Anal. Bioanal. Electrochem., Vol. 8, No. 5, 2016, 547-556

Analytical & Bioanalytical Electrochemistry

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Full Paper

Construction of a Nanostructure based Voltammetric Sensor for the Determination of Dopamine

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Received: 11 May 2016 / Accepted with minor revision: 15 June 2016 / Published online: 15 August 2016

Abstract- 2-(4-Oxo-3-phenyl-3,4-dihydroquinazolinyl)-*N′*-phenyl-hydrazinecarbothio amide was synthesized and used to construct a modified-graphene oxide nano sheets paste electrode. The electrocatalytic oxidation of dopamine at the surface of this electrode was studied using cyclic voltammetry (CV), chronoamperometry (CHA), and square wave voltammetry (SWV). Under the optimized conditions, the square wave voltammetric peak current of dopamine increased linearly with dopamine concentration in the ranges of 5.0×10^{-7} to 4.0×10^{-4} M. The detection limit of 9.5×10^{-8} M was obtained for dopamine. Finally this modified electrode was used for determination of dopamine in some real samples.

Keywords- Dopamine, Graphene oxide nano sheets, Chemically modified electrodes, Electrocatalysis

1. INTRODUCTION

Dopamine (scheme 1), has been of interest to neuroscientists and chemists since its discovery in the 1950 s [1]. As the most important neurotransmitter in the mammalian central nervous system, the amount of dopamine distributed in organs has great influences on human

movements and emotions. The abnormal low concentration level of this neurotransmitter can cause Tourette's syndrome, schizophrenia, Parkinson's disease, Huntington's disease, HIV infection and other similar neurological disorders [2,3]. The normal level of dopamine concentration in the extracellular fluid of the brain tissue is about (10^{-8} to 10^{-6} M). Hence, there is an enormous interest in the determining of the concentration of dopamine in the pharmaceutical and clinical samples.

Various commonly usable analytical methods have been developed for the determination of dopamine, including rapid liquid chromatography/tandem mass spectrometry (LC-MS/MS), fluorimetric method, chemiluminescence method, electrochemistry and capillary electrophoresis mass spectrometry method [4-6].

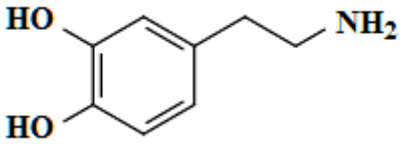
In 1976, Adams [7] proposed the use of voltammetric methods for determination of such neurotransmitters species in the brain. Therefore, given the advantages of having a lower cost, providing faster response, simple instrumentation, high sensitivity, facile miniaturization, and low power requirement, numerous electrochemical methods for the determination of drugs have been developed [8-21].

Carbon paste electrodes (CPEs), is an inexpensive kind of electrode and possess many advantages including wide range of potential application, low background current, easy fabrication, compatibility with various types of modifiers and rapid surface renewal, have been widely used as suitable matrixes for preparation of modified electrodes [22-26]. Over recent years, various materials including polymers, nanorods, nanocomposites, carbon nanotubes, and metal oxide nanoparticles have been employed for the electrode surface modification [27-35].

Another important electrocatalytic material is graphene, which was successfully employed as an electrode material for sensing drugs because of its rich edge defects, unique electronic properties, strong mechanical strength, and large surface area. Graphene is made of a two-dimensional (2D) sheet of covalently bonded carbon atoms, also some organic or inorganic synthetic procedures have been employed to add special functions to graphene to improve its selectivity and sensitivity. Graphene can be synthesized via chemical reduction of exfoliated graphitic oxide (GO) [36-40]. GO can be produced by any of the oxidative treatments of graphite reported by Hummers, Brodie, and Staudenmaeir. Graphene exhibits 60-fold better conductivity, higher carrier mobility, higher stability, and greater sp^2 characteristics, and possesses more negative surface charge densities than single-walled carbon nanotubes [41-48]. Thus, it is an important electro-catalytic material that may be used in the determination of a variety of electro-active species.

