



Decoration of chemically reduced graphene oxide modified carbon paste electrode with yttrium hexacyanoferrate nanoparticles for nanomolar detection of rutin



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ABSTRACT

Through a simple, rapid and green method, a small size of yttrium hexacyanoferrate nanoparticles (YHCFNPs) was synthesized firstly. As the novel sensing materials, a sensor of YHCFNPs/chemically reduced graphene oxide (CRGO) nanocomposite modified carbon paste electrode (CPE) was fabricated. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM), inductive coupled plasma emission spectrometer (ICPES) and electrochemistry were performed to characterize the modified electrode. SEM images showed that the average diameter of the prepared YHCFNPs was about 40 nm. The electrochemical behavior of the YHCFNPs/CRGO/CPE in response to rutin was studied. The response current of rutin at the YHCFNPs/CRGO/CPE was obviously higher than that at the other modified CPE. Under the optimal conditions, YHCFNPs/CRGO/CPE exhibited a broader detection range from 2.0 to 4000 nmol/L with a nanomolar detection limit of 0.82 nmol/L ($S/N=3$). This novel method was successfully used to determine rutin in pharmaceutical tablets.

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1. Introduction

Rutin, also called vitamin P, is a kind of flavonoid glycoside compounds. The antioxidant activity and therapeutic activity of the flavonoid are closely related to the structure of these compounds. Especially, rutin has many physiological functions, such as diluting the blood, reducing capillary permeability, as well as lowering blood pressure [1]. It is often clinically used as a therapeutically drug. Many analytical methods have been developed for the detection of rutin, including high performance liquid chromatography (HPLC) [2], chemiluminescence [3], capillary electrophoresis [4] and spectrophotometry [5]. Nevertheless, some of the above mentioned methods, for example HPLC, need complicated separation processes, large amounts of toxic organic solvents, expensive instruments, and professional technicians. Electrochemical methods provide with some advantages, such as rapid and simple procedure, low cost equipment and on-site test. Even for

pharmaceuticals analysis, electrochemical method is very effective. Gupta and co-workers [6] critically reviewed the voltammetric techniques for the assay of pharmaceuticals. The review not only discussed the use and advantages of techniques to pharmaceutical compounds in dosage forms and biological media, but also clearly provided the matrix in which pharmaceuticals were analyzed. Furthermore, important information, like the peak potential of the electroactive substance, was included. Due to the presence of phenolic hydroxyl groups in rutin structure, rutin has good electrochemical activity, and the electrochemical methods have been widely used to investigate the oxidation mechanism of rutin. For example, Ziyatdinova et al. [7] demonstrated that in the presence of cationic surfactant media, as for rutin, hydroxyl groups of B and A aromatic rings are oxidized with formation of corresponding carbonyl derivatives in reaction with electrogenerated hexacyanoferrate(III) ions by coulometric titration. Fatibello-Filho and co-workers [8] constructed carbon composite electrode modified with copper(II)-resin for voltammetric determination of rutin, and pointed out that the mechanism of the voltammetric response of the modified electrode can be divided in two stages: electrochemical and chemical. Initially, a process of electrochemical oxidation involving two electrons ($\text{Cu}^0/\text{Cu}^{2+}$) in the surface of the electrode was observed, followed by the complex formation of $\text{Cu(II)-[rutin]-resin}$. Malagutti and co-workers [9] fabricated

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a rigid carbon-polyurethane composite electrode (RCPE) for the determination of rutin in green tea infusions using square-wave voltammetry, and revealed that on the RCPE, the oxidation reaction of rutin was quasireversible, and coupled with a losing of 2-electron and 2-protons, with adsorption of the reactant on the electrode surface. The RCPE electrode could be electrochemically cleaned after each experiment. Although various electrochemical techniques including many types of modified electrodes were developed to investigate the electrochemical reaction of rutin, the oxidation of phenolic compounds at solid electrodes produced phenoxy radicals which coupled to form a passivating polymeric film on the electrode surface. Many efforts should not only be devoted to improve the sensitivity of the determination of rutin, but also be developed to address these surface fouling problems, including the use of electrochemical pretreatment or laser activation, as well as carbon-polymer [9,10].

Since the discovery of graphene (GR) in 2004, it has attracted strong scientific and technological interests due to its remarkable high specific surface area, electron transport capability, thermal and electrical properties [11]. The application of graphene in electrochemical sensing and biosensing is wide [12]. However, graphene is hydrophobic. Especially, it is easy to form irreversible agglomerates due to its strong π - π stacking and van der Waals interactions [13], which is a disadvantage for its further application. Graphene oxide (GO) can be considered as a precursor for graphene preparation. GO consists of a single-layer graphite oxide with various oxygen containing functional groups, such as hydroxyl groups, epoxy group, carbonyl, and quinone etc. The oxygenated groups in GO can remarkably affect its mechanical and electrochemical properties. They can account for the differences between GO and graphene [14]. Compared with graphene, the polar oxygen functional groups render GO strongly hydrophilic. This provides GO with good dispersibility in many solvents, especially in water [15–18]. The resulting stable GO dispersion can be subsequently deposited on various substrates to obtain thin films. Nevertheless, The existence of those oxygenated functional groups in GO can indeed give rise to a remarkable loss of the electrical conductivity [19], which may limit the direct application of GO in the electrochemical field. Generally speaking, graphene can be prepared through chemical reduction of graphene oxide using chemical reducing agents [20,21], such as sodium borohydride and hydrazine hydrate.

