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Original article

Electrochemical determination of quercetin by self-assembled platinum nanoparticles/poly(hydroxymethylated-3,4-ethylenedioxylthiophene) nanocomposite modified glassy carbon electrode

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ABSTRACT

A simple and sensitive platinum nanoparticles/poly(hydroxymethylated-3,4-ethylenedioxylthiophene) nanocomposite (PtNPs/PEDOT-MeOH) modified glassy carbon electrode (GCE) was successfully developed for the electrochemical determination of quercetin. Scanning electron microscopy and energy dispersive X-ray spectroscopy results indicated that the PtNPs were inserted into the PEDOT-MeOH layer. Compared with the bare GCE and poly(3,4-ethylenedioxythiophene) (PEDOT) electrodes, the PtNPs/PEDOT-MeOH/GCE modified electrode exhibited a higher electrocatalytic ability toward the oxidation of quercetin due to the synergic effects of the electrocatalytic activity and strong adsorption ability of PtNPs together with the good water solubility and high conductivity of PEDOT-MeOH. The electrochemical sensor can be applied to the quantification of quercetin with a linear range covering 0.04–91 μmol L^{-1} and a low detection limit of 5.2 nmol L^{-1}. Furthermore, the modified electrode also exhibited good reproducibility and long-term stability, as well as high selectivity.

1. Introduction

Quercetin (3,3′,4′,5,7-penta hydroxyl flavones), one of the most abundant natural flavonoids, has been widely distributed in various vegetables and fruits, especially in traditional Chinese herbs. Its average human daily intake is estimated to be 16–25 mg per person. Over the past years, quercetin has drawn much attention because of its various beneficial effects on human health, including anti-cancer, anti-inflammatory, anti-tumor, anti-ulcer, anti-allergy, anti-viral, and anti-oxidant effects [1,2], and quercetin also can protect human DNA from oxidative attack *in vitro* [3]. Hence, it is extremely important to determine and study it.

Several techniques have been utilized in the determination of quercetin, for example, HPLC-UV [4], spectrophotometry [5], liquid chromatography with mass spectrometry [6], and solid phase extraction [7]. These methods are highly sensitive and effective, but often require some complicated and time consuming sample pretreatment. Due to the advantages of time-saving, simple operation, sensitivity, low-cost, and on-field detection, some electrochemical methods have been proposed for the electrochemical study of quercetin. Several materials have been used to fabricate the modified electrode, such as carbon nanotubes [3,8–10], copper microparticles [11], and graphene nanosheets [12]. However, to date, the application of conductive polymer with metal nanoparticles for the electroanalytical detection of quercetin has not been reported.

In recent years, metal nanoparticles have been the focus of much current research in designing and constructing of chemo/biosensors owing to their large surface-to-volume ratio, strong adsorption ability, good electrical properties, high surface reaction activity, small particle size and good surface properties. In particular, platinum nanoparticles (PtNPs) have been the subject of intensive research in the design of electrodes [13,14]. Conducting polymers (CPs) are a fascinating modified electrode material by virtue of their good electrical properties and high specific capacity. Especially due to easy processing, biocompatibility, and conductivity, CPs or the composites of CPs with nanomaterials (such as carbon nanotubes, metal particles or graphene) have been successfully employed in electrochemical sensors [15–19]. Poly(3,4-ethylenedioxythiophene) (PEDOT), known as one of the most stable and successful commercially available CPs today, has attracted a great deal of

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attention for the application of chemo/bio-sensors materials because of the high conductivity, good stability, friendly biocompatibility, low toxicity, and relatively low band gap [20–24]. Hydroxymethylated-3,4-ethylenedioxylthiophene (EDOT-MeOH), a polar derivative of EDOT, exhibited better water-solubility and a lower onset oxidation potential compared with EDOT monomer [25–29]. In addition, our group has reported a new and efficient synthetic route to obtain EDOT-MeOH monomer and the fabricated PEDOT-MeOH chemo/bio-sensors were successfully used in the electrochemical determination of the anticancer herbal drug, shikonin [27], and VC in commercial fruit juice [27,28]. Therefore, it is very meaningful to construct an electrochemical sensor for the determination of quercetin by incorporating the merits of EDOT-MeOH and PtNPs.

In this contribution, in view of the merits of conducting polymer PEDOT-MeOH and metal nanoparticles PtNPs, a simple and sensitive PtNPs/PEDOT-MeOH nanocomposite modified glassy carbon electrode (GCE) was constructed for the electrochemical determination of quercetin. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) results showed that the PtNPs were inserted into the PEDOT layer and formed a porous 3D structure, which exhibited large surface area and excellent electrocatalytic activity for the oxidation of quercetin. Moreover, the electrochemical properties of the PtNPs/PEDOT-MeOH/GCE modified electrode for the voltammetric detection of quercetin were studied.

2. Experimental

2.1. Chemicals

3,4-Dibromothiophene (EDOT) (98%, Shanghai Bangcheng Chemical Co., Ltd.), Quercetin (>98%) and platinum powder (99.99%) were obtained from Aladdin Reagent Co., Ltd. All other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. with analytical grade and were used as received without any further purification. All solutions were prepared using double-distilled deionized water.