In the present work, we described the preparation of a 2-(4-oxo-3-phenyl-3,4-dihydroquinazolinyl)-*N′*-phenyl-hydrazinecarbothioamide modified graphene oxide nano sheets paste electrode (2PHCGPE) as a new sensor in the electrocatalysis of dopamine in an aqueous buffer solution. Then, in order to demonstrate the catalytic ability of the modified

electrode in the electrooxidation of dopamine in real samples, we examined this method for the determination of dopamine in dopamine injection and urine samples.



Scheme 1. Chemical structure of dopamine

2. EXPERIMENTAL

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302 N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and 2PHCGPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

All reagents were of analytical grade and were obtained from Merck (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0-9.0. 2PHC [16] and graphene oxide nano sheets [31] were synthesized in our laboratory as reported previously.

2.2. Preparation of the electrode

The modified electrodes were prepared by mixing 0.01 g of 2PHC with 0.89 g graphite powder and 0.1 g graphene oxide nano sheets with a mortar and pestle. Then, ~0.7 mL of paraffin oil was added to the above mixture and mixed for 20 min until a uniformly-wetted paste was obtained. The paste was then packed into the end of a glass tube (ca. 3.4 mm i.d. and 10 cm long). A copper wire was inserted into the carbon paste provide the electrical contact. For surface regeneration, a new surface was obtained by pushing an excess of the paste out of the tube and polishing with a weighing paper.

For comparison, 2PHC modified CPE electrode (2PHCCPE) without graphene oxide nano sheets, also, graphene oxide nano sheets paste electrode (GPE) without 2PHC, and unmodified CPE in the absence of both 2PHC and graphene oxide nano sheets were also prepared in the same way.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Behavior of 2PHCGPE

2PHCGPE was constructed and its electrochemical behaviors were studied in a 0.1 M PBS (pH 7.0) using CV. The experimental results show well-defined and reproducible anodic and cathodic peaks, with E_{pa}, E_{pc} and E°´ of 210, 110 and 160 mV *vs*. Ag/AgCl/KCl (3.0 M) respectively. The observed peak separation potential, $\Delta E_p=(E_{pa}-E_{pc})$ of 100 mV, was greater than the value of 59/n mV expected for a reversible system [49] suggesting that the redox couple of 2PHC in 2PHCGPE has a quasi-reversible behavior in aqueous medium.

3.2. Electrocatalytic oxidation of dopamine at a 2PHCGPE

Fig. 1 shows the CV responses for the electrochemical oxidation of 0.3 mM dopamine at unmodified CPE (curve b), GPE (curve d), 2PHCCPE (curve e) and 2PHCGPE (curve f). As it is seen, while the anodic peak potential for dopamine oxidation at the GPE, and unmodified CPE are 350 and 400 mV, respectively, the corresponding potentials at 2PHCGPE and 2PHCCPE are ~210 mV. These results indicate that the peak potential for dopamine oxidation at the 2PHCGPE and 2PHCCPE shift by ~140 and 190 mV toward negative values compared to GPE and unmodified CPE, respectively. However, 2PHCGPE shows much higher anodic peak current for the oxidation of dopamine compared to 2PHCCPE, indicating that the combination of graphene oxide nano sheets and the mediator (2PHC) has significantly improved the performance of the electrode toward dopamine oxidation. In fact, 2PHCGPE in the absence of dopamine exhibited a well-behaved redox reaction (Fig. 1, curve c) in 0.1 M PBS (pH 7.0). However, there was a drastic increase in the anodic peak current in the presence of 0.3 mM dopamine (curve f), which can be related to the strong electrocatalytic effect of the 2PHCGPE towards this compound.

The potential scan rate effect on the electrocatalytic oxidation of dopamine at the 2PHCGPE was investigated by LSV (Fig. 2). As can be observed in Fig. 2, the oxidation peak potential shifted to more positive potentials with increasing scan rate, confirming the kinetic limitation in the electrochemical reaction. Also, a plot of peak height (I_p) *vs*. the square root of scan rate ($\nu^{1/2}$) was found to be linear in the range of 5-70 mV s^{-1}, suggesting that, at sufficient overpotential, the process is diffusion rather than surface controlled (Fig. 2A). A plot of the scan rate-normalized current ($I_p/\nu^{1/2}$) *vs*. scan rate (Fig. 2B) exhibited the characteristic shape typical of an EC' process [49].