Transition metal hexacyanoferrates (MHCs), an important kind of multicore inorganic polymers, have recently attracted considerable attention due to their open zeolite-like structure and attractive magnetic, optical, and electroactive characteristics [22]. They are widely used in many fields, such as sensing [23], electroanalysis [24], and electrochromic devices [25]. Nevertheless, the stability and analytical properties of the MHCs modified electrodes need further improvements. In order to obtain this aim, many efforts have been contributed to fabricate various composites containing MHCs. On the basis of the role of the introduced materials, some of them can increase the electrical conductivity of the hybrid, such as carbon nanotubes [26]; some of them can work as an fixed material to increase the mechanical properties of the composites, such as chitosan [27,28]; some can provide both high conductivity and mechanical properties of the hybrid films, such as polyaniline [29], polypyrrole [30] and poly(1-naphthol) [31]. As the electrode materials, the stability and electrochemical performance of the hybrid composites are superior to the single MHCs due to their synergetic effect.

In this paper, GO-stable dispersion was mixed with graphite firstly to get a uniform suspension, which was added into chemical reducing agents for further reduction of GO to obtain chemically reduced GO (CRGO). The obtained uniform CRGO/graphite

dispersion was homogeneous doped with freshly prepared YHCFNPs to achieve YHCFNPs/CRGO/graphite composite. Then silicone oil was dropped into the above composite to prepare YHCFNPs/CRGO modified CPE. The YHCFNPs/CRGO in the CPE exhibited the synergistic properties of CRGO and YHCFNPs simultaneously, such as large specific surface area, unique electrochemical properties and strong catalytic activity. Electrochemical behaviors of rutin on YHCFNPs/CRGO/CPE were further carefully investigated. Nanomolar detection limit as the lower value for rutin determination was achieved.

2. Experimental

2.1. Apparatus and reagents

CHI 660E electrochemical system (Shanghai Chenhua Instrument Co., Ltd. Shanghai, China) was performed for all the voltammetric measurement. A conventional three-electrode system was used, YHCFNPs/CRGO/CPE as working electrode, an Ag/AgCl (3 mol/L) as reference electrode and a platinum wire electrode as auxiliary electrode. The X-ray diffraction (XRD) spectra of the as-prepared samples were obtained by a powder X-ray diffractometer (Rigaku Ultima III), using K_{α} radiation ($\lambda = 1.5418 \text{ \AA}$). Morphologies of the products were examined by scanning electron microscopy (SEM; Hitachi, JSM-6701F) at an accelerating voltage of 5 kV. FTIR absorption spectra of selected samples were obtained using KBr disks on a FTIR 6300. Elemental analysis of the as-prepared samples was obtained by inductive coupled plasma emission spectrometer (ICPES; USA, PE, Optima8000). All the pH values were measured with a PHS-3C precision pH meter (Leici Devices Factory of Shanghai, China), which was calibrated with standard buffer solution every day.

Rutin (purchased from National Institute for the Control of Pharmaceutical and Biological Products, China) was used without further purification. $K_4[Fe(CN)_6]$ and Ytterbium nitrate hexahydrate $[Y(NO_3)_3 \cdot 6H_2O]$ with purity of >99% were got from Merck Company (Germany). Na_2HPO_4 NaH_2PO_4 , hydrazine solution (80 wt% in water) and ammonia solution (28 wt% in water) were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). The stock solution of rutin ($2.0 \times 10^{-2} \text{ mol/L}$) was diluted with 0.1 mol/L pH 1.5 phosphate buffer solutions (PBS) before used. The Compound Rutin Tablets were purchased from Shanghai Zhaohui Pharmaceutical Co. Ltd (Shanghai, China). Rutin Tablets were purchased from Shanxi Fenhe Pharmaceutical Co. Ltd (Shanxi, China), respectively, with the specified amount of 20 mg per-tablet. Spectral graphite (average particle size $30 \mu\text{m}$) was obtained from Shanghai Carbon Co., Ltd. All the other chemicals used were analytical grade without further purification and prepared with double-distilled water.

2.2. Preparation of YHCFNPs

YHCFNPs were synthesized according to our previous report [26] with a slight modification. In brief, all glassware was thoroughly dipped in aqua regia (3 HCl:1 HNO₃, v/v), and then dried in air before use after rinsed with distilled water. Subsequently, 50.0 mL $3.0 \times 10^{-3} \text{ mol/L}$ $Y(NO_3)_3$ was dropwise added into a vigorous ultrasonic solution of 50.0 mL $3.0 \times 10^{-3} \text{ mol/L}$ $K_4[Fe(CN)_6]$ solution which was protected by pure nitrogen gas. The resulting milky precipitates were collected by centrifugation, and washed with ultrapure water to remove any unreacted impurities. Finally, the purified solid was dispersed in 10 mL water with the aid of sonication. The suspension was stored at 4 °C.

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