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An electrochemical sensor based on graphene/poly(brilliant cresyl blue) nanocomposite for determination of epinephrine

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ABSTRACT

A graphene modified with poly(brilliant cresyl blue) (PBCB) glassy carbon electrode was fabricated by a simple method of drop-casting and two-step-electropolymerization for facilitating electrocatalytic detection of epinephrine (EP). Surface characterization of PBCB/graphene/GCE was conducted by electrochemical impedance spectroscopy (EIS), whose results showed that the electron transfer process at PBCB/graphene is faster than at bare GCE, graphene/GCE and PBCB/GCE. And the scanning electron microscopy (SEM) image confirmed the graphene dispersion incorporated with PBCB on the GCE. A noticeable enhancement in the microscopic area of the electrode resulted in an appreciable increase of the peak current of EP oxidation (~9.4 times). The catalytic oxidation peak currents obtained from cyclic voltammetry (CV) increased linearly with EP concentrations in the range of 1.0×10^{-6} to 1.0×10^{-3} mol/L with the limit of detection 2.4×10^{-7} mol/L ($S/N = 3$). Furthermore, the fabricated PBCB/graphene/GCE nanocomposite can determine EP in the presence of a large excess of ascorbic acid (AA) and uric acid (UA) by differential pulse voltammetry (DPV). The modified electrode can be used for the determination of EP in practical pharmaceutical formulation.

1. Introduction

Nowadays, due to its obvious redox effect and high electric conductivity, conducting polymers (CPs) have been of central importance in materials science since their discovery in 1976 [1]. As one of excellent CPs materials, organic dyes were used to fabricate CPs chemical modified electrode. Albery et al. [2] first explored that organic dye could easily form film at metal electrode surface in acid solution when they electropolymerized organic dyes to study photoelectric tube. After that, the modification of the electrode surface with organic dyes by electropolymerizing has been extensively studied [3–5], and poly(azine) [6–8] has been applied in sensing and biosensing.

Graphene, a two-dimensional monolayer of SP^2-hybridized carbon atomic crystal, is highlighted in the field of materials science and condensed-matter physics [9]. The unique nanostructure possesses the features of extreme mechanical strength, high-speed electron mobility at room temperature, as well as many other supreme properties [10,11]. These make it highly attractive for application in numerous technological fields, such as energy and environment [12], sensing and energy storage [13], especially at electrochemical biosensors [14–16]. Vashist et al. [17] provided a comprehensive overview of the field and electrochemical applications of graphene.

Although many researches have focused on graphene-based material [18] and the polymeric film [19–21], respectively, little attention is paid to the preparation of the graphene surface interfaced with PBCB. Some researches have been conducted continually to the development of carbon nanotube nanocomposite [22,23], and the PBCB film electropolymerized on the single-walled carbon nanotube/GCE can provide even higher porous 3D-structure and electron transfer rate [24]. A polymeric BCB and dihexadecy phosphate dispersed multiwalled carbon nanotube composite film modified GCE as epinephrine (EP) sensor was reported that the improvement of EP response was mainly arises from the enhanced adsorption of EP at modified film [25]. Therefore, it is shown that PBCB/graphene can be expected to be a promising nanocomposite material. Nevertheless, as previous reports show, adsorption of EP would cause the passivation of the electrode [26] and foul the electrode surface. So far, the fabrication of PBCB/graphene/GCE as electrochemical sensor or biosensor has not been reported.

With the continuously increasing requirement of a modified electrode sensing ability (i.e., electrocatalytic activity, conductivity, and surface properties), the research of using composite film based on CPs as modified electrode has generated considerable interest [1,27]. And combination of CPs with various materials such as inorganic, metal, and carbon nanomaterials was successfully achieved [28–30]. What's more, preparation method of composite is mainly including chemical (impregnation, polymerization) and electrochemical methods (electrodeposition,

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Table 1
Comparison of different modified electrodes for EP determination.

Electrode	Detection method	Linear range (μM)	Detection limit (μM)	Reference
f-MWCNTs/BR9/GCE	DPV	19.6–82.5	9	[31]
MCPE-MWCNTs$_{ox}$-BTB	Amperometry	0.8–100	0.8	[32]
DH-CN/CPE	DPV	5–600	1	[33]
CNTSSEs	DPV	2–100	2	[34]
o-DA/Au*	CV	2–800	0.3	[35]
Poly(taurine)/GCE	DPV	2–600	3	[36]
Poly(isonicotinic acid)/CPE	CV	5–100	1	[37]
PBCB/graphene/GCE	CV	1–1000	0.24	This work

* Over-oxidized dopamine modified gold electrode.

doping), and the combination of these methods (electropolymerization, secondary doping by surface modified structures). Due to the synthetic rout and surface properties of resulted composite films, there exist different advantages to different applications [1].

In this paper, we fabricated a nanocomposite electrode based on graphene and PBCB by drop-casting and two-step-electropolymerization method. The attachment of PBCB and graphene on GCE electrode was confirmed by scanning electron microscopy and electrochemical impedance spectroscopy. Under the experimental conditions, it was found that PBCB/graphene/GCE exhibited high electrocatalytic properties toward the oxidation of EP. Good linearity was observed between the cyclic voltammetry peak current and the concentration of EP in the range from 1 μM to1000 μM. Compared to the existing methods for determination of EP (Table 1), the proposed method exhibited wider linear range, fair sensitive, high selectivity and could obtain satisfactory recovery at the study of biopharmaceutical sample analysis application.