The Tafel slope (b) can be obtained from the slope of Ep *vs*. log v using Eq. (1) [49]:

$$Ep=b/2 \log v+\text{constant} \quad (1)$$

The Tafel slope was found to be 0.0862 V (Fig. 2C), which indicates that an one-electron transfer process is the rate limiting step assuming a transfer coefficient (*a*) is about 0.32.

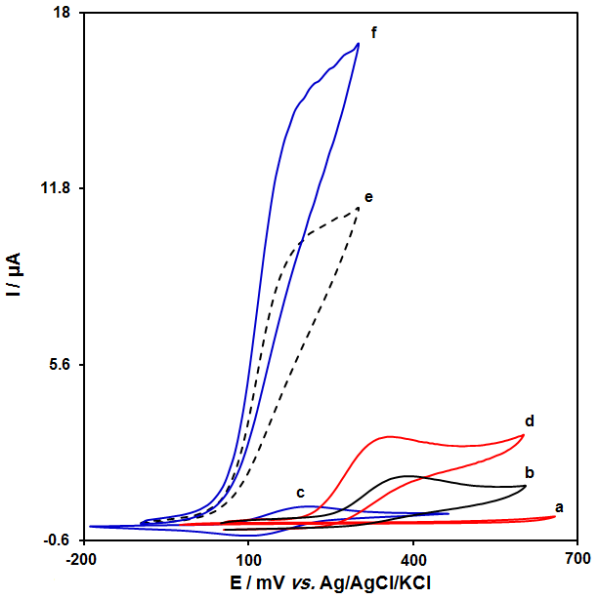


Fig. 1. CVs of (a) unmodified CPE in 0.1 M PBS (pH 7.0); (b) unmodified CPE in 0.1 M PBS (pH 7.0) containing 300.0 µM dopamine, (c) 2PHCGPE in 0.1 M PBS (pH 7.0) (d) GPE in 0.1 M PBS (pH 7.0) containing 300.0 µM dopamine, (e) 2PHCCPE in 0.1 M PBS (pH 7.0) containing 300.0 µM dopamine and (f) 2PHCGPE in 0.1 M PBS (pH 7.0) containing 300.0 µM dopamine In all cases scan rate is 10 mV s^{-1}

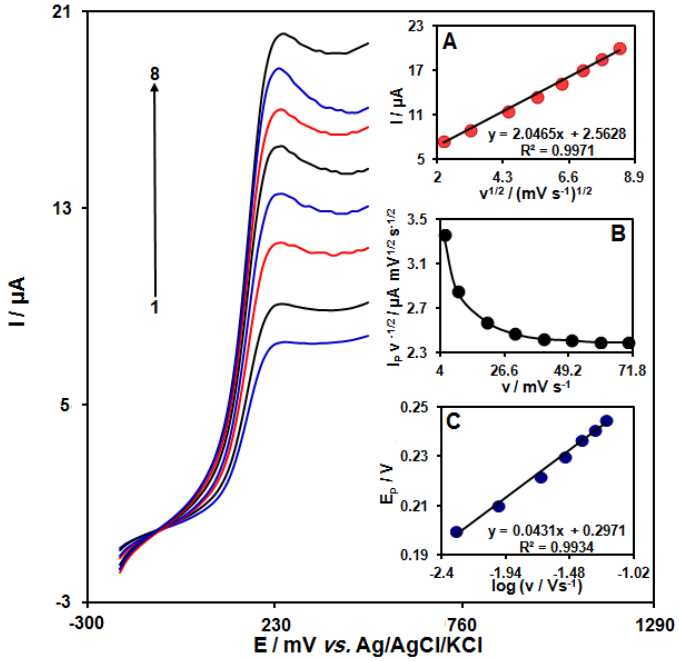


Fig. 2. LSVs of 2PHCGPE in 0.1 M PBS (pH 7.0) containing 150.0 µM dopamine at various potential scan rates; numbers 1-8 correspond to 5, 10, 20, 30, 40, 50, 60 and 70 mV s^{-1}, respectively. Insets: Variation of (A) anodic peak current *vs.* $v^{1/2}$; (B) normalized current ($I_p/v^{1/2}$) *vs.* v, and (C) anodic peak potential *vs.* log v

