Fabrication of a graphene oxide nano-sheet modified electrode for determination of dopamine in the presence of tyrosine: A multivariate optimization strategy

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ABSTRACT

In the present study, the oxidation peak current of dopamine (DA) in a 0.2 M Britton–Robinson (B–R) buffer solution was optimized by experimental design for its determination in the presence of tyrosine (Tyr) at the surface of graphene oxide modified carbon paste electrode (CPE/GO). A central composite rotatable design (CCRD) and response surface methodology (RSM) were used to evaluate the effects of the variables by the differential pulse voltammetry (DPV) method. These variables include scan rate, step potential, modulation amplitude, graphene oxide amount and pH. Characterizing of the CPE/GO was investigated by electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and cyclic voltammetry (CV) techniques. Also other voltammetric techniques such as chronocoulometry and linear sweep voltammetry (LSV) were applied for electrochemical studies of DA. Using these methods, diffusion coefficient ($D = 9.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and kinetic parameters such as electron transfer coefficient ($\alpha = 0.6$) and exchanging current density ($j_0 = 14.6 \text{ μA cm}^{-2}$) of DA were determined. Then, under the optimized conditions linear concentration range for DA was from 0.08 to 2.30 μM and the detection limit was found to be 8.60 nM. Finally CPE/GO could be employed for determination of DA in real samples such as human blood plasma.

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1. Introduction

A significant discharge from mammalian cell that contributes in the central nerve system is dopamine (DA) which is categorized in the catecholaminse neurotransmitter [1]. In some cases DA is responsible for some nerves and physiological diseases such as Parkinsonism and schizophrenia [2]. Because of the important role of DA chemical, the study of this analyte is useful to understand physiological and physical function [3]. DA was studied using some methods, including titrimetry [4], spectrophotometry [5] and potentiometry [6]. But because of DA is an electroactive component, electrochemical studies of the analyte are useful; moreover this method has many advantages such as selectivity, sensitivity, low cost and rapid detection [7]. However, these methods have some difficulties such as high over potential and sediment by oxidation or reduction [8]. To resolve these problems many studies focus on the electrode surfaces modified by several material including carbon materials [9], polymers [10], enzymes [11] and self-assemble monolayers [12]. Lately, a new two dimensional (2-D) carbon material graphene has been used in the fabrication of electrochemical biosensors [13]. Graphene oxide (GO) is a graphite derivative and has unique

electrical, thermal and mechanical properties as well as usually is made out of chemical oxidation and scratch of graphene [14]. GO is a 2-D plate with 1.0 nm thickness and big lateral dimensions in the range of a few nanometer to hundred micrometers [15]. GO was used as modifier in some studies such as DNA sensing [16], detection of single nucleotide polymorphisms of DNA [17], detection of leukemia [18,19].

Tyrosine (Tyr) is a semi-essential amino acid in the body and is primarily derived from phenylalanine by phenylalanine hydroxylase [20]. Abnormal concentrations of DA and Tyr have been linked with several neurological disorders such as the debilitating ailment schizophrenia and Parkinson's disease [21]. Thus determination of DA in the presence of tyrosine (Tyr) seemed to be significant.

Most of the processes studied in the laboratory are the result of the interaction and influence of several chemical and instrumental factors. Traditionally the study of the interaction of these factors is done by modifying one factor at a time. This univariate analysis causes carrying out many experiments, but it does not allow statistical interpreting results and does not detect the interactions between variables, which can often lead to a mistaken interpreting results. Experimental design methodology makes a joint study of the relation between a number of factors and a specific response using a mathematical model. The designed experiments allow one, through the controlled modification of the experimental factors, to study the effect of a variation of experimental variables on the response [22].

The main aim of optimization is to find the experimental conditions which give the best response. Response surface methodology [23] is an area of the experimental design that deals with the optimization and modeling of a system. This methodology was introduced by Box and Wilson [24] at the beginning of the 1950s.

In this work, we introduce a new method for determination of DA in the presence of Tyr based on a sensitive and simple nanostructured sensor and multivariate optimization strategy. This method presents electrochemical studies along with central composite rotatable design (CCRD) and response surface methodology (RSM) for optimization of all effective factors on electrochemical responses. Moreover, we described preparation a GO modified carbon paste electrode (CPE/GO) as a sensitive sensor for the determination of DA in the presence of Tyr. Finally, to demonstrate the potential of the modified electrode for electrooxidation of DA in real samples, we have examined this method for the voltammetric determination of DA in human blood plasma samples.

2. Experimental

2.1. Chemicals

All solutions were prepared using deionized water. All reagents were from Merck with analytical grade and used without any other purification. Graphite powder with high purity and paraffin oil (DC 350, $\rho = 0.88$ g cm^{-3}) were used as a binding factor for the graphene paste. Britton–Robinson (B–R) buffer solution (0.2 M) was used as supporting electrolyte that containing 0.2 M of phosphoric acid, boric acid and acetic acid. The value of pH was adjusted using a saturated solution of sodium hydroxide. GO was obtained from Nanjing XFNano Materials Tech Co., Ltd. All experiments were done at the room temperature (25 ± 0.5 °C).

