

Sensitive voltammetric determination of rutin at a carbon nanotubes-ionic liquid composite electrode

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Abstract A new composite electrode of multiwall carbon nanotubes (MWNTs) and 1-dodecyl-3-methylimidazolium hexafluorophosphate (DDMIMPF₆) was fabricated to determine rutin. This electrode showed very attractive electrochemical performances compared to other kinds of ionic liquid modified electrodes and notably improved sensitivity and stability. Electrochemical behavior of rutin at the composite electrode had been investigated in pH 2.09 Britton–Robinson buffer solution by cyclic voltammetry and square wave voltammetry. The experimental results suggested that the composite electrode exhibited an electrocatalytic activity toward the redox of rutin. The electrochemical parameters of rutin were calculated with the results of the charge transfer coefficient (α) and the standard rate constant (k_s) as 0.48 and 2.09 s⁻¹. Under the selected conditions, the reduction peak current was linearly dependent on the concentration of rutin in the range of 0.03–1.5 μ M, with a detection limit of 0.01 μ M ($S/N=3$). The relative standard deviation for six times successive determination of 1 μ M rutin was 1.6 %. The method was

successfully applied to the determination of rutin in tablets and urine samples without the influence of the coexisting substances. In addition, the MWNTs/DDMIMPF₆ composite electrode exhibits a distinct advantage of simple preparation, surface renewal, good reproducibility, and stability.

Keywords 1-dodecyl-3-methylimidazolium hexafluorophosphate · Multiwall carbon nanotubes · Rutin · Composite electrode

Introduction

Room temperature ionic liquids (RTILs) can be defined as liquid electrolytes composed entirely of ions which have melting points below 100 °C [1]. As a new “green” media, RTILs have attracted extensive attention due to their special characters such as thermal stability, relative inertness, negligible vapor pressure, good ionic conductivity, high polarity, low melting temperature, and wide electrochemical windows [2–5]. They have been widely used in various research fields, including electrochemistry [6, 7], synthetic chemistry [8, 9], material science [10], extraction processes [11], and biocatalysis [12]. The applications of ILs in electrochemistry and biological sciences have drawn considerable and increasing interest. A few ILs were used for composite modified electrode preparation [13–17]. Maleki et al. [13] used *n*-octylpyridinium hexafluorophosphate (OPFP) as a new binder to fabricate a carbon ionic liquid electrode (CILE), which provided a remarkable increase in the rate of electron transfer and decreased the overpotentials of some organic substances. Zhang et al. [15] constructed a carbon composite electrode (IL/CPE) using hydrophilic ionic liquid 1-amy1-3-methylimidazolium bromide as a modifier, demonstrating the electrocatalytic activity toward the redox of rutin. Liu et al. [16]

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fabricated a new CILE electrochemiluminescence sensor composed of graphite powder and 1-butyl-3-methylimidazoliumhexafluorophosphate (BMIMPF₆), and the detection limit of tripropylamine of the MCM-41-modified CILE was 7.2 nM, which was two orders of magnitude lower than that observed at the traditional CPEs. Natalya et al. [17] used 1-dodecyl-3-methylimidazolium hexafluorophosphate (DDMIMPF₆) and metallated phthalocyanine to fabricate iodide-selective screen-printed electrodes. Although various IL composite modified electrodes have already been reported, it is still significant to exploit more economical and efficient ILs to fit the need of composite modified electrodes.

