



A simple, rapid and green method based on pulsed potentiostatic electrodeposition of reduced graphene oxide on glass carbon electrode for sensitive voltammetric detection of sophoridine



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ABSTRACT

A simple, rapid and green method was described for sensitive voltammetric detection of sophoridine based on graphene nanosheets directly deposited onto a glassy carbon electrode (GCE) by pulsed potentiostatic reduction of a graphene oxide (GO) colloidal solution. The resulting electrodes (PP-ERGO/GCE) were characterized by electrochemical methods and scanning electron microscopy. Moreover, the electrochemical behaviors of sophoridine at the modified electrode were investigated in detail by cyclic voltammetry (CV), chronoamperometry (CA) and chronocoulometry (CC). Compared with the bare GCE and the preparation of reduced graphene oxide (RGO) films by potentiostatic method (PM) modified GCE, PP-ERGO/GCE could intensively enhance the oxidation peak currents and decrease the overpotential of sophoridine. Under the selected conditions, the modified electrode showed a linear voltammetric response to sophoridine within the concentration range of $8.0 \times 10^{-7} \sim 1.0 \times 10^{-4} \text{ mol L}^{-1}$, with the detection limit of $2.0 \times 10^{-7} \text{ mol L}^{-1}$. And, the method was also applied to detect sophoridine in spiked human urine with wonderful satisfactory.

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1. Introduction

Sophoridine, a quinolizidine alkaloid, is a main active ingredient of kinds of Sophora plants in traditional Chinese herbal drug [1]. The studies of pharmacological effect have shown that sophoridine has wide pharmacological effects including anti-arrhythmic [2], antiviral effects [3] and immunological enhancement [4]. And, it also exhibits the potential therapeutic efficacy on malignant tumors in the digestive tract such as colorectal carcinoma, gastric cancer, and esophageal cancer [5,6]. Accordingly, accurate analytical method for sophoridine is necessary and some determination techniques have been developed, such as high performance liquid chromatography (HPLC) [7,8], gas chromatography–mass spectrometer (GC–MS) [9], nonaqueous capillary electrophoresis (CE) [10] and electrogenerated chemiluminescence (ECL) [11]. But, some of them are time-consuming, expensive or involve a tedious extraction

process before detection. In contrast, electrochemical method is simple, rapid, sensitive and inexpensive. Furthermore, the redox properties of drugs can provide insight into their metabolic fate, their in vivo redox processes, and their pharmacological activity [12]. Recently, the report regarding the voltammetric and amperometric determination of sophoridine is raised [13,14], but very limited.

In the past decades, several forms of carbon materials (e.g. ordered mesoporous carbon [15], carbon nanofiber [16], carbon nanotube [17]) have been studied to use for developing electrochemical sensors. Graphene, a perfect two-dimensional carbon material found in 2004 [18,19], is an ideal material for electrochemistry [20] because of its very large 2D electrical conductivity, large surface area and low cost. At present, graphene is usually prepared in large quantities by a chemical method [21] or an electrochemical reduction [22] of graphene oxide (GO). A series of investigations showed that chemically reduced graphene oxide (CRGO) always needs excessive reducing agents, and additionally some oxygenated species cannot be completely reduced by chemical treatment, which may degrade the electrochemical performance. As compared with the chemical method, electrochemical reduction provides several advantages, including being simple, rapid, green and efficient [23–26]. More importantly, the

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highly negative potential used in the electrochemical reduction of graphene oxide (ERGO) efficiently reduces the oxygen-containing functional groups [27]. Recently, the synthesis and applications of ERGO as electrochemical sensors [28–30], biosensors [31], and supercapacitors [32] have attracted considerable interest because of its unique properties. The ERGO has usually been obtained by two steps: (1) drop-casting of graphene oxide solution on basal electrodes; (2) then, electrochemical reduction of above modified electrodes. And, a series of electrochemical methods, such as cyclic voltammetry (CV) [28,30–32] and potentiostatic method [29], has been employed. However, the pulse potentiostatic method (PPM) [33], having advantages, including simplicity, time savings and high purity of the deposits, has little been adopted in the ERGO field.