2.2. Instruments

Electrochemical determinations involving cyclic voltammetry (CV), differential pulse voltammetry (DPV), chronocoulometry and linear sweep voltammetry (LSV), were done using a Sama 500 potentiostate (Isfahan, Iran). Electrochemical impedance spectroscopy (EIS) measurements were done by an Autolab potentiostat-galvanostat PGSTAT 35 (Eco Chemie Utrecht, Netherlands), equipped with NOVA 1.6 software and a personal computer (Pentium IV) was used for data storage and processing. Scanning electron microscopy (SEM) micrographs were performed using a KYKY-EM3200. A digital pH meter (metrohm model 691) was used for pH adjusting, and an ultrasonic bath (Bandelin Sonorex, Germany) at a constant frequency of 35 kHz was used for dispersing of GO during the experiment. Our electrochemical cell contained three electrodes including CPE/GO, a platinum electrode (Metrohm, Switzerland) and a silver/silver chloride (Ag/AgCl/KCl (sat.)) (Metrohm, Switzerland) as working, counter and reference electrode, respectively. Carbon paste was pushed into a polyethylene tube with 2 mm diameter and 5 mm deep.

2.3. Preparation of the modified electrode

The bare electrode was prepared by mixing of 0.5 g graphite powder with 0.18 g paraffin oil. For preparation of the CPE/GO, 0.01 g graphene oxide (optimum amount) was added to 5.0 mL deionized water and sonicated for 30 min using ultrasonic bath to achieve a homogenous suspension and then added into 0.5 g graphite powder and allow this mixture to stay in the room temperature to evaporate the water. Then 0.18 g of paraffin oil was added to this mixture and mixed for 30 min till uniformly carbon paste was formed.

3. Results and discussion

3.1. Surface analysis by EIS and SEM studies

EIS technique is very sensitive for the investigations of electrode/ electrolyte interaction. EIS spectrums in Fig. 1 show two distinct parts: (1) a semi-circle part related to the charge transfer process, (2) a line defining a region of semi-infinite diffusion of species in the electrode, recognizable different of charge-transfer resistance (R_{ct}) value was observed upon the stepwise formation of the modified electrode. The R_{ct} value for the bare CPE was 5.87 kΩ while it was 1.53 kΩ for CPE/GO. It might be because of the presence of GO on the CPE surface, which played an important role in accelerating the transfer of the electrons. In addition to EIS measurements, SEM was used to investigate the surface morphological characters of the CPE and GO (Fig. 2A [25] and Fig. 2B, respectively). Fig. 2B shows the GO has a typical flake-like shape with slight wrinkles on the surfaces.

3.2. Electrochemical properties of the modified CPE/GO

The catalytic function of the CPE/GO at pH 6.0 is shown in Fig. 3 in the absence (curve a) and presence of 2.30 μM DA (curves b and c) at the surface of the bare CPE and the CPE/GO by DPV. As can be seen by scanning from 0.15 V toward a positive potential at a bare CPE, a relatively small anodic peak at 0.25 V was observed (Fig. 3, curve b), while at the surface of CPE/GO large enhancement in current response at + 0.217 V is observed (Fig. 3, curve c).

3.3. Experimental design and data analysis

Optimizing of effective chemical and instrumental variables for determination of DA in the presence of Tyr was carried out by CCRD. CCRD is a good method for simultaneous optimization of factors and investigating the interaction between variables with minimum number of experiments. These experiments were performed based on two group of factors containing concentration of GO and the pH value as chemical factors and the values of scan rate, step potential and modulation amplitude as instrumental factors. For optimizing of the first group, 11 experiments were designed and carried out for pH ranging between 2.0 to 6.0 and the GO amount between 6 to 14 mg. The second group contained 17 experiments that the range of variables was 0.02–0.18 V s^{-1} for scan rate, 0.001–0.005 V for step potential and 0.01–0.09 V for modulation amplitude. Also three replication experiments were designed in this optimization. Figs. 4 and 5 show the optimum response values can be obtained by the graphical analysis of the surface related to chemical
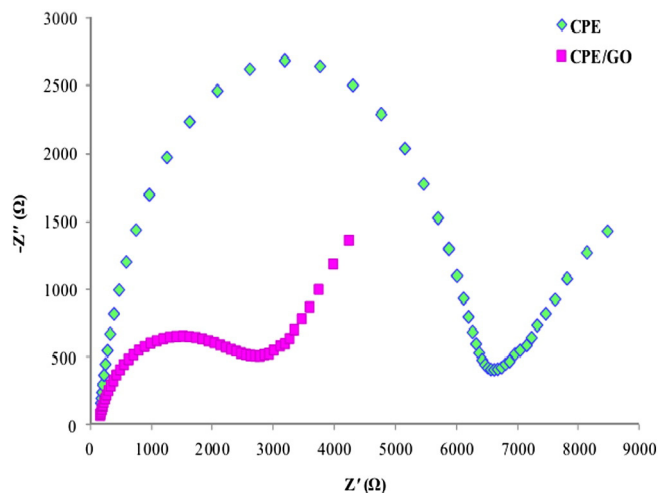
Fig. 1. (A) The Nyquist plot of the bare CPE and modified CPE/GO in 0.2 M B–R buffer solution containing 5.0 mM [Fe(CN)$_6$]$^{3-/4-}$.