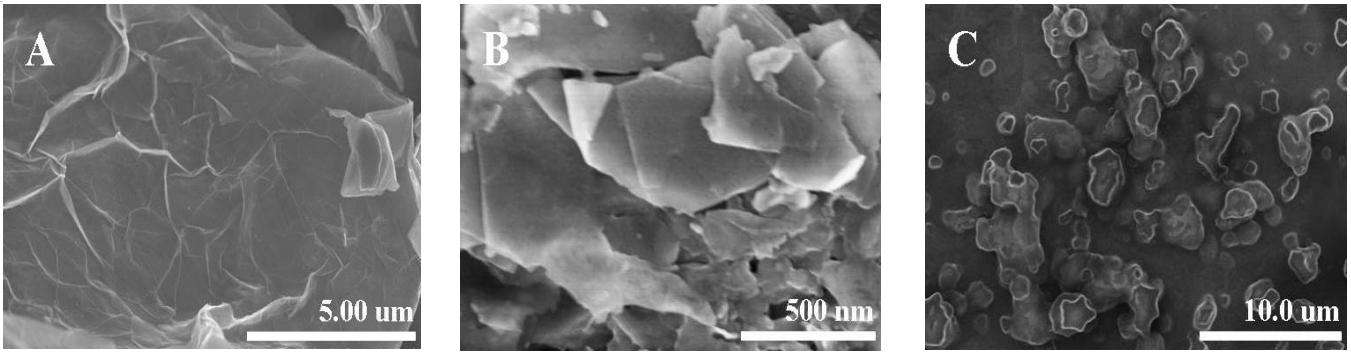

Fig. 1. Scanning electron microscope of images of graphene (a), Graphene/tetraphenylboron-dopamine complexes (b) and graphene/tetraphenylboron-dopamine/graphite electrode (c)

Effect of pH: The effects of pH on the graphene/tetraphenylboron-dopamine/graphite electrode were investigated in the concentration of 1×10^{-4} mol/L dopamine solution. Fig. 3a shows the relationship between the anodic peak potential of dopamine and the pH value. It can be seen that the anodic peak potential decreases obviously with the increase of pH. The linear regression equation is as follows: Epa (mV) = 646.095-53.63 pH and the correlation coefficient is -0.9975. A slope of -53.63 mV/pH indicates that the proportion of the electron and proton involved in the reactions is equal. The maximum current was obtained at pH 7 and close to the physiological pH conditions (Fig. 3b). Therefore, pH 7 was chosen for the subsequent experiments and provides the possibility of real samples' determination.

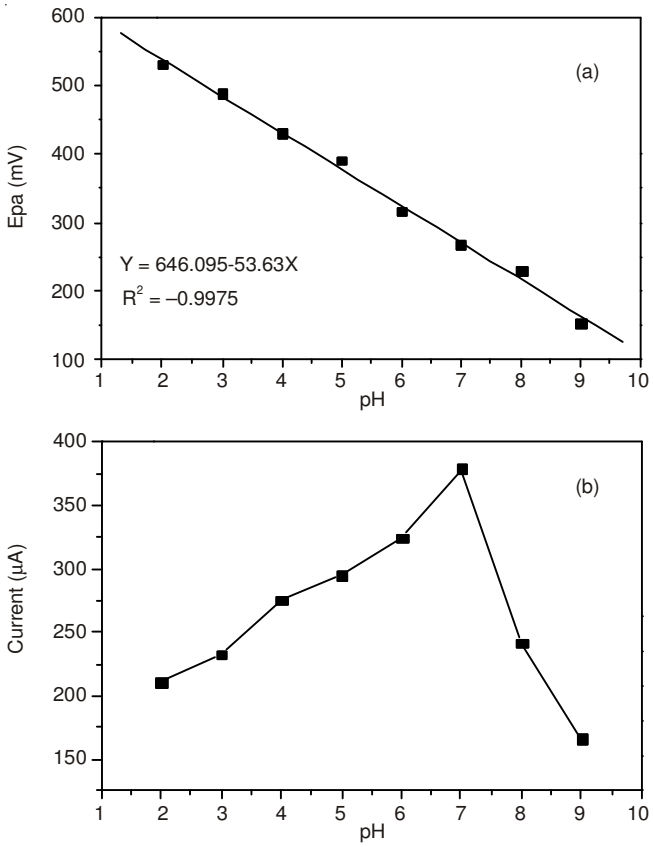

Fig. 3. Plots of variation of Epa (a) and Ipa (b) with pH change in the concentration of 1×10^{-4} mol/L dopamine solution at the surface of graphene/tetraphenylboron-dopamine/graphite electrode. Scan rate: 100 mV s^{-1}

