



Application of ionic liquid modified carbon ceramic electrode for the sensitive voltammetric detection of rutin

Tianrong Zhan^{a,b}, Xiaoying Sun^b, Xiuzhen Wang^b, Wei Sun^{b,*}, Wanguo Hou^{a,b,**}

^a Key Laboratory of Colloid and Interface Chemistry, Ministry of Education, College of Chemistry and Chemical Engineering, Shandong University, Jinan 250000, China

^b Key Laboratory of Eco-chemical Engineering, Ministry of Education, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, 53 Zhenzhou Road, Qingdao 266042, China

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ABSTRACT

An ionic liquid (IL) modified carbon ceramic electrode (CCE) was designed and further used for the voltammetric detection of rutin in this paper. IL-CCE was prepared by mixing graphite powder with 1-butyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) doped silicate sol–gel matrix together and further characterized by different methods. Then electrochemical behaviors of rutin on the IL-CCE were investigated by different electrochemical methods such as cyclic voltammetry and differential pulse voltammetry (DPV). Due to the presence of IL in the CCE, an enhanced electrochemical response of rutin appeared with a pair of well-defined redox peaks in pH 2.5 phosphate buffer solution (PBS). The electrochemical behaviors of rutin on the IL-CCE were carefully investigated. Under the selected conditions the oxidation peak currents exhibited good linear relationship with the rutin concentration in the range from 0.3 to 100.0 μmol/L with the detection limit as 0.09 μmol/L (3σ). The proposed method was further applied to the rutin tablets sample detection with satisfactory results.

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1. Introduction

The sol–gel derived carbon ceramic electrodes (CCEs), which are fabricated by mixing graphite powder with silicate gel matrix, have aroused great interests in recent years [1]. In 1994 Tsionsky et al. firstly introduced CCE into the field of electroanalysis [2]. Then CCEs have been widely used as the working electrode with the advantages such as low cost, high-stability, easy to preparation, bulk modification and the convenience of surface renew. Different kinds of conductive particles such as glassy carbon [3], gold [4] and carbon nanotube [5] have been used in the preparation of the ceramic composite electrodes. Various modified CCEs have also been fabricated to improve the performance of the working electrode. For example, Razmi and Heidari applied a lead pentacyanonitrosylferrate film modified CCE for the electrocatalytic reduction of peroxodisulfate [6]. Shen et al. used a pyrocatechol modified CCE for the sensitive detection of hydrogen peroxide [7]. Salimi et al. fabricated a Ru-complex modified CCE for the amperometric detection of L-cysteine [8]. Ni powder doped CCE was also used for the electrocatalytic oxidation of some sulfur containing amino acids [9].

Ionic liquid (IL) is a kind of green solvent with the characteristics such as high conductivity, wide electrochemical windows and good solubility. Due to these specific properties IL had been used as the electrolyte and the modifier in the field of electrochemical sensor [10]. Carbon ionic liquid electrode (CILE) is a new type of working electrode, which is prepared by using IL as the binder and the modifier in the traditional carbon paste electrode (CPE). Due to the presence of IL, CILE had shown the advantages such as easy preparation, good reversibility, high sensitivity and the ability to lower the overpotential of electroactive compounds [11]. Maleki et al. [12,13] applied 1-octylpyridinium hexafluorophosphate based CILE for the detection of some electroactive molecules. Sun et al. studied the electrochemical behaviors of electroactive compounds with different ILs modified carbon paste electrodes [14–16]. Zheng and co-workers also applied CILE in the electrochemical detection of paracetamol [17]. In recent years Opallo and co-workers investigated the electrochemical activity of CCE modified with ionic liquids [18,19]. Li and co-workers also fabricated an ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate based silica sol–gel matrix modified gold electrode [20]. Shi et al. investigated the reaction mechanism of IL in the sol–gel process as a new attempt for the development of supported nano-liquid catalyst [21].

Rutin (vitamin P) is a commonly used clinical drug with the physiological functions such as anti-inflammatory, anti-tumor and anticancer [22]. Many analytical methods such as capillary electrophoresis [23], chemiluminescence [24], HPLC [25] and spec-

* Corresponding author. Tel.: +86 532 84023927; fax: +86 532 84023927.

** Corresponding author at: Key Laboratory of Colloid and Interface Chemistry, Ministry of Education, College of Chemistry and Chemical Engineering, Shandong University, Jinan 250000, China. Tel.: +86 0531 88564750; fax: +86 0531 88564750.

E-mail addresses: sunwei@qust.edu.cn (W. Sun), wghou@sdu.edu.cn (W. Hou).

trophotometry [26] have been devised for the sensitive rutin detection. Some of these methods involved complicated operation, high cost with large amounts of toxic organic solvents used or the separation processes. Rutin can be directly detected by different electrochemical methods due to its electroactivity, which show the advantages such as high sensitivity with simple and speedy procedure. Different kinds of working electrodes, such as glassy carbon electrode (GCE) [27], ionic liquid modified carbon paste electrode [28] and CeO₂ nanoparticle modified electrode [29], had been used for the electrochemical detection of rutin. The mechanism of rutin electro-oxidation is first a predissociation of a proton to give the monoanionic species, which is then oxidized to form a radical anion. The radical anion undergoes a second reversible 1e-oxidation to form dehydro-rutin. The latter species is rapidly dehydrated to yield the final product of 3',4'-diquinone.