Carbon nanotubes (CNTs) are considered an important group of nanomaterials with attractive electronic, chemical, mechanical, and physical properties [18, 19]. More importantly, as a kind of electrically conductive carbon-based materials, MWNTs have the excellent electrocatalytic properties to the redox reaction of different biomolecules [20, 21]. Their unique properties make them extremely attractive for fabricating chemical sensors, in general, and electrochemical ones [22], in particular. The use of electrodes prepared from carbon nanotubes and ILs have been reported in a number of articles [23, 24]. However, the preparation of CNTs/IL pastes and composites by direct mixing of the nanotubes with a suitable IL (either solid or liquid at room temperature) has been limited by the very high background currents, which could limit monitoring the analytical faradic current and limit the use of such useful combination. Kachoosangi et al. [25] fabricated a new composite electrode using multiwall carbon nanotubes and the ionic liquid *n*-octylpyridinium hexafluorophosphate (OPFP) with very low background currents, which improved sensitivity toward a number of compounds. This kind of electrode shows very attractive electrochemical performances, compared to other conventional electrodes using graphite and mineral oil, notably improved sensitivity, and stability. To our knowledge, 1-dodecyl-3-methylimidazolium hexafluorophosphate (DDMIMPF₆) has not been used as a binder combining with either carbon graphite or multiwall carbon nanotubes for an electrode preparation.

Rutin is a kind of flavonoid glycoside, called as vitamin P, which can dilute the blood, reduce capillary permeability, and lower blood pressure [26]. Many analytical methods, including capillary electrophoresis [27], adsorptive stripping voltammetry [28], chemiluminescence [29], HPLC [30], spectrophotometry [31], and electrochemistry [14, 15, 32–34] have been developed to determine rutin. Of these methods, the electrochemistry is preferred over others because of its low detection limits, fast response time, low cost, and simplicity. However, applications of multiwall carbon nanotubes combining with DDMIMPF₆ have never been used to fabricate electrochemical electrode for detection of rutin. In the present work, we fabricated a composite electrode by direct mixing of multiwall carbon nanotubes with DDMIMPF₆ to determine rutin. The

composite electrode was characterized by scanning electron microscopy (SEM). The electrochemical behaviors of rutin at the electrode were investigated in detail by cyclic voltammetry (CV) and square wave voltammetry (SWV). A novel method was developed to determine rutin with simple, sensitive, and rapid characteristics.

Experimental

Reagents and chemicals

Rutin was purchased from Wako (Japan) and used as received. 1-dodecyl-3-methylimidazolium hexafluoro-phosphate (purity >99 %) and *n*-octylpyridinium hexafluorophosphate (purity >99 %) were purchased from Shanghai Chengjie Chemical Co. Ltd.. Multiwall carbon nanotubes (MWNTs) were obtained from Shenzhen Nanotech. Port Co. Ltd., China. The compound rutin tablets were purchased from Tianjin Lisheng Pharmaceutical Co. Ltd., China. Graphite powder was from Shanghai Colloid Chemical Plant, China. All other chemicals used were of analytical grade and prepared with double distilled water. B–R buffer solution (0.04 M) of various pH values were used as supporting electrolyte. A 0.2-mM stock solution of rutin was dissolved with ethanol.