Effect of scan rate: Fig. 4a shows the cyclic-voltammogram curves of 1×10^{-4} mol/L dopamine at the surface of graphene/tetraphenylboron-dopamine/graphite electrode with different scan rates in the range of 20-200 mV/s. The proportional increase of anodic peak current *versus* increase of scan rate is shown in Fig. 4b. The ideal correlation coefficient proves that the redox reaction of dopamine toward the graphene/tetraphenylboron-dopamine/graphite electrode is a typically adsorption-controlled process. Fig. 4c shows a good linear relationship between the anodic peak current and the square root of the scan rate. It indicates that the reaction of electron transfer is a diffusion-controlled process. So our electrode process is controlled by both process of adsorption and diffusion simultaneously.

Selective determination of dopamine: The selectivity of graphene/tetraphenylboron-dopamine/graphite electrode for dopamine had been researched in the mixture containing conventional interference. Fig. 5a shows the cyclic-voltammogram curves of 1×10^{-4} mol/L dopamine, 0.1 mol/L ascorbic acid and 0.1 mol/L uric acid (a), 0.1 mol/L ascorbic acid (b), 0.1 mol/L uric acid (c) and blank phosphate buffer (d) at the modified electrode with a scan rate of 100 mV/s. In 1000 times presence of ascorbic acid and uric acid than the dopamine, the oxidation peak current and ΔE_p of dopamine on the surface of graphene/tetraphenylboron-dopamine/graphite electrode are 379.6 uA and 137.3 mV which are extremely similar to only presence of dopamine. It means our graphene/tetraphenylboron-dopamine/graphite electrode provides its excellent selectivity for dopamine because dopamine is only positive charge comparing with ascorbic acid and uric acid when they are dissolved into water. According to a principle of ion-selective electrodes based on permselectivity, the tetraphenylborate ions of tetraphenylboron-dopamine with the negative charges just allow ions with positive charge such as dopamine passing through the membrane phase. Additionally, graphene was wrapped in tetraphenylboron-dopamine, the feasible electron transfer between graphene and phenyl structure of dopamine promotes the selectivity and sensitivity of modified electrode since special π-π interaction unlike ascorbic acid and uric acid. Fig. 5b shows calibrating plots of the anodic peak current *versus* logarithm of the dopamine concentrations. The linear regression equation follows as: I(μA) = 572.559 + 49.605 log C (mol/L) and the correlation coefficient is 0.9969. Then the detection limit is gotten as 7.39×10^{-11} mol/L with noise-signal ratio in 3.