3.2. Chronoamperometric measurements

Chronoamperometric measurements of dopamine at 2PHCGPE were carried out by setting the working electrode potential at 0.3 V *vs*. reference electrode for the various concentrations of dopamine in PBS (pH 7.0) (Fig. 3).

For an electroactive analyte (dopamine in this case) with a diffusion coefficient of D, the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation [49]. Experimental plots of I *vs*. $t^{-1/2}$ were employed, with the best fits for different concentrations of dopamine (Fig. 3A). The slopes of the resulting lines were plotted *vs*. dopamine concentration (Fig. 3B). From the resulting slope and Cottrell equation the mean value of the D for dopamine was found to be 1.1×10^{-6} cm^2/s.

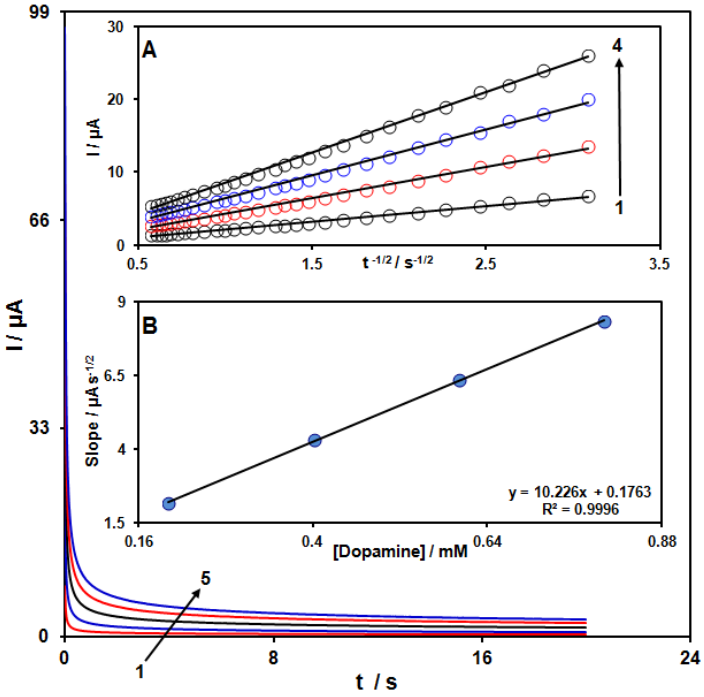


Fig. 3. Chronoamperograms of 2PHCGPE in 0.1 M PBS (pH 7.0) for different concentrations of dopamine The numbers 1–5 correspond to 0.0, 0.2, 0.4, 0.6 and 0.8 mM of dopamine. Insets: (A) Plots of I *vs*. $t^{-1/2}$ obtained from chronoamperograms 2–5; (B) Plot of the slopes of the straight lines obtained in (A) against dopamine concentration

3.3. Calibration plot and limit of detection

The peak currents of dopamine oxidation at the surface of the modified electrode can be used for determination of dopamine in solution. Therefore, square wave voltammetry (SWV) experiments were done for different concentrations of dopamine (Fig. 4).

The oxidation peak currents of dopamine at the surface of a modified electrode were proportional to the concentration of the dopamine within the range 5.0×10^{-7} to 4.0×10^{-4} M

with detection limit (3σ) of 9.5×10^{-8} M. These values are comparable with values reported by other research groups for electro-oxidation of dopamine at the surface of chemically modified electrodes by other modifiers (see Table 1).