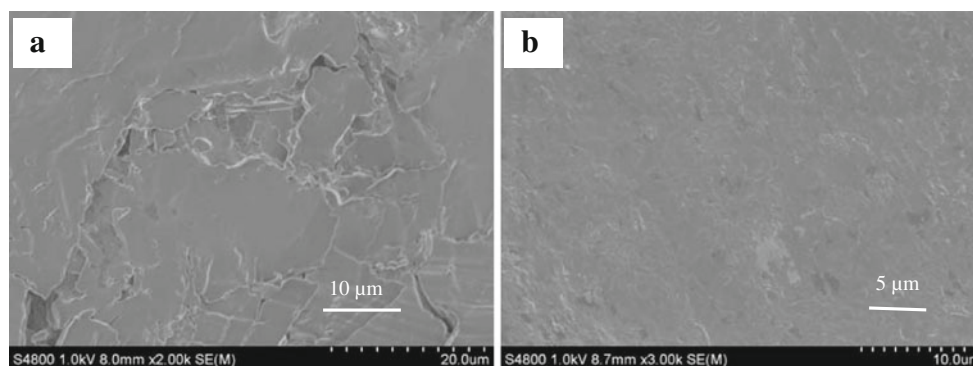
Apparatus

Cyclic voltammetry and SWV experiments were performed on a LK2005 electrochemical workstation (Tianjin Lanlike Chemistry & Electron High Technology Co. Ltd., China). A three-electrode system was used, including a saturated calomel electrode (SCE) as a reference electrode, a platinum wire electrode as an auxiliary electrode, and a MWNTs/IL composite electrode or a DDMIMPF₆-CPE as a working electrode. All the following potentials reported in this work were versus the SCE. The surface morphologies of the prepared electrodes were observed through S-4800 ultra-high resolution scanning electron microscopy.

Electrode fabrication

The MWNTs/DDMIMPF₆ composite electrode was fabricated with the following procedures: 0.5 g DDMIMPF₆ and 0.1 g MWNTs were mixed thoroughly in a mortar to form a uniform carbon nanotube-ionic liquid composite. The mixture was filled into one end of a quartz glass tube (3-mm diameter and 3-cm depth), and a copper wire was inserted through the opposite end to establish an electrical contact. Then the resulting electrode was heated at 80 °C for about 20 s. The preparation process of the MWNTs/OPFP composite electrode was similar to that of the MWNTs/DDMIMPF₆ composite electrode, but a replacement of the mixture with *n*-octylpyridinium

Fig. 1 SEM images of **a** DDMIMPF₆-CPE and **b** MWNTs/DDMIMPF₆ composite electrode



hexafluorophosphate. The ionic liquid of DDMIMPF₆ modified carbon paste electrode (DDMIMPF₆-CPE) was prepared by mixing graphite powder with ILs at a ratio of 1/5 (*w/w*), which was heated at 80 °C for about 20 s after being packed into the glass sleeve.

Analytical procedures

Except as otherwise stated, 0.04 M B–R buffer solution (pH 2.09) was used as supporting electrolyte for the determination of rutin. Voltammograms were obtained by scanning the potential from 0 to 800 mV (vs. SCE). The quantitative determination of rutin was achieved by measuring the oxidation peak currents using SWV. The compound rutin tablets were ground into powder and mixed adequately, dissolved in ethanol with the aid of ultrasonic agitation, and then diluted with buffer solution.

Results and discussion

Characterization of the MWNTs/DDMIMPF₆ composite electrode

The morphologies of the MWNTs/DDMIMPF₆ composite electrode and DDMIMPF₆-CPE are characterized by SEM observation, as shown in Fig. 1. The DDMIMPF₆-CPE surface is a multilayer surface distribution reflecting the arrangement of graphene sheets in graphite (Fig. 1a). The SEM image of the MWNTs/DDMIMPF₆ composite electrode presents more uniform and homogeneous and no clearly separated layers could be observed, indicating better and stronger interaction between the MWNTs and DDMIMPF₆ (Fig. 1b). This is due to the possible specific interaction between the imidazolium ion component and the π -electronic nanotube surface [36]. One can see the good adherence of this solid binder to nanotubes due to its high viscosity.

Potassium ferricyanide was selected as a probe to evaluate the performance of the MWNTs/IL electrodes and DDMIMPF₆-CPE. Figure 2 shows the cyclic voltammograms of the DDMIMPF₆-CPE, MWNTs/OPFP composite electrode,