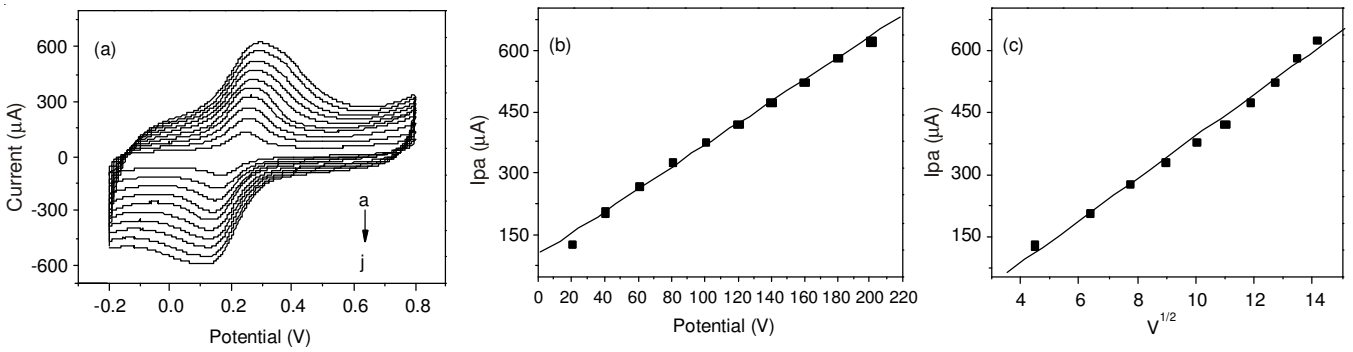

Fig. 4. Cyclic voltammograms of graphene/tetraphenylboron-dopamine/graphite electrode in 0.1 M phosphate buffer containing 1×10^{-4} mol/L dopamine at different scan rate (a-j): 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 mV s^{-1} (a); Graph of anodic peak current *versus* scan rate (b); Graph of anodic peak current *versus* the square root of the scan rate (c)

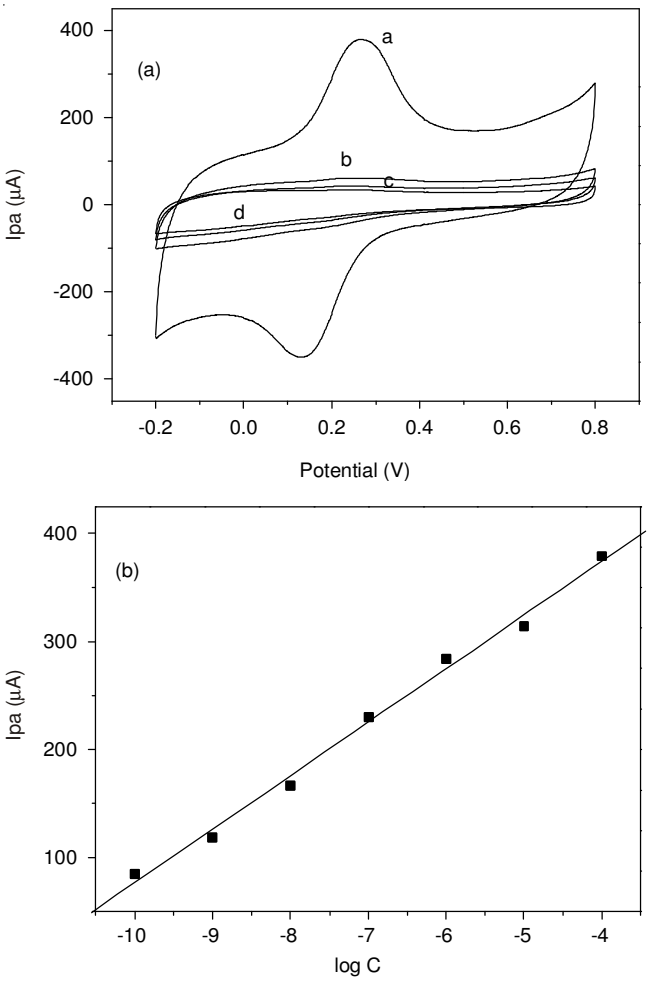

Fig. 5. Cyclic voltammograms scanned by graphene/tetraphenylboron-dopamine/graphite electrode in the presence of 1×10^{-4} mol/L dopamine, 0.1 mol/L ascorbic acid and 0.1 mol/L uric acid (a), 0.1 mol/L ascorbic acid (b), 0.1 mol/L uric acid (c) in 0.1 M phosphate buffer (d) at scan rate of 100 mV s^{-1} (A); Calibrating plots of the anodic peak current *versus* logarithm of the dopamine concentrations in the presence of ascorbic acid and uric acid (B)

Stability and reproducibility: The stability and reproducibility of the graphene/tetraphenylboron-dopamine/graphite electrode were investigated in the PBS solution containing 1×10^{-4} mol/L dopamine, 0.1 mol/L ascorbic acid and 0.1mol/L uric acid. For the dopamine, the relative standard deviation of the oxidation peak currents is 1.83 % in 10 times successive measurements. The peak currents of the electrodes keep more than 90.2 % comparing with initial values after 30 days stored in 4 ºC.

Conclusion

In this study, graphene/tetraphenylboron-dopamine modified graphite electrode developed for dopamine determination in the presence of ascorbic acid and uric acid shows the excellent selectivity and sensitivity at physiological pH. Moreover, modified electrode own the wide linear range and low detection limit. All results suggest that our investigation describe here provide a great promise for clinical diagnosis and long-term monitoring of dopamine.

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