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Facile preparation of molecularly imprinted polypyrrole-graphene-multiwalled carbon nanotubes composite film modified electrode for rutin sensing

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ABSTRACT

In this paper, a novel molecularly imprinted composite film modified electrode was presented for rutin (RT) detection. The modified electrode was fabricated by electropolymerization of pyrrole on a graphene-multiwalled carbon nanotubes composite (G-MWCNTs) coated glassy carbon electrode in the presence of RT. The netlike G-MWCNTs composite, prepared by *in situ* hydrothermal process, had high conductivity and electrocatalytic activity. At the resulting MIP/G-MWCNTs/GCE electrode RT could produce a sensitive anodic peak in pH 1.87 Britton-Robinson buffer solution. The factors affecting the electrochemical behavior and response of RT on the modified electrode were carefully investigated and optimized. Under the selected conditions, the linear response range of RT was 0.01–1.0 μmol L^{-1} and the detection limit (S/N=3) was 5.0 nmol L^{-1}. The electrode was successfully applied to the determination of RT in buckwheat tea and orange juice samples, and the recoveries for standards added were 93.4–105%.

1. Introduction

Rutin (i.e. quercetin-3-rhamnosylglucoside, RT) (Scheme S1) is a polyphenolic compound that is widely found in plants [1,2], such as in buckwheat, fruits and berries as well as in many Chinese herbs [3]. It can strengthen the capillaries and inhibit platelet aggregation, making the blood thinner and improving circulation [4]. RT is also well-recognized as a therapeutic medicine with the physiological functions of anti-inflammatory, anti-tumor and anti-bacteria [5,6].

At present, high performance liquid chromatography (HPLC) [7], capillary electrophoresis (CE) [8,9], chemiluminescence [10] and ultraviolet spectrophotometry (UV) [11] are often used for RT assay. Owing to its electroactivity, electrochemical methods are also developed for it [12–14]. For examples, Wu et al. constructed a single-sided heated graphite cylindrical electrode for the detection of RT [15]. Yang et al. determined RT with a gold nanoparticles/ethylenediamine/carbon nanotube modified glassy carbon electrode (GCE) [16]. RT was also detected by using Nafion-graphene oxide-ionic liquid modified electrode [17], and acetylene black nanoparticle modified GCE [18]. However, as a natural flavonoid, RT generally coexist with quercetin and morin in medicinal plants, fruits, vegetables and variety of beverages [2,19]. Therefore, its electrochemical determination usually suffers from the interference of the coexistants.

Molecular imprinting is a technology to introduce recognition properties into synthetic functional polymers [20]. It is widely used in fabricating sensors because it can enhance selectivity and/or sensitivity [21,22]. Furthermore, molecularly imprinted polymer (MIP) can be easily prepared and possess good physical, chemical and mechanical stability [23]. When MIP is prepared by electropolymerization, the thickness and morphology of polymer film can be conveniently controlled by changing deposition conditions, so does the property of the resulting sensors [24,25]. Polypyrrole (PPy) is one of the most extensively studied conductive polymers and it has been widely used for the preparation of MIP based electrochemical sensors [26,27], due to its unique biocompatibility, high conductivity etc.

To enhance sensitivity MIP is generally combined with nanomaterials in constructing sensors [28–31]. Among various nanomaterials, graphene-multiwall carbon nanotubes (G-MWCNTs) composite becomes popular recently because it has superior electronic, thermal and mechanical properties [32]. Some researchers have revealed that G-MWCNTs nanocomposite is a promising material for fabricating modified electrodes and electrochemical sensors [33,34].

In the present work, a facile and green method was employed to synthesize G-MWCNTs nanocomposite, and the nanocomposite

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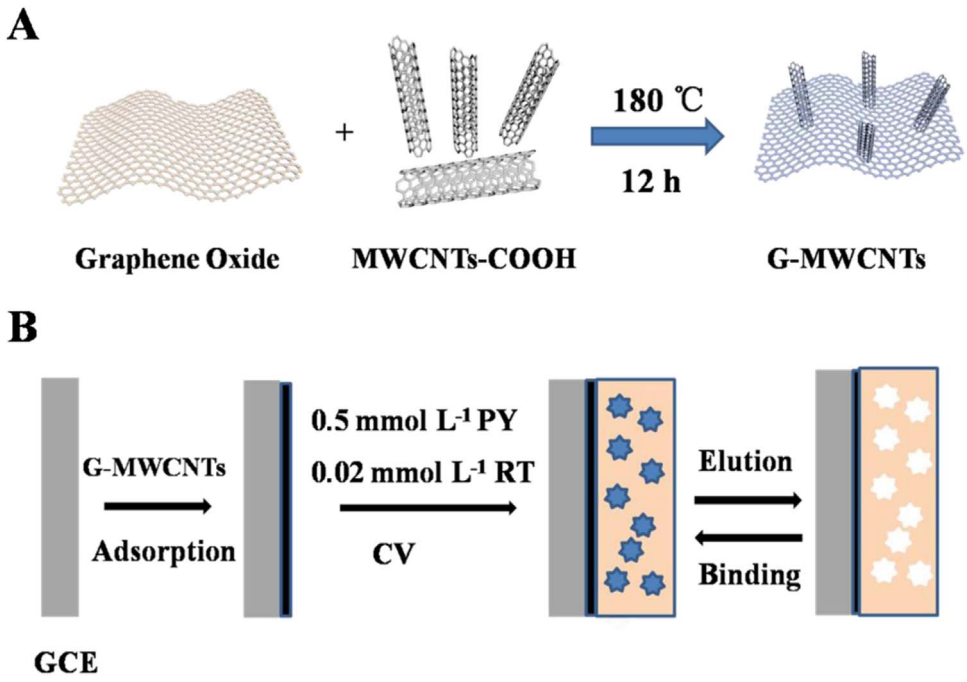