and MWNTs/DDMIMPF₆ composite electrode in 1 M KCl solution with 5 mM K₃[Fe(CN)₆], respectively. For the DDMIMPF₆-CPE, the peak-to-peak potential separation (ΔE_p) is 180 mV, corresponding to an irreversible electron transfer process (Fig. 2a). While for the MWNTs/OPFP and MWNTs/DDMIMPF₆ composite electrodes (Fig. 2b, c), the ΔE_p values are decreased to 110 and 90 mV, respectively, indicating a quasireversible electron transfer process. This observation reflects the superior performance of carbon nanotubes over graphite as a conductive material. Furthermore, the peak currents of K₃[Fe(CN)₆] at the MWNTs/IL electrodes are much bigger than that at the DDMIMPF₆-CPE. The MWNTs/DDMIMPF₆ composite electrode is superior to the OPFP-based electrode (Fig. 2b) in terms of having a much lower background response. The experimental results above reflect the superiority of MWNTs/DDMIMPF₆ composite electrode to two other ionic liquid modified electrodes, which are attributed to improve reversibility and lower background response. Otherwise, the melting point of DDMIMPF₆ (46 ± 1 °C) is much higher compared with BMIMPF₆, being at solid state at room temperature. Owing to the lubrication property of CNTs, BMIMPF₆-CNT paste electrode tends to drop a few of its component into solution, and its reproducibility is worse than that of MWNTs/DDMIMPF₆ composite electrode.

Electrodes with a ratio of MWNTs/DDMIMPF₆ ranging from 90 to 10 % (*w/w*) were prepared. When the ratio of

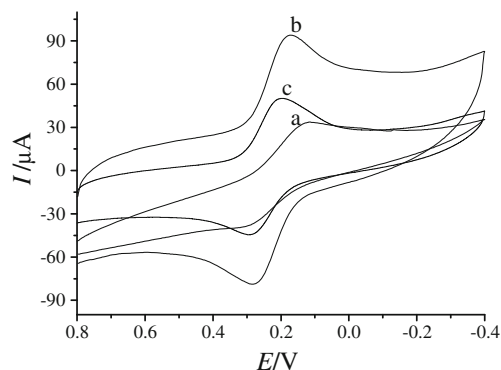
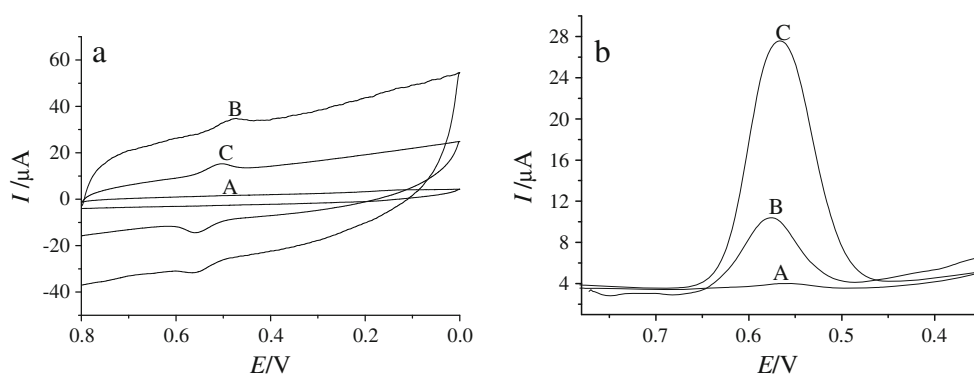


Fig. 2 CV curves of **a** DDMIMPF₆-CPE, **b** MWNTs/OPFP composite electrode, and **c** MWNTs/DDMIMPF₆ composite electrode in 1 mM KCl solution with 5 mM K₃[Fe(CN)₆], at scan rate of 0.10 V s⁻¹

Fig. 3 CV (a) and SWV (b) curves of 5 μM rutin in pH 2.09 B–R buffer solution at A DDMIMPF₆-CPE, B MWNTs/OPFP composite electrode, and C MWNTs/DDMIMPF₆ composite electrode. In scan rate 0.10 V s^{-1} (a) and in amplitude 0.03 V, frequency 10 Hz, and quiet time 130 s (b)



MWNTs/DDMIMPF₆ was less than 60 %, the prepared electrodes yielded consistent composites and improved electrochemical behavior after compressions and heating to the melting point of DDMIMPF₆. However, the electrode prepared with a MWNTs/DDMIMPF₆ ratio of 20 % (*w/w*) offered the lowest background and was used in further studies.