In this paper the IL 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) was used in the preparation of an IL incorporated sol-gel solution, which was further mixed with graphite powder to make an IL modified CCE. The electrochemical behavior of IL-CCE was carefully characterized and rutin was selected as an example for the electrochemical application by IL-CCE. Experimental results indicated that IL-CCE showed great improvement to the electrocatalytic oxidation of rutin with enhanced electrochemical responses. The proposed method was applied to the rutin tablet samples detection with satisfactory results.

2. Experimental

2.1. Apparatus and reagent

Electrochemical measurements such as cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were performed on a CHI 750B electrochemical analyzer (Shanghai CH Instrument, China) with a conventional three-electrode system composed of a IL-CCE as working electrode, a platinum wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. Scanning electron microscopy (SEM) was recorded on a JSM-6700F scanning electron microscope (Japan Electron Company, Japan).

Ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄, Hangzhou Kemer Chemical Company), methyltrimethoxysilane (MTMOS, ≥98%, Sigma-Aldrich), graphite powder (average particle size 30 μm, Shanghai Colloid Chemical Plant) and rutin (Sinopharm Chemical Reagent Co. Ltd.) were used as received without further purification. 0.1 mol/L phosphate buffer solution (PBS) was used as the supporting electrolyte. All the other chemicals used were of analytical reagent grade and doubly distilled water was used throughout the experiments.

2.2. Fabrication of the modified electrode

Carbon ceramic electrode (CCE) was prepared according to the procedure proposed by Lev's group with a minor modification [2]. In general the solution of 1.5 mL methanol, 1.0 mL MTMOS and 70 μL hydrochloric acid (11.8 M) catalyst were ultrasonically mixed for 2 min until a clear and homogeneous solution resulted, then the carbon ceramic composite electrodes (CCE) were prepared by hand-mixing 3.75 g of graphite powder with the silica sol thoroughly.

Ionic liquid modified carbon ceramic electrode (IL-CCE) was fabricated with the following procedure. The solution of 1.5 mL methanol, 1.0 mL MTMOS and 140 μL EMIMBF₄ were ultrasonically mixed for 5 min, then 50 μL hydrochloric acid (11.8 M) catalyst was added and ultrasonically mixed for 2 min until a clear and homogeneous solution resulted. Then 3.75 g of graphite powder was mixed

with the silica sol solution thoroughly and a portion of the resulted paste was filled into one end of a glass tube ($\Phi = 4$ mm) with a copper wire inserted through the opposite end to establish an electrical contact. The surface of IL-CCE was smoothed on a piece of polishing paper just before use.

3. Results and discussion

3.1. Characteristics of the IL-CCE

The electrochemical properties of IL-CCE were carefully investigated by different electrochemical methods. Electrochemical impedance spectroscopy (EIS) can give information on the impedance changes of the electrode interface and the semicircle diameter in the EIS curve equals to the electron transfer resistance (R_{et}). The EIS of CCE and IL-CCE were recorded in 10.0 mmol/L [Fe(CN)₆]^{3-/4-} solution with the results shown in Fig. 1A. On the traditional CCE a big semicircle appeared with the R_{et} value as 1366 Ω, indicating a high electron transfer resistance existed (curve a). While on the IL-CCE a nearly straight line was got with the R_{et} value close to zero (curve b), indicating that the presence of high conductive IL in the CCE facilitated the electron transfer rate of the electrochemical probe. Cyclic voltammetric responses on CCE and IL-CCE were further recorded in a 10.0 mmol/L K₃[Fe(CN)₆] and 0.1 mol/L KCl mixture solution with the results shown in Fig. 1B. On the CCE the peak-to-peak potential separation (ΔE_p) was got as 0.200 V (versus SCE) with small redox peak currents (curve a), corresponding to a quasi-reversible electron transfer process. While on the IL-CCE the value of ΔE_p decreased to 0.053 V with greatly increase of the redox peak currents (curve b), indicating a more reversible electron transfer process. The redox peak currents on IL-CCE were 3.2 times higher than that of CCE, indicating that the presence of high conductive IL in the CCE resulted in the enhancement of the whole conductivity of the electrode. The experimental results exhibited the superiority of IL-CCE to CCE in terms of improved reversibility and enhanced electrochemical responses, which was attributed to the usage of IL as a modifier. The presence of IL in the carbon ceramic material can form a film on the graphite powder and filled into the void spaces inside the ceramic structure. So the presence of IL played an important role in improving the performance of the working electrode.

Cyclic voltammograms of IL-CCE in pH 7.4 PBS with different scan rates were further recorded with the results shown in Fig. 1C. The background current increased gradually with the increase of scan rate, indicating the presence of IL film on the electrode surface as the double layer. The observed capacitance of IL-CCE can be calculated according to the following equation [2]: $C_{app} = I/Sv$. Here I is the average of the positive and negative charging current obtained from the cyclic voltammetric curves at 0.4 V, which were performed in the 0.05 mmol/L pH 7.4 PBS between 0.0 and 0.6 V, S is the geometric area of the electrodes and v is the scan rate. By exploring the slope of the straight line of I versus v , the observed capacitance value of IL-CCE was found to be 29.79 μF/cm². By the same method the observed capacitance value of CCE was calculated as 3.35 μF/cm², which was much smaller than that of IL-CCE. The result also indicated the presence of IL film on the surface of IL-CCE, which acted as a double layer and resulted in the accessible capacitance of IL at the graphite surface.

Scanning electron microscopic (SEM) image of IL-CCE was further recorded with the image shown in Fig. 1D. It could be observed that a rough and uniform surface appeared without the micrometer sized flakes of graphite sheets. The result can be attributed to the high viscosity of IL present in the sol-gel solution, which can adhere the graphite powder together and filled into the void space between the graphite powder.

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