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A sensitive voltammetric sensor for taxifolin based on graphene nanosheets with certain orientation modified glassy carbon electrode

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ABSTRACT

The electrodeposition of reduced graphene oxide (ERGO) film with preferred vertical orientation was fabricated on a glassy carbon electrode by using pulse potential method in a graphene oxide colloidal solution. Using square wave adsorptive stripping voltammetry (SWASV), the ERGO film was applied for the first time, in developing a high-sensitive electrochemical sensor for detection of taxifolin. Compared with bare glassy carbon electrode (GCE), the resulting electrodes (ERGO/GCE) exhibited excellent response toward the redox of taxifolin by significantly enhancing the redox peak currents and decreasing the peak-to-peak separation. Under the selected conditions, the peak currents were linear relationship with taxifolin concentration in the range of 1.0×10^{-8}–1.0×10^{-6} mol L^{-1}, with detection limit of 2.0×10^{-9} mol L^{-1}. Besides, the ERGO/GCE also exhibited an excellent selectivity, stability, reproducibility and repeatability.

1. Introduction

Flavonoids have aroused increasing awareness because of their potential health beneficial effect [1]. Taxifolin, 3,3′,4′,5,7-pentahydroxiflavanon, is the main constituent in extract from the rind of siberian larch *Larix sibirica* leder, and dahurian larch *Larix gmelini* rupr. (Rupr.), syn. *Larix dahurica* turoz. (Pinaceae). It has been widely used in the treatment of cerebral infarction and sequelae, cerebral thrombus, coronary heart disease and angina pectoris [2,3]. Accordingly, accurate analytical method for taxifolin is interesting and necessary. Some detection techniques have been developed, such as high performance liquid chromatography (HPLC) [4–6], UV–vis spectrophotometry [7], thin layer chromatography (TLC) [8] and capillary zone electrophoresis (CZE) [9]. However, some of these methods are time-consuming, expensive or involve a tedious extraction process before detection, which hampers their further application. In contrast, electrochemical method can provide sensitive, fast, facile, and low-cost detection. Recently, some effort has been devoted to electrochemical sensor of taxifolin [10,11], but very limited.

Graphene, a perfect two-dimensional carbon material found in 2004 [12,13], is an ideal material for electrochemistry [14] because of unusual electronic conductivity, high surface area, high mechanical, thermal and chemical stabilities [15–17]. Hence grapheme-based modified electrodes prepared by various methods have been explored as electrochemical sensors platforms [18–22]. Among these, direct electrodeposition of reduced graphene oxide (ERGO) on glassy carbon electrode (GCE) has attracted considerable interest because of its unique several advantages, such as simple, rapid, green and efficient [23–26]. More recently, it has been widely used in both analytical [27–31] and industrial electrochemistry [32,33]. The electrodeposition technique may be cyclic voltammetry (CV) [27–30] or potentiostatic method (PM) [31–33]. As we know, the pulse potentiostatic method (PPM) [34], having advantages, including simplicity, time savings and high purity of the deposits, has little been applied in preparing the ERGO.

In this work, the ERGO film with preferred vertical orientation was fabricated on a glassy carbon electrode by using pulse potential method in a graphene oxide colloidal solution. Using square wave adsorptive stripping voltammetry (SWASV), the ERGO film was applied for the first time, in developing a high-sensitive electrochemical sensor for detection of taxifolin. Compared with bare glassy carbon electrode (GCE), the resulting electrodes (ERGO/GCE) exhibited excellent response toward the redox of taxifolin by significantly enhancing the redox peak currents and decreasing the peak-to-peak separation. Under the selected conditions, the peak currents were linear relationship with taxifolin concentration in the range of 1.0×10^{-8}–1.0×10^{-6} mol L^{-1}, with detection limit of 2.0×10^{-9} mol L^{-1}. Besides, the ERGO/GCE also exhibited an

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excellent selectivity, stability, reproducibility and repeatability. Based on these results, we believe it is a simple, rapid, green and promising method for determination of taxifolin. And, this work firstly raises an approach to fabricate graphene nanosheets with a certain orientation on the electrode surface.

2. Experimental

2.1. Apparatus and reagents

All the electrochemical measurements were carried out using a CHI 650A electrochemical analyzer (CHI Instrumental, Shanghai, China) and a RST5000 electrochemical workstation (Zhengzhou Shiruisi Instrument Co., Ltd., Zhengzhou, China). A conventional three-electrode system was used, including a GCE (d = 3 mm) or a modified GCE as the working electrode, a platinum (Pt) wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode (KCl saturation). Atomic force microscopy (AFM) images were obtained with a BenYuan CSPM-5500 atomic force microscopy (Guangzhou BenYuan Nanometer Instrument Co., Ltd., Guangzhou, China). Scanning electron microscopy (SEM) images were obtained with a Quonxe-2000 field emission scanning electron microscope (FEI Company, Holland). All the pH measurements were made with a PHS-3C precision pH meter (Leici Devices Factory of Shanghai, China), which was calibrated with a standard buffer solution at 25 ± 0.1 °C every day.

