



Poly (crystal violet) - Multi-walled carbon nanotubes modified electrode for electroanalytical determination of luteolin



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ABSTRACT

With the aim of sensitive determination of luteolin, a new poly (crystal violet)/multi-walled carbon nanotubes modified electrode (PCV/MWCNTs/GCE) was fabricated by casting multi-walled carbon nanotubes (MWCNTs) onto the surface of glassy carbon electrode (GCE), then electro-polymerizing crystal violet (CV) on the MWCNTs/GCE matrix. Characterization of the novel modified electrode was carried out by cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy. The electrochemical behaviors of luteolin indicated that the PCV/MWCNTs/GCE can greatly enhance the electrocatalytic activity in the redox process of luteolin. It leads to a considerable improvement of the redox peak current for luteolin and allows the development of a sensitive voltammetric sensor for the determination of luteolin. Under optimized conditions, the oxidative peak currents increased linearly for the concentration of luteolin in the range of 2.0×10^{-8} to 7.0×10^{-5} M with a detection limit of 5.0×10^{-9} M ($S/N = 3$). The novel modified electrode demonstrated high sensitivity, good reproducibility and long-term stability. The proposed method was adopted for detection of luteolin in Chrysanthemum as a real sample with satisfactory results.

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1. Introduction

Luteolin (3', 4', 5, 7-tetrahydroxyflavone, Fig. 1), belongs to the class flavonoids, has the important biology effects including anti-inflammatory and anti-oxidant, which has been widely distributed in various vegetables and fruits, especially in drugs [1–4]. Furthermore, recent studies have also shown that it has anti-proliferative activity against cancer cells [5]. Therefore, investigating the redox process and control of the content of luteolin is of great importance. To achieve the sensitive determination of luteolin, several instrumental techniques such as high-performance liquid chromatography (HPLC) [6,7], spectrophotometry [8], capillary electrophoresis [9,10], and gas chromatography [11] have been developed. Although these methods have advantages of sensitivity and accuracy, their high cost and complicated sample pretreatment limit their extensive application. In comparison, electrochemical method offers the advantages of great speed, low cost, simplicity and feasibility of miniaturization. In this context luteolin is an electroactive compound because of the catechol group on the B ring (3', 4'-dihydroxyl), the development and application of electrochemical methods for the determination of luteolin has attracted widespread attention in recent years [12–15].

The application of polymer modified electrodes for electroanalysis and similar topics have been investigated [16–19]. Crystal violet (CV) is a triphenylmethane water-soluble dye and can be polymerized on the electrode surface by different electrochemical methods. By controlling the conditions of electropolymerization, stable composite film can be formed on the electrode surface with multi-functions and exhibiting interesting features such as fast rate of charge transfer and ion transport and good catalytic ability toward small biomolecules [20,21].

Carbon nanotubes (CNTs) have drawn wide attention due to possess interesting chemical and physical properties such as electric conductivity, chemical stability, mechanical and tensile strength [22–27]. A large number of studies have been established in various fields using CNTs for example sensors [28]. Many efforts have been focus on the fabrication of CNT/polymer composites electrode due to the CNTs can improve the electrical and mechanical properties of polymers [29,30]. CNTs might play a role as a template in the immobilization of polymers [31–35] and the obtained CNT/polymer composites lead to synergistic effects in terms of sensitivity [36] and can improve the access of analyte to the electrode surface as well as leading to electrocatalytic effects. For example, Brett et.al has reported polymerization of thionine on MWCNT-modified glassy carbon electrode that can be used for sensing acetaminophen and dipyrone to increase the sensitivity and reduce the detection limit [37].

In this work, poly (crystal violet) (PCV) and carbon nanotube nanocomposites was used to act as modifier in the direct electrochemistry of luteolin. There exists favorable electrostatic interaction between the

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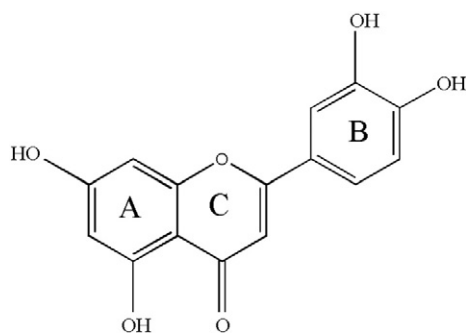


Fig. 1. Chemical structure of luteolin.

electron-rich π system and carboxylate groups of MWCNT and the positively charged species crystal violet. The PCV film acts as an electron transfer mediator to accelerate electron transfer rate for the oxidation reaction of luteolin. The goal of the study is to fabricate a novel poly (crystal violet)/multi-walled carbon nanotubes (MWCNTs) composite electrode and to investigate the synergetic catalytic effect of MWCNTs and PCV toward the redox reaction of luteolin.

Herein, a poly(crystal violet)/multi-walled carbon nanotubes modified glass carbon electrode (PCV/MWCNTs/GCE) was fabricated using a two-step procedure by electropolymerizing crystal violet on the MWCNTs/GCE matrix, which was obtained by casting a certain amount of well-dispersed MWCNTs suspension onto a prior polished glassy carbon electrode. The electrochemical behavior of the luteolin at the PCV/MWCNTs/GCE was investigated in detail. This composite film exhibited large surface area and good electroactivity for the oxidation of luteolin. Under the optimum conditions, differential pulse voltammetry (DPV) was developed for the direct determination of luteolin, and a detection limit of 5.0×10^{-9} M was achieved by this method. With such a PCV/MWCNTs modified electrode, luteolin from Chrysanthemum was successfully detected.

