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A novel voltammetric sensor based on poly(L-Citrulline)/SWCNTs composite film modified electrode for sensitive determination of picroside II

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ABSTRACT

A novel voltammetric sensor was constructed by simple dripping single-walled carbon nanotubes (SWCNTs) on to the glass carbon electrode (GCE) firstly and electro-polymerizing L-Citrulline film subsequently. The resulting poly(L-Citrulline)/SWCNTs/GCE showed a significant voltammetric response to picroside II due to the synergistic effect of SWCNTs and poly(L-Citrulline) film. The first electroanalytical method of picroside II was proposed with detection linear range from 8.0×10^{-8} to 5.0×10^{-6} mol L^{-1} and a detection limit of 3×10^{-8} mol L^{-1}.The high sensitivity, selectivity and long-term stability made the sensor suitable for the determination of picroside II. Moreover, based on the systematically investigation and some kinetics parameters calculated in the experimentation, the reaction mechanism of picroside II at the poly(L-Citrulline)/SWCNTs modified GCE was obtained reliably. Lastly, the proposed sensor was used for the determination of picroside II in real sample with satisfactory results. This work promoted the potential applications of amino acid materials and SWCNTs in electro-chemical sensors.

1. Introduction

Picroside II (Scheme 1) is one of the most effective components extracted from picrorhizae (family: Scrophulariaceae [1]) which used as traditional medical systems in India, China, Tibet, Nepal and Sri Lanka for various immune-related diseases [2]. Previous studies have shown that picroside II has a wide range of pharmacological effects, including antioxidant [2], anti-inflammation [3], neuroprotective [4]. It can also improve accelerated atherosclerosis [1], inhibit hepatocyte apoptosis [5], protect myocardial ischemia reperfusion injury [6], protect cardiomyocyte [7], and decrease oxidative stress [8]. Analytical methods for picroside II have been developed using liquid chromatography–electrospray ionization ion-trap mass spectrometry (LC–ESI-IT-MS) [9], high-performance liquid chromatography–electrospray ionization-mass spectrometry (LC–ESI-MS) [10], LC–MS [11], LC–PDA [12], liquid chromatographic separation with tandem mass spectrometric detection (LC–Tandem-MS) [13], HPLC [14,15], high-performance liquid chromatography with evaporative light scattering detection (HPLC–ELSD) [16], and high-performance liquid chromatography–electrospray ionization tandem mass spectrometry (LC–ESI-MS/MS) [17]. However, there has no report about the determination of picroside II by electrochemical techniques. As we know, electrochemical method has many advantages comparing with above mentioned techniques, such as high sensitivity, simple equipment, cheapness and easy to realize automation. The mechanism of the electrochemical oxidation of pricroside II was investigated, providing important information about its pharmacological actions. Therefore, it is valuable to develop an electroanalytical method for picroside II.

Amino acids are the most fundamental material of the organism. They have many unique properties for containing amino and carboxyl functional groups. Amino acid modified electrodes have caused the extensive research interest for their strong electrochemical response, good stability and simple preparation [18–22]. L-Citrulline (Scheme 2), a kind of α-amino acid isolated from watermelon juice, is beneficial to the cardiovascular system [23,24]. At present, the reports of L-citrulline are mainly focused on its pharmacological aspects [25,26]. Nevertheless, literature about L-citrulline modified electrodes has not been reported so far.

Because of the larger specific surface area and good electrical conductivity, carbon nanotubes (CNTs) have caused great interest in the field of electrochemistry since their first report in 1991 [27]. CNTs modified electrodes have been applied to the analysis of various materials as voltammetric sensors [28–31]. Nowadays, composite materials combining CNTs and poly amino acid have increased attentions due to the synergistic contribution of two or more functional components and many potential applications [32–34].

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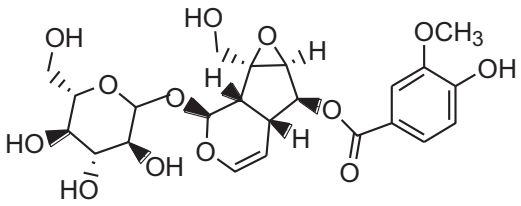
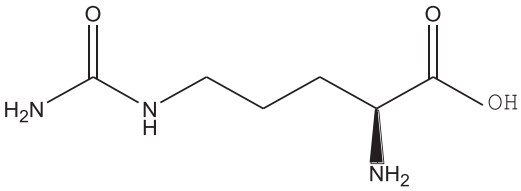


Scheme 1. The chemical structure of picroside II.



Scheme 2. The structure of L-Citrulline.

In the current work, a novel voltammetric sensor, composite materials combining SWCNTs and poly(L-Citrulline) modified glassy carbon electrode (poly(L-Citrulline)/SWCNTs/GCE), was fabricated and used for investigating the electrochemical characters of picroside II. At the proposed sensor, picroside II had sensitive electrochemical response. The redox mechanism and dynamics parameters of the electrode process were investigated systematically by various electrochemical techniques. Moreover, a sensitive and reliable electroanalytical method for determination of picroside II was established with detection linear range and low detection limit. This is the first report about the electrochemical informations and electroanalytical method for picroside II. Finally, the proposed method was applied to determine picroside II in real samples with satisfactory results.