2.2. Apparatus

Electrochemical measurements were performed on a CHI660B electrochemical workstation (Chenhua Instrument Company, Shanghai, China) with a conventional electrochemical cell containing a three-electrode system. The modified electrode or bare glassy carbon electrode (GCE) (Φ = 3 mm) was served as a working electrode, a platinum wire (Φ = 1 mm) was used as a counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The addition of samples was performed with a microsyringe (Shanghai Gaoge Industry & Trade Co., Ltd., China). The pH values of PBS were measured with a PHB-5 portable pH meter (Hangzhou Qiwei Instrument, China). SEM measurements were taken with a JEOL JSM-6701F scanning electron microscope (Tokyo, Japan).

2.3. Preparation of modified electrode

Prior to modification, the working electrode bare GCE was carefully polished with 0.05 μm alumina slurry until a mirror-shine surface was obtained, followed by successively sonicating in doubly distilled deionized water and ethanol, and then dried in air. The PEDOT-MeOH/GCE modified electrode was prepared facilely by one-step electropolymerization of EDOT-MeOH (10 mmol L^{-1}) in 0.1 mol L^{-1} $LiClO_4$. The deposition potential was 1.1 *vs.* SCE and the deposition time is 70 s. After drying at room temperature under a clean environment, the PEDOT-MeOH/GCE was electrodeposited in 5 mmol L^{-1} $HPtCl_6$ solution by cyclic voltammetry (CV) at the scan rate of 100 mV s^{-1} from −0.3 V to +1.0 V *vs.* SCE for 10 cycles. Then, the resulting PtNPs/PEDOT-MeOH/GCE modified electrode was washed repeatedly with double-distilled deionized water to remove the electrolyte and monomer from electrode surface and naturally dried at room temperature.

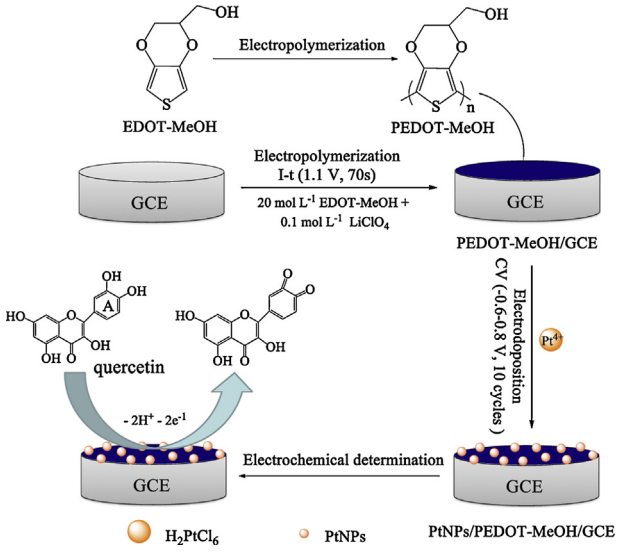
2.4. Experimental measurements

Five milliliters of 0.1 mol L^{-1} PBS (pH 7.0) with a specific amount of quercetin solution was transferred into the sealed electrochemical cell by microsyringe. The voltammetric detection of quercetin was studied by differential pulse voltammetry (DPV). The DPV conditions were as follows: potential increase, 0.004 V; amplitude, 0.05 V; pulse width, 0.05 s; and pulse interval, 0.2 s. Prior to each experiment, all solutions were deoxygenated by purging with nitrogen for 10 min. The fabrication process of the modified electrode and the working mechanism for the electrochemical analysis of quercetin are shown in Scheme 1.

3. Results and discussion

3.1. Characterization of modified electrodes

The surface morphology of the PEDOT-MeOH film and the PtNPs/PEDOT-MeOH composite deposited on the indium-tin oxide (ITO) transparent electrode was investigated by SEM. As shown in Fig. 1A, The PEDOT-MeOH film obtained from the aqueous solution was rough and compact structure, while the morphology of PtNPs/PEDOT-MeOH film exhibited a three-dimensional (3D) morphological structure (Fig. 1B). The 3D structure of PtNPs/PEDOT-MeOH modified electrode could produce a large surface area structure, which is beneficial to maintaining large electroactive area on the electrode surface. Moreover, the 3D structure may give a high sensitivity for the detection of analytes. In addition, energy dispersive spectrum (EDS) analysis was performed to further confirm the components of the PtNPs/PEDOT-MeOH film shown in Fig. 1C. The presence of C, S, O, and Pt come from the component elements of the PEDOT-MeOH–PtNPs composite. Other elements mainly originated from electrolysis solution and ITO. The content of PtNPs is shown in Table 1. All the results confirm the presence of Pt on PEDOT-MeOH–PtNPs composite.



Scheme 1. The process of construct PtNPs/PEDOT-MeOH/GCE and trace determination of quercetin.