2. Experimental

2.1. Materials

Graphene dispersion (0.5 mg mL^{-1}) in water, supplied by Nanjing XFNANO Materials Tech Co., Ltd. (Nanjing, China), was synthesized from graphene oxide using high-temperature thermal treatment. EP was purchased from Sigma-Aldrich Trade Co., Ltd. (Shanghai, China). Brilliant cresyl blue, uric acid, and ascorbic acid were provided by Sinopharm Chemical Reagent Beijing Co., Ltd. (Beijing, China). EP pharmaceutical formulation was obtained from Tianjin Jinyao Amino Acid Co., Ltd. (Tianjin, China) and was used as supplied. 0.1 M phosphate buffer solution (PBS) was prepared under different conditions by mixing the stock solution of KH_2PO_4 and K_2HPO_4. The EP standard solution was made by EP in pH 7.0 PBS. All aqueous solutions were prepared with double-distilled water (DDW) from BYT-120A quartz sub-boiling distillation apparatus (Jiangsu, China).

2.2. Measurement and apparatus

The morphology of the modified electrodes was observed using NNS450 scanning electron microscopy (FEI Czech Co., Ltd., Czech). The cyclic voltammetry, differential pulse voltammetry, and electrochemical impedance spectroscopy experiments were carried out using a CHI660D electrochemical workstation (Shanghai ChenHua Instrument Co., Ltd., China). A conventional three electrode system has GCE (Φ 3 mm), graphene/GCE, PBCB/GCE, and PBCB/graphene/GCE as working electrode, a Pt foil electrode as counter electrode and a saturated calomel electrode (SCE) as reference electrode. KQ3200B ultrasonic cleaner (Kunshan Ultrasonic Instrument Co., Ltd. China) with operating frequency of 40 kHz and ultrasonic power output of 150 W has been used for ultrasonic at room temperature.

2.3. Electrode preparation

Prior to electrode modification, the GCE was carefully polished to a mirror with silicon carbide sandpaper and followed by a series of alumina slurries with successively smaller particles size, typically finishing with 0.05 μm [38], rinsed conscientiously with DDW between each polishing step, next ultrasonicated with C_2H_5OH (1:1), HNO_3 (1:1), and DDW for 5–8 min to remove any adsorbed alumina particles or dirt from the electrode surface.

2.3.1. PBCB/GCE

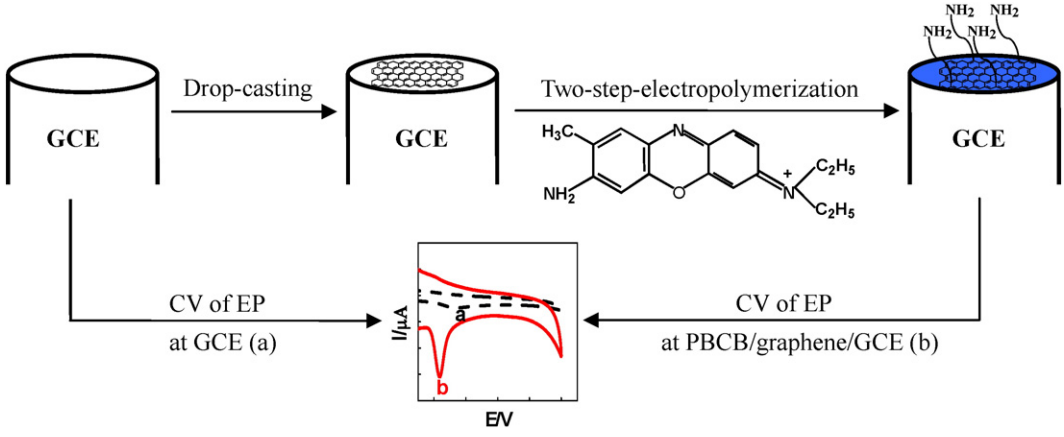
After cleaning, the three electrodes system was bathed with DDW thoroughly, and then immersed into the BCB solution, and treated by cyclic voltammetry sweeping 12 laps in the potential range of 0.8–1.8 V. After initiation, the electropolymerization of BCB by performing continuous potential cycling (15 laps) from −0.8 to 0.8 V at a scan rate of 50 mV s^{-1}, after washed with DDW, the PBCB/GCE modified electrode was put in PBS (pH 7.0) solution for further study [21].

2.3.2. Graphene/GCE

Graphene/GCE was fabricated on the GCE surface. Prior to using, the dispersed graphene was ultrasonicated for 30 min to make the graphene disperse evenly. Then 10 μL of the graphene dispersion was cast on the pretreated GCE surface with a micro-injector, followed by drying under the infrared lamp (20 min) and flushed with DDW.

2.3.3. PBCB/graphene/GCE

PBCB/graphene/GCE was also fabricated for comparison using similar procedure of PBCB/GCE, except for using graphene/GCE electrode instead of GCE. The schematic illustration of the preparation steps is



Scheme 1. Schematic illustration the preparation steps of PBCB/graphene/GCE.