2. Experimental

2.1. Reagents

MWCNTs used came from Chengdu Organic Chemicals Co. Ltd., treated with HNO_3 for purification and dried in air. Crystal violet was purchased from Sigma-Aldrich. The standard of luteolin was obtained from Chinese Chemical and Biological Drugs Institute (Beijing, China). All other chemicals were of analytical reagent grade and purchased from Shanghai Chemical Reagent Co., Ltd. (China). All solutions were prepared using Millipore Milli-Q nanopure water (resistivity $>18 \text{ M}\Omega \text{ cm}$). The supporting electrolyte was 0.1 M phosphate buffer solutions (PBS) of pH 5.5–8.0.

2.2. Apparatus

Voltammetric experiments were done using a CHI660C electrochemical workstation (Shanghai ChenHua Instruments, China). A conventional three-electrode cell was employed, which consisted of bare GCE (3 mm diameter), PCV/GCE, MWCNTs/GCE or PCV/MWCNTs/GCE as the working electrode, an Ag/AgCl as the reference electrode and a platinum wire as the counter electrode, respectively. The morphological characterization of electrode was examined by means of a scanning electron microscopy (SEM, EVO18, Carl Zeiss). Electrochemical impedance spectroscopy (EIS) was carried out using Princeton PARSTAT4000 with the frequency range from 10 kHz to 0.1 Hz at 0.25 V. Measurements of pH were performed with a pHS-3C model meter (Leici Devices Factory of Shanghai, China).

2.3. Fabrication of modified electrode

Prior to the modification, the bare glassy carbon electrode (GCE) was pretreated as following: polished with 1, 0.3 and 0.05 μm alumina powder on chamois leather respectively, followed by washed ultrasonically in ethanol and doubly distilled water for 30 s, respectively.

The MWCNTs modified electrodes were prepared by drop-casting. 9 μL of a DMF/ H_2O (1:1) solution containing $0.50 \text{ mg} \cdot \text{mL}^{-1}$ MWCNTs was directly dropped on a bare electrode and dried for 4 h at room temperature. The electropolymerization of crystal violet was carried out under cyclic voltammetry sweeping from -1.5 to 2.0 V at a scan rate of $100 \text{ mV} \cdot \text{s}^{-1}$ [38] for 5 cycles on the MWCNTs/GCE. The concentration of crystal violet was $2.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ in PBS (pH 6.8) solution. The modified electrode was donated as the PCV/MWCNTs/GCE. The MWCNTs/GCE and the PCV/GCE were individually prepared through aforementioned procedures for comparison. The electrodes were stored at 4°C before use.

2.4. Experimental measurements

The cyclic voltammogram was recorded between -0.2 V and 0.6 V at a scan rate of 100 mV s^{-1} . The determination of luteolin was performed by differential pulse voltammetry (DPV). The DPV was recorded from -0.2 V to 0.6 V (with an amplitude of 50 mV and a pulse width of 50 ms). High-purity nitrogen was used for purging oxygen before each experiment. All measurements were carried through at ambient temperature.

2.5. Sample preparation

The air-dried Chrysanthemum (I and II) samples were acquired from a local drugstore (Anhui, China). The samples were prepared by extracting 1.0 g of sample with 5 mL of anhydrous ethanol in ultrasonic bath for 30 min and filtering. Next each of the samples was centrifuged in 1500 rev/s for 10 min. The obtained supernatant was filtered through 0.45 μm syringe cellulose acetate filter, 1 mL filter liquor was diluted with PBS (pH 7.0) to 10 mL in a calibrated flask. The extract was transferred to an electrochemical cell and analyzed by DPV.

3. Results and discussion

3.1. Characterizations of modified electrode

SEM images were employed to characterize the typical morphologies of the bare GCE (Fig. 2a), the prepared PCV (Fig. 2b), MWCNTs (Fig. 2c) and PCV/MWCNTs composite (Fig. 2d). At the bare GCE a uniform and smooth surface appeared (Fig. 2a). At PCV/GCE (Fig. 2b) a three-dimensional film appeared with increased roughness, indicating that crystal violet was successfully electropolymerized on the electrode surface with increase of the effective area. At MWCNTs/GCE (Fig. 2c), a wrinkled structure could be observed and indicated that the MWCNTs were successfully incorporated into the GCE. This structure can effectively increase the surface-to-volume ratio and facilitate electron transfer [39]. In comparison, when crystal violet were electropolymerized on the surface of MWCNTs/GCE matrix to get a composite, the interface was different from that of PCV/GCE and MWCNTs/GCE, which indicated that the PCV film covered on the MWCNTs/GCE (Fig. 2d). This PCV film may enhance the interaction between the modified electrode and the luteolin to further improve the sensitivity and stability of PCV/MWCNTs/GCE.

The electrochemical properties of the different electrodes were characterized by $\text{K}_3[\text{Fe}(\text{CN})_6]$ as a probe by cyclic voltammetry. Fig. 3A presents the cyclic voltammetric responses of different electrodes in 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 M KCl. Compared with other electrodes, it could be seen that the redox peaks were significantly increased due to the larger surface area and good conductivity of PCV/

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