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A rapid, green and controllable method to fabricate the electrodeposition of a film of reduced graphene oxide as sensing materials for the determination of matrine

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ABSTRACT

The electrodeposition of a film of reduced graphene oxide (ERGO) on a glassy carbon electrode (GCE) was achieved using pulse potential method (PPM) in the graphene oxide colloidal solution. For the first time, the electrodeposition of a film was applied to develop a high-sensitive electrochemical sensor for determination of matrine using linear sweep adsorptive stripping voltammetry (LSASV). Compared with bare GCE and ERGO film prepared by potentiostatic method (PM) modified electrode, the resulting electrodes (PP-ERGO/GCE) exhibited excellent response toward the oxidation of matrine by significantly enhancing the oxidation peak currents and decreasing the overpotential of matrine. Under the selected conditions, there exist the linear relation between the oxidation peak currents and matrine concentration in the range of 2.0×10^{-6}–1.2×10^{-4} mol L^{-1}, with detection limit of 5.0×10^{-7} mol L^{-1}. At the same time, the method can be successfully applied to the quantitative determination of matrine in injection and its result is satisfactory.

1. Introduction

Matrine, a typical quinolizidine alkaloid, is a main active ingredient of kinds of Sophora plants in traditional Chinese herbal drug. It has been extensively used in China for the treatment of viral hepatitis, cancer, cardiac and skin diseases [1–4]. Accordingly, accurate analytical method for matrine is necessary and some determination techniques have been developed, such as high performance liquid chromatography (HPLC) [5–8], liquid chromatography – mass spectrometer (LC-MS) [9–11], capillary electrophoresis (CE) [12] and chemiluminescence (CL) [13]. However, some of them are time-consuming and 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 redox processes in vivo, and their pharmacological activity. Recently, some effort has been made to design the electrochemical sensor of matrine [14,15], but very limited.

Graphene, a perfect two-dimensional carbon material found in 2004 [16,17], is an ideal electrochemical material because of its very large 2D electrical conductivity [18], large surface area and low cost. Hence graphene-based modified electrodes, which can be prepared by various methods, have been explored as electrochemical sensors platforms [19–23]. Among these methods, the way of direct electrodeposition of reduced graphene oxide (ERGO) on glassy carbon electrode (GCE) has attracted considerable interest because it is simple, rapid, green and efficient [24–27]. Recently, it has been widely used in analytical [28–32] and industrial electrochemistry [33,34]. The electrochemical methods, such as cyclic voltammetry (CV) [28–31] and potentiostatic method (PM) [32–34], have been used. As we know, the pulse potential method (PPM) [35] is rarely applied in preparing the ERGO.

In this work, the ERGO film was directly achieved on GCE using PPM in the graphene oxide colloidal solution. The ERGO film were characterized by electrochemical methods and scanning electron microscopy. For the first time, the electrodeposition of a film was applied to develop a high-sensitive electrochemical sensor for determination of matrine using linear sweep adsorptive stripping voltammetry (LSASV). Electrochemical behaviors of matrine at the modified electrode were investigated by cyclic voltammetry (CV) and chronocoulometry (CC). At the same time, the method can be successfully applied to the quantitative determination of matrine in injection and its result is satisfactory.

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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. Scanning electron microscopy (SEM) images were obtained with a Quanta 250 scanning electron microscope (FEI Company, Czech). Atomic Force Microscopy (AFM) images were obtained with a BenYuan CSPM-5500 atomic force microscopy (Guangzhou BenYuan nanometer Instrument Co., Ltd., Guangzhou, China). A standard three-electrode electrochemical cell was used with GCE (d = 3 mm) or modified GCE as a working electrode, platinum (Pt) wire as an auxiliary electrode and a saturated calomel electrode (SCE) as a 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 ± 0.1 °C every day.

Matrine was purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). Stock solution (5.0×10^{-2} mol L^{-1}) of matrine was prepared with doubly distilled water and stored at 4 °C in the dark. Matrine injection was purchased from Jilin Yuhuang Pharma. Co., Ltd (Jilin, China). Graphite was purchased from Nanjing Xfnano Materials Tech Co., Ltd (Nanjing, China). All 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

Prior to modification, the bare GCE was polished successively with 0.3 and 0.05 μm Al_2O_3 powder 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 0.85 mg mL^{-1} GO, and electrodeposited the GO by PPM under constant stirring. Graphene oxide (GO) was synthesized from graphite by the modified Hummers method [36]. 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}, 150 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 obtained electrode was denoted as PP-ERGO/GCE. For comparison, the ERGO/GCE was also fabricated with the similar procedure by the PM. The reduction time of two methods is exactly the same.