Voltammetric behavior of rutin at the MWNTs/DDMIMPF₆ composite electrode

Figure 3 shows the electrochemical responses of these three paste electrodes to 5 μM rutin in B–R solution (pH 2.09), respectively. At the DDMIMPF₆-CPE, almost no signal can be observed (curve a in Fig. 3), indicating that it has the very poor sensitivity to rutin. However, well-shaped CV peaks have been reported for rutin at graphite–wax CPEs [35]; it is possible that DDMIMPF₆ is not a good binder for carbon paste in comparison with wax. At the MWNTs/IL composite electrodes, rutin shows a pair of redox peaks (curves b and c in Fig. 3a). The redox peak potentials are at 559 mV (E_{pa}) and 475 mV (E_{pc}) at the MWNTs/OPFP composite electrode, with oxidation peak potential (E_{pa}) of 557 mV and reduction peak potential (E_{pc}) of 506 mV at the MWNTs/DDMIMPF₆ composite electrode. However, the peak current of rutin at the MWNTs/DDMIMPF₆ electrode is much larger than that at the MWNTs/OPFP electrode; it is about 3.6 times of that at the MWNTs/OPFP electrode by SWV (Fig. 3b). Thus, this new composite electrode exhibited better electrocatalytic activity toward the redox of rutin. This result further testified its superiority to DDMIMPF₆-CPE and MWNTs/OPFP composite electrode, indicating that the use of DDMIMPF₆ and carbon nanotubes facilitated the electron transfer between rutin and electrode. So, the significant improvement of the reversibility and sensitivity was achieved on the DDMIMPF₆ modified new electrode.

Influence of supporting electrolyte and pH

The types of supporting electrolytes play a key role in the voltammetric responses of rutin. The current responses of

1 μM rutin were estimated in different supporting electrolytes such as $\text{Na}_2\text{HPO}_4\text{--NaH}_2\text{PO}_4$, NaAc--HAc , citric acid–sodium citrate, and B–R buffer solution. The results showed that higher peak current and better peak shape could be obtained in B–R buffer solution. Therefore, B–R buffer solution was adopted.

The effect of the pH of B–R buffer solution, which ranged from 1.89 to 7.0, on the electrochemical response of 1 μM rutin was investigated by SWV. In Fig. 4, it could be seen that the maximum value of reduction peak current is at the pH value of 2.09 and decreases gradually with the further increase of buffer pH. Therefore, pH 2.09 was chosen for the determination of rutin. It was also found that the reduction peak potential was negatively shifted with the increase of pH value, and the relationship between E_{pc} and pH was linear. The linear regression equation was obtained as $E_{\text{pc}} = -0.057 \text{ pH} + 0.69$ ($n = 5$, $r = 0.9995$). The slope of -0.057 is close to the theoretical value of -0.059 V/pH at 25 °C. According to the equation $-0.057x/n = -0.059$, where n is the electron transfer number and x is the number of hydrogen ion participating in the reaction, the uptake of electron was accompanied by an equal number of hydrogen ion and $x = n = 2$. Thus, the electro-oxidation reaction of rutin on the MWNTs/DDMIMPF₆ composite electrode was a two-electron with two-proton process, and the electrode reaction equation was the same as described in reference [14].