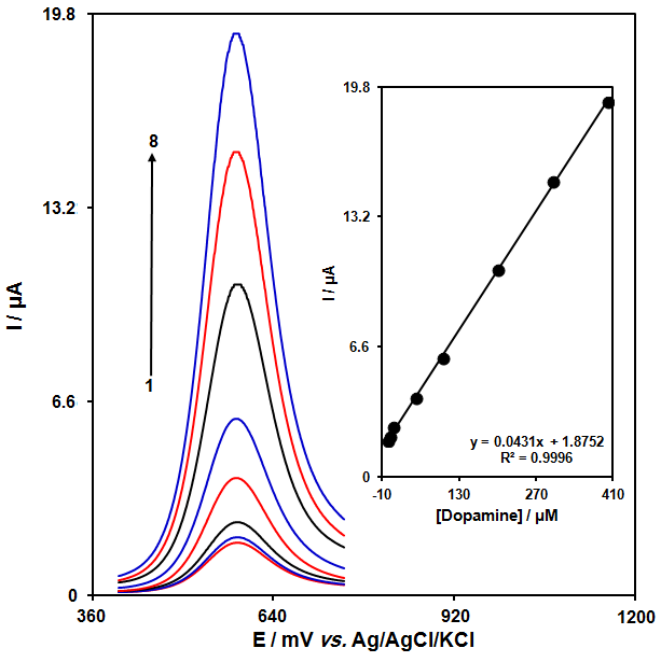


Fig. 4. SWVs of 2PHCGPE in 0.1 M PBS (pH 7.0) containing different concentrations of dopamine Numbers 1-8 correspond to 0.5, 2.5, 10.0, 50.0, 100.0, 200.0, 300.0 and 400.0µM of dopamine. Inset show the plots of the peak current as a function of dopamine concentration in the range of 0.5-400.0 µM

Table 1. Comparison of the efficiency of some modified electrodes used in the electro-oxidation of dopamine

Electrode	Modifier	LOD (M)	LDR (M)	Ref.
Glassy carbon	Poly(l-leucine)/DNA composite film	4.0×10^{-8}	1.0×10^{-7}–1.0×10^{-4}	[17]
Carbon fiber	Reduced graphene oxide	7.7×10^{-7}	1.4×10^{-6}–2.24×10^{-4}	[18]
Glassy carbon	Carbon nanohorns/poly(glycine)	3.0×10^{-8}	1.0×10^{-6}-2.8×10^{-4}	[19]
Glassy carbon	l-tyrosine (l-Tyr) covalently functionalized graphene oxide (GO) composite	2.8×10^{-7}	1.0×10^{-6}-5.0×10^{-4}	[20]
Glassy carbon	Graphene quantum dots	1.15×10^{-7}	1.0×10^{-6}–1.5×10^{-4}	[21]
Carbon paste	2-(4-Oxo-3-phenyl-3,4-dihydroquinazolinyl)-*N*′-phenyl-hydrazinecarbothioamide	9.5×10^{-8}	5.0×10^{-7}-4.0×10^{-4}	This Work

3.4. Real sample analysis

In order to evaluate the analytical capability of the proposed method, it was applied to the determination of dopamine in dopamine injection and urine samples (Table 2). Satisfactory recovery of the experimental results was found for dopamine.

Table 2. The application of 2PHCGPE for determination of dopamine in real samples

Sample	Spiked (μM)	Found (μM)	Recovery (%)	R.S.D. (%)
Dopamine injection	0	10.0	-	3.3
	5.0	14.8	98.7	2.5
	10.0	20.5	102.5	1.8
	15.0	25.2	100.8	2.6
	20.0	29.8	99.3	3.2
Urine	0	ND[a]	-	-
	7.5	7.7	102.7	1.7
	12.5	12.4	99.2	2.7
	17.5	17.6	100.6	3.1
	22.5	21.9	97.3	2.5

[a] ND: Not detected

4. CONCLUSION

The 2PHCGPE was constructed and used for the study of the electrochemical behavior of dopamine. The 2PHCGPE showed excellent electrocatalytic activity toward dopamine. The SWV currents of dopamine at 2PHCGPE increased linearly with the concentration of dopamine in the range from 5.0×10^{-7} to 4.0×10^{-4} M with a detection limit of 9.5×10^{-8} M. Finally, this method was used for the determination of dopamine in some real samples.

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