3. Results and discussion

3.1. Morphologic characterization of the GO

The structure and morphology of the resulting GO deposited on the mica were characterized by AFM. The results showed that the GO sheets were almost single-layer, seen in Fig. 1. And the average thickness of single-layer GO sheets was about 1 nm.

3.2. Pulsed potentiostatic electrodeposition of RGO film on GCE

As applying a positive potential, GO sheets could be deposited on the electrode surface; because GO colloids exhibit negative charges in weak acid [37]. According to the literature [38], the as-deposited GO sheets can be electrochemically reduced at E = −1.1 V *vs.* SCE. Here we use the PPM to achieve the ERGO 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. The voltage profiles for the electrodeposition modes are schematically shown in the inset of Fig. 2.

To illustrate the pulse procedure used for the ERGO film, Fig. 2 shows the evolution in time of the E and i for the process of PPM. After the potential E_a is applied, the i increases sharply, reaching values close to zero. GO sheets were deposited on the electrode surface during the period. As potential E_c is imposed, the GO sheets close to the electrode surface start to react. The i drops sharply and then decreases tending to reach a steady value in potentiostatic mode. And then, when a new pulse starts, GO sheets could be diffused to areas where they have been quickly consumed while applying E_c. The distribution of GO sheets on the electrode surface is supposed to be more efficient and homogenous [39]. Therefore, the PPM can gain more uniform thin films.

3.3. Morphological characterization of ERGO film

To get more information on the successful preparation of ERGO films by PPM and illustrate the difference of electrochemical properties, morphologies of the ERGO/GCE (Fig. 3A) and PP-ERGO/GCE (Fig. 3B) were characterized using SEM. As showed in Fig. 3A, preparation of ERGO films by PM showed a loose, disorder and stacked surface. In contrast, preparation of ERGO films by PPM display closely associated with each other to form thin and crumpled sheets, and the edges of individual sheets were distinguishable with kinked and wrinkled areas, which is highly beneficial in maintaining a high surface area on the electrode and helpful in constructing an interface for the electrochemical sensors. Moreover, films barely show aggregation, indicating that the assembly of ERGO films by PPM on a solid substrate is a good way to achieve well-dispersed ERGO films and can prevent the aggregation.

3.4. Electrochemical characterization of PP-ERGO/GCE

The redox probe $[Fe(CN)_6]^{3-/4-}$ is sensitive to surface chemistry of carbon-based electrodes [40], and therefore was used to directly investigate the charge transfer property of the PP-ERGO/GCE. Fig. 4A shows the cyclic voltammograms (CVs) of bare GCE (curve a), ERGO/GCE (curve b) and PP-ERGO/GCE (curve c) in 1.0×10^{-3} mol L^{-1} $K_3[Fe(CN)_6]$ + 0.1 mol L^{-1} KCl solution. It proved the enhanced current response of the ERGO films toward $[Fe(CN)_6]^{3-/4-}$, indicating increased electrochemical active sites by ERGO surface modification. Moreover, the largest peak currents and the smallest ΔE_p of redox probe $[Fe(CN)_6]^{3-/4-}$ are observed on PP-ERGO/GCE, suggesting that the properties of the ERGO films prepared by PPM were superior to that of PM in increasing the active surface area of electrode and accelerating the electron transfer rate. Besides, Fig. 4B shows the influence of thickness of ERGO films on the peaks current of the redox probe. It is clear that the redox peaks current is directly proportional to the t_{re} (see the inset of Fig. 4B), indicating that PPM is an easily controllable and distinct advantage over CRGO methods.

At the same time, the average electroactive area of different electrode can obtain according to Randles–Sevcik formula [41]: $i_{pa} = 2.69 \times 10^5 n^{3/2} A D_o^{1/2} c_o v^{1/2}$, where i_{pa} refers to the anodic peak current (A); n is the electron transfer number; A is the surface area of the electrode (cm^2); D_o is the diffusion coefficient (cm^2 s^{-1}); c_o is the concentration of $K_3[Fe(CN)_6]$ (mol L^{-1}) and v is the scan rate (V s^{-1}). By exploring the redox peak current with scan rate, the average electroactive area of bare GCE, ERGO/GCE and PP-ERGO/GCE was calculated as 0.049, 0.080 and 0.139 cm^2, respectively. The results further indicated the preparation of the ERGO films