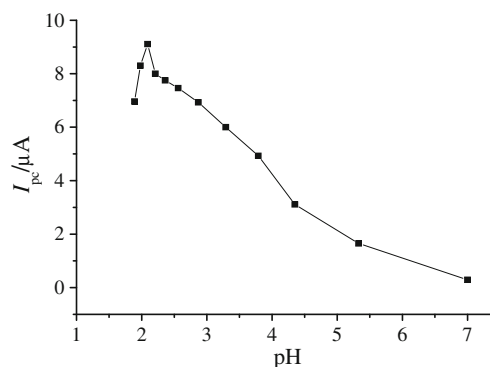
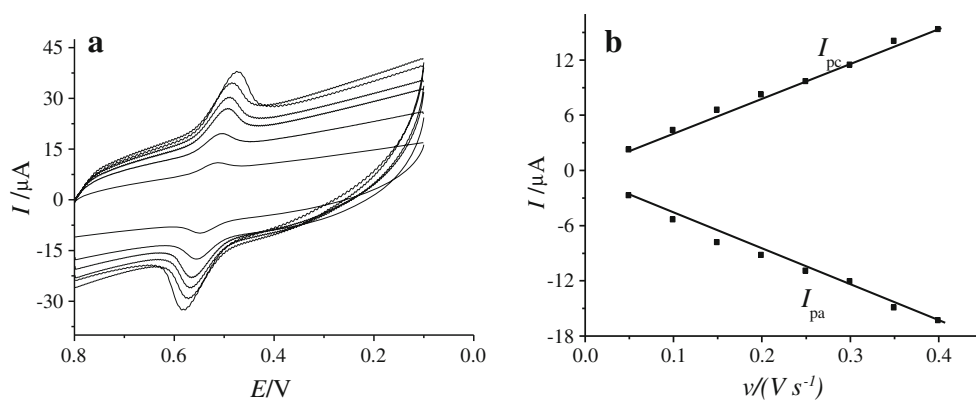


Fig. 4 pH dependence of reduction peak currents with 1 μM rutin. Amplitude 0.03 V, frequency 10 Hz, and quiet time 130 s

Fig. 5 **a** CV curves of 5 μM rutin in pH 2.09 B–R buffer solution at the MWNTs/DDMIMPF₆ composite electrode; scan rate (inner to outer): 0.05, 0.10, 0.20, 0.25, 0.30, and 0.40 V s⁻¹. **b** Linear relationship of I_p vs. ν



Influence of rutin concentration and potential scan rate

The influence of potential scan rate (ν) on the electrochemical response of 5 μM rutin was studied by CV in the range from 0.05 to 0.4 V s⁻¹, and the results were shown in Fig. 5a. It can be seen that with the increase of the scan rate, the redox peak current increased gradually, and there were good linear relationships between the peak currents and ν (Fig. 5b). The regression equation was I_{pc}=0.556+37.27ν (r=0.9980); I_{pa}=-1.459-37.86ν (r=0.9996), indicating that the redox process of 5 μM rutin at the MWNTs/DDMIMPF₆ composite electrode was adsorption-controlled.

As shown in Fig. 5a, with the increase of ν, the oxidation peak potential positively shifted and the reduction peak potential negatively shifted, indicating that the redox reversibility of rutin was impaired. The peak potential and log ν showed a linear relationship: the regression equations were obtained as E_{pa} (V)=0.588+0.0317 log ν (n=6, r=0.996) and E_{pc} (V)=0.467-0.0334 log ν (n=6, r=0.997). According to the Laviron's Eq. [37], the charge transfer coefficient α can be calculated to be 0.48. And k_s, the electrode reaction constant, is expressed in Eq. (1):

$$\log k_s = \alpha \log(1 - \alpha) + (1 - \alpha) \log \alpha - \log \frac{RT}{nF\nu} - \frac{(1 - \alpha)n\alpha F \Delta E_p}{2.3RT} \tag{1}$$

where α is the charge transfer coefficient, n the number of electron transfer, ν the scan rate, ΔE_p the peak-to-peak potential separation, and F the Faraday's constant. The resulting value of k_s was 2.09 s⁻¹.

Influence of accumulation time, potential and SWV parameters

For considering the adsorption of rutin on the MWNTs/DDMIMPF₆ composite electrode surface, SWV technique coupled with accumulation procedure was used for the study. With the increase in accumulation time, the peak current increased. When accumulation time was 130 s, the peak current achieved a maximum value. So 130 s was chosen as the accumulation time. The accumulation potential had little effect on the peak current of 1 μM rutin in the range from 1.3 to 0.8 V. To reduce scanning time, 0.8 V was selected as the accumulation potential.