2. Experimental

2.1. Apparatus and reagents

Model CHI650A electrochemical system (Chenhua Instrument Company, Shanghai, China) was employed for electrochemical techniques. A standard three-electrode system was used for electrochemical measurement with a bare GCE or modified GCE ($d=3$ mm) used as working electrode; A platinum (Pt) wire used as an auxiliary electrode and a saturated calomel electrode (SCE) used as a reference electrode, respectively.

L-Citrulline and the standard reagent of picroside II were obtained from Aladdin Co. Ltd. (Shanghai, China). A stock solution of picroside II (1×10^{-3} mol L^{-1}) was prepared using ethyl alcohol and stored under 4 °C. It was diluted to suitable concentration when used. SWCNTs were purchased from Shenzhen Nanotech Port Co., Ltd. Phosphate buffer solution (PBS, 0.1 mol L^{-1}) were prepared using the mixture of the stock solutions (0.1 mol L^{-1} NaH_2PO_4 and Na_2HPO_4). All other reagents were of analytical grade and were used without any further purification. Doubly distilled water was used for all preparations.

2.2. Preparation of carboxylic SWCNTs

Carboxylic acid groups were grafted onto the SWCNTs by means of ultrasound for 4 h in acid mixture (98% concentrated sulfuric and 70% nitric acid, 3:1). The resulting SWCNTs were washed with water until the pH of the cleaning fluid was about 7.0 [35]. The carboxylation-functionalized SWCNTs were ready after drying at 120 °C. Then the functionalized SWCNTs were dispersed in Dimethylformamide (DMF) and sonicated for 24 h to obtain a suspension of 0.1 mg mL^{-1}.

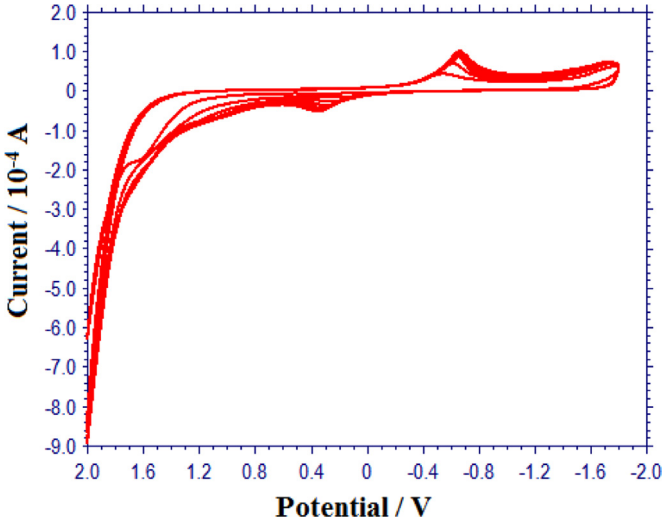


Fig. 1. Cyclic voltammograms for the electropolymerization of L-Citrulline. Supporting electrolyte: PBS buffer solution (pH 8.0); scan rate: 0.1 V s^{-1}; L-Citrulline concentration: 2.5×10^{-3} mol L^{-1}.

2.3. Fabricated of poly(L-Citrulline)/SWCNTs/GCE

The GCE was polished with 0.1 μm aluminum slurry, then rinsed ultrasonically with ethanol and double distilled water, each for 3 min. Afterwards, The fresh GCE surface was coated with 1 μL SWCNTs suspension and dried under IR-lamp. Then the poly(L-Citrulline)/SWCNTs modified GCE (poly(L-Citrulline)/SWCNTs/GCE) was obtained by cyclic sweeping between −1.8 V and 2.0 V at the rate of 0.1 V s^{-1} for 8 cycles in a PBS (pH 8.0) containing 2.5×10^{-3} mol L^{-1} L-Citrulline. This was the optimal depositional condition for fabricating the poly(L-Citrulline)/SWCNTs/GCE from test. As shown in Fig. 1, an oxidation peak (+1.6 V) and a reduction peak (−0.65 V) were observed. In subsequent scans, a new oxidation peak appeared at 0.35 V and the peak currents increased with the scanning cycles, indicating the continuous growth of the film. When scanning at high positive potential, L-Citrulline monomer is oxidized to form α-amino free radical, which can be linked on the electrode surface. Then poly(L-Citrulline) films can be formed. As is well known, amino acid monomer could be electro-polymerized onto the carboxylic SWCNTs surface by forming a carbon-nitrogen linkage at GCE surface [32–34,36]. The proposed schematic representation of the poly(L-Citrulline)/SWCNTs/GCE was shown in Scheme 3. For comparison, a poly(L-Citrulline) modified GCE (denoted as poly(L-Citrulline)/GCE) was prepared using the same electro-polymerizing method and a SWCNTs modified GCE (named as SWCNTs/GCE)was established by deposited the above SWCNTs suspension (1 μL) on the fresh GCE surface.

2.4. Treatment of herbal samples

Picrorhiza kurroa Royle ex Benth (Zhengzhou Ruikang Pharmaceutical Co., Ltd., China), was employed to determine the picroside II content and evaluate the performance in practical applicability of the proposed voltammetric sensor. 2 g Picrorhiza kurroa was weighed and ground into powder. Then the powder was dispersed in 10 mL methanol and soaked for 2 h under the condition of ultrasonic [37]. After that, the solution was centrifuged for 5 min at 5000 rpm and the supernatant was taken for further use. The residue was leaching in another 10 mL methanol, repeated the above operation for four times. Lastly, the filtrates was merged and concentrated to 8 mL, which was used as detection sample.