Taxifolin was acquired from Shanghai Jinsui Biological Technology Co., Ltd. (Shanghai, China). Stock solution (1.0×10^{-3} mol L^{-1}) of taxifolin was prepared with absolute ethyl alcohol and stored at 4 °C darkly. Graphite was purchased from Nanjing Xfnano Materials Tech Co., Ltd. (Nanjing, China). All other reagents were of analytical grade and were used as received. Double distilled water was used for all preparations.

2.2. Preparation of the modified electrode

Firstly, graphene oxide (GO) was synthesized from graphite by the modified Hummers method [35]. The exfoliated GO was obtained by ultrasound of the GO dispersion, and centrifugation at 4000 rpm for 10 min. The resulting GO deposited on the mica were characterized by AFM. The results revealed that the GO sheets were almost single-layer, see Fig. S1. And the average thickness of single-layer GO sheets was approximately 1 nm.

Prior to modification, the bare GCE was polished successively with 0.3 and 0.05 μm Al_2O_3 power and rinsed thoroughly with doubly distilled water between each polishing step. After that, the GCE was sonicated in ethanol and doubly distilled water each for 2 min, and dried under N_2 blowing. After that, the cleaned GCE was immersed in phosphate buffer solutions (PBS, pH 5.0) containing 1.2 mg mL^{-1} GO, and electrodeposited the GO by PPM under constant stirring. The optimal parameters of electrodeposition were listed as follows: upper limit potential E_a, 0.1 V; lower limit potential E_c, −1.5 V; anodic pulse duration t_a, 0.6 s; cathodic pulse duration t_c, 0.3 s; experimental time t_{exp}, 60 s. The overall reduction time (t_{re}) can be calculated from the following equation: $t_{re} = t_{exp} \times t_c/(t_c + t_a)$. The optimal parameters of electrodeposition (t_a, t_c and t_{re}) were described in Fig. S1. The obtained electrode was denoted as ERGO/GCE.

2.3. Experimental procedures for electrochemical analysis

A certain volume of stock solution of taxifolin and 10 mL 0.1 mol L^{-1} H_2SO_4 solutions (pH 0.95) were added into an electrochemical cell, and then the electrode was immersed into the cell. The CV, chronocoulometry (CC) or square wave voltammetry (SWV) were performed to investigate the electrochemical behavior of taxifolin at ERGO/GCE.

2.4. Real sample assay procedures

The real sample was processed according to the literature [11]. The sample powder was obtained by grinding a certain amount of dried *princes-feather fruit*. About 2 g of the powder was weighed and extracted with 50 mL 80% ethanol for 2 h in an ultrasonic bath. Finally, the extractum was extracted with ethyl acetate. Sample solution was stored in the dark. Just before each measurement, the sample solution was diluted quantitatively using the supporting electrolyte.

3. Results and discussion

3.1. Pulse potential electrodeposition of ERGO film on GCE

As applying a positive potential, GO sheets could be adsorbed on the electrode, because GO colloids exhibit negative charges in weak acid [36]. According to the literature [18], the as-adsorbed GO sheets can be electrochemically reduced at E = −1.1 V (versus SCE). Here, we used the PPM to achieve the electrodeposition of ERGO films, in which 0.1 V (versus SCE) was used to adsorb GO sheets on GCE, followed by applying −1.5 V to electrochemically reduce the as-adsorbed GO sheets to ERGO sheets.

To illustrate the pulse procedure used for the ERGO film, Fig. 1 shows the evolution in time of the E and i for the process of PPM. After the potential E_c is applied, the i increases sharply and then decreases tending to a steady value as in potentiostatic mode. As potential E_a is imposed, the i drops sharply, reaching values close to zero. This is a so-called "relaxation period" that allows the diffusion of GO sheets to areas where they have been quickly consumed while applying E_a. When a new pulse start, the distribution of GO sheets on the electrode surface is supposed to be more homogenous [37]. Therefore, the PPM can gain more uniform thin films.

3.2. Morphological characterization of the ERGO/GCE

To obtain further information as called ERGO films prepared by PPM and illustrate the difference of electrochemical properties, morphologies of ERGO/GCE were characterized by SEM. As showed in Fig. 2A and B, ERGO film modified GCE showed a cluster of close

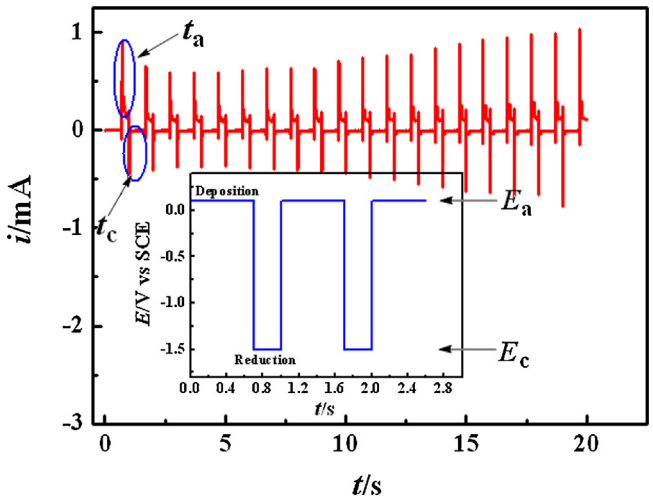

Fig. 1. Characteristic i–t response registered for pulsed electrodeposition; the inset outlines the E–t profile imposed for the method, during the electrodeposition of ERGO films.