In this work, an ERGO film was prepared onto the glassy carbon electrode (GCE) directly from GO dispersions by PPM, and the resulting electrode was used to determine sophoridine. The electrochemical behaviors of sophoridine at the modified electrode were investigated in detail by cyclic voltammetry (CV), chronoamperometry (CA) and chronocoulometry (CC). Compared with the bare GCE and the preparation of reduced graphene oxide (RGO) films by PM modified GCE, the modified electrode could intensively enhance the oxidation peak currents and decrease the overpotential of sophoridine. In addition, oxidation peak currents were found to be sensitively responding to the sophoridine, and a linear voltammetric response to sophoridine within the concentration range of $8.0 \times 10^{-7} \sim 1.0 \times 10^{-4} \text{ mol L}^{-1}$ was obtained under the selected conditions. Based on these results, we believe it is a simple, rapid, green and promising method for determination of sophoridine. And, this work would enlarge the application range of graphene in electroanalytical chemistry.

2. Experimental

2.1. Apparatus and Reagents

Model CHI 650A electrochemical system (CHI Instrumental, Shanghai, China) and RST5000 electrochemical workstation (Zhengzhou Shiruisi Instrument Co., Ltd., Zhengzhou, China) were employed for electrochemical techniques. 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). A standard three-electrode electrochemical cell was used with glassy carbon electrode ($d=3 \text{ mm}$) or modified GCE as working electrode, platinum (Pt) wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode (the internal solution was saturated KCl solution). All the pH measurements were made with a PHS-3C precision pH meter (Leici Devices Factory of Shanghai, China), which was calibrated with standard buffer solution at $25 \pm 0.1 \text{ }^\circ\text{C}$ every day.

All reagents were of analytical grade and were used as received. Double distilled water was used for all preparations. Sophoridine was purchased from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Stock solution ($2.0 \times 10^{-3} \text{ mol L}^{-1}$) of sophoridine was prepared with doubly distilled water and stored at 4°C in the dark.

2.2. Preparation of the modified electrode

Firstly, GO was synthesized from graphite by the modified Hummers method [34]. The exfoliated GO was obtained by ultrasound of the GO dispersion, and centrifugating at 3000 rpm for 15 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 $\mu\text{m Al}_2\text{O}_3$ 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 bare GCE was immersed in pH 6.0 phosphate buffer solutions (PBS) containing 0.8 mg mL^{-1} GO, and prepared for electrodeposition 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 , -1.2 V; anodic pulse duration t_a , 0.6 s; cathodic pulse duration t_c , 0.3 s; experimental time t_{exp} , 180 s. The overall reduction time (t_{re}) can be calculated from the following equation: $t_{\text{re}} = t_{\text{exp}} \times t_c / (t_c + t_a)$. The optimal parameters of electrodeposition (t_a , t_c and t_{re}) were described in the S1. The obtained electrode was denoted as PP-ERGO/GCE. For comparison, the ERGO/GCE was also fabricated with the similar procedure by the potentiostatic method (PM).

2.3. Analysis of spiked urine samples

The urine samples were drawn from healthy individuals immediately before the experiments. Spiked urine samples were obtained by treating 1.0 mL aliquots of urine with appropriate amount of sophoridine standard solutions. A 20 μL aliquot of spiked urine was diluted with 10 mL 0.2 mol L^{-1} pH = 7.5 phosphate buffer solutions (PBS), without any pre-treatment, and transferred into the voltammetric cell. The SWV was recorded to achieve the quantitative analysis (with a scan increment of 4 mV, pulse amplitude of 30 mV, and pulse frequency of 25 Hz).

3. Results and Discussion

3.1. Pulsed potentiostatic electrodeposition of RGO film on GCE

As applying a positive potential, GO sheets could be deposited on the electrode; because GO colloids exhibit negative charges in weak acid [35]. According to the literature [30], the as-deposited GO sheets can be electrochemically reduced at $E = -1.1 \text{ V vs SCE}$. Here, we use the PPM to achieve the electrodeposition of RGO films, in which 0.1 V vs SCE is used to deposit GO sheets on GCE, followed by applying -1.2 V vs SCE to electrochemically reduce the as-deposited GO sheets to RGO sheets.

To illustrate the pulse procedure used for the ERGO film, the evolution in time of the E and the i for the process of PM and PPM was investigated, see Fig. 1. When the E is constant and uninterrupted (see the inset of Fig. 1A), the i decays quickly as soon as the potential is imposed, probably due to the change in the precursor's concentration when the GO sheets close the electrode surface start to react. Later, the i attains a limiting value (see Fig. 1A), typical of a deposition process controlled by mass transport. The i - t response is altered when the E is pulsed (see the inset of Fig. 1B). After the potential E_c is applied, the i increases sharply and then decreases tending to a steady value as in potentiostatic mode (see Fig. 1B). 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 [36]. Therefore, the PPM can gain more uniform the thin films.

3.2. Morphological characterization of the PP-ERGO/GCE

To obtain further information on the successful preparation of RGO films by PPM and illustrate the difference of electrochemical

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