Scheme 1. Schematic diagram of the construction procedure of sensor.

was used as support for the electrodeposition of RT imprinted PPy film. The resulting new modified electrode showed highly selective and sensitive response to RT. It could be applied to the determination of RT in real samples, such as buckwheat tea and orange juice.

2. Experimental

2.1. Chemicals and apparatus

Graphite oxide (GO, purity: 99%) and MWCNTs were obtained from Nanjing XF NANO Materials Tech Co., Ltd (Nanjing, China). RT (purity: ≥95%) and pyrrole (PY, purity: ≥98%) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Morin (MR, purity: ≥99%) was purchased from Beijing Chemical Works (Beijing, China). Quercetin (QR, purity: 99%) came from Fluka (Switzerland). The stock solution of RT (0.010 mol L^{-1}) was prepared with ethanol and stored in a refrigerator at 4 °C. A Britton-Robinson (BR) buffer solution (containing 0.04 mol L^{-1} of glacial acetic acid, 0.04 mol L^{-1} orthophosphoric acid and 0.04 mol L^{-1} boric acid) was employed as supporting electrolyte. Unless stated otherwise, other reagents used were analytical grade. All the solutions were prepared with ultrapure water.

Cyclic voltammetry, differential pulse voltammetry and electrochemical impedance spectroscopy (EIS) experiments were performed with a CHI 660B electrochemical workstation (CH Instrument Company, Shanghai, China). A conventional three-electrode system was employed. The working electrode was a modified glassy carbon electrode (GCE, diameter: 3 mm), the auxiliary and reference electrodes were a Pt wire and a saturated calomel electrode (SCE), respectively. Scanning electron microscope (SEM) images were obtained by using a Zeiss (German) with an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images were recorded with a JEM-2100 transmission electron microscope with an accelerating voltage of 200 kV. X-ray diffraction data (XRD) was obtained by a Bruke D8 diffractometer (Germany) using Cu Kα radiation (40 kV, 40 mA) with a Ni filter. All experiments were carried out at room temperature.

2.2. Preparation of G-MWCNTs composite

The G-MWCNTs nanocomposite was prepared according to literature with minor modification [35]. Briefly, GO was dispersed into water with the aid of sonication, then 1.0 mg MWCNTs and 0.4 mL NaOH solution (0.1 mol L^{-1}) were added to 10 mL GO suspension (0.2 mg mL^{-1}), followed by ultrasonication for 2 h, and then the solution was transferred to a Teflon-lined autoclave for hydrothermal reaction at 180 °C for 12 h. The as-prepared homogeneous black hybrid was cooled to room temperature. The precipitate was collected by centrifugation and washed with water, and then it was dispersed in 10 mL water for electrode modification.

2.3. Fabrication of modified electrode

Prior to surface modification, the GCE was polished with alumina slurries (Φ=0.5 μm) and washed with 1:1 nitric acid aqueous solution, ethanol and deionized water, respectively. After dried, the clean GCE was modified by dropping 10 μL G-MWCNTs suspension and the solvent was evaporated under an infrared lamp. After that, the modified electrode was immersed into 0.1 mol L^{-1} $LiClO_4$ solution containing 0.5 mmol L^{-1} pyrrole and 0.02 mmol L^{-1} RT, electropolymerization was performed by cycling potential between −0.6 V and +1.8 V for 8 cycles. The scan rate was 50 mV s^{-1}. Then the modified electrode was washed with sodium hydroxide solution (0.2 mol L^{-1}) and ethanol repeatedly to remove the template RT. Thus, an MIP composite modified electrode (i.e. MIP/G-MWCNTs/GCE) was obtained (Scheme 1). The non-imprinted composite modified electrode (i.e. NIP/G-MWCNTs/GCE) was prepared by the same method but without RT.

2.4. Sample preparation

Buckwheat tea was pretreated according to Ref. [36]. Briefly, the buckwheat tea sample (46.0 mg) was extracted with ethanol through reflux in a water bath at 80 °C for 1 h, and the solid was removed by filtration. The collected solid was extracted once again