The influence of the square wave parameters such as amplitude and frequency on the I_{pc} was also investigated. The peak current increased with the increasing of the square wave amplitude from 0.005 to 0.075 V or square wave frequency in the range of 5–45 Hz, but the peak potential shifted to less negative values and the peak changed unshapely. So 0.030 V was chosen as the optimum amplitude, and 10 Hz was chosen as the optimum frequency.

Fig. 6 **a** SWV curves of different concentrations of rutin in B–R buffer solution of pH 2.09 at the MWNTs/DDMIMPF₆ composite electrode: A 0.03, B 0.3, C 0.6, D 1, and E 1.5 μM. Amplitude 0.03 V, frequency 10 Hz, and accumulation time 130 s. **b** Calibration curve, insert: curves of I_{pc} vs. low rutin concentration

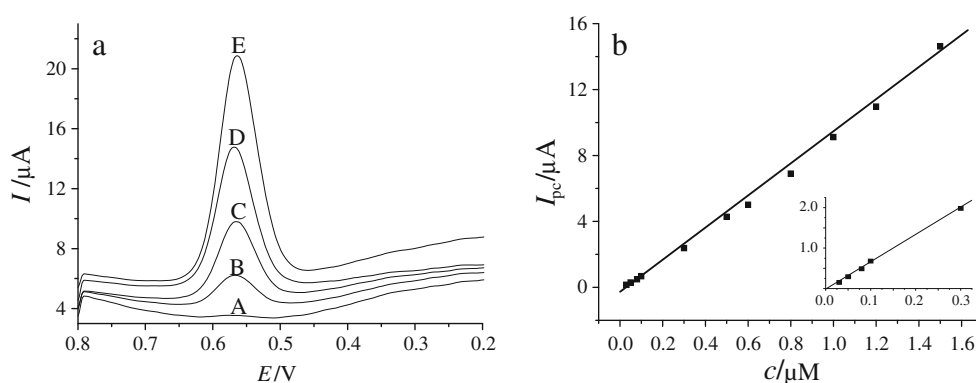


Table 1 Comparison of different modified electrodes for rutin determination

Electrode	Line range (μM)	Detection limit (μM)	Reference
PABSA/GCE	0.25–10	0.1	[32]
SWNTs/Au	0.02–5	0.01	[33]
PVP/CPE	0.39–13	0.15	[34]
BPPF ₆ /CPE	0.5–100	0.358	[14]
MWNTs/DDMIMPF ₆ composite electrode	0.03–1.5	0.01	This work

Determination of rutin using SWV

Figure 6a presents SWV curves of five different concentrations of rutin at the MWNTs/DDMIMPF₆ composite electrode under the optimum conditions. A linear relationship (Fig. 6b) could be established between I_{pc} and the concentration of rutin in the range of 0.03–1.5 μM . In the above scope of concentration in sections (0.03–0.3 μM and 0.3–1.5 μM), the linear regression equation was $I_{pc}=6.768 \times 10^6 c - 0.040$ ($r=0.9994$) and $I_{pc}=10.106 \times 10^6 c - 0.909$ ($r=0.9980$) respectively, where I_{pc} was the reduction peak current in microampere and c was the rutin concentration in molar, where the detection limit of rutin was found to be 0.01 μM ($S/N=3$). In this paper, the proposed method showed a significant improvement with simple electrode preparation and low cost.

Compared with other kinds of modified electrode, the proposed new composite electrode exhibited sensitivity for rutin determination, and the results are listed in Table 1. We can see that this method can provide comparable linear range and detection limit with a simple electrode preparation procedure.

The repeatability and stability of MWNTs/DDMIMPF₆ composite electrode

To estimate the reproducibility of the proposed electrode with the SWV method, the RSD of six times successful measurement, the peak current of 1 μM rutin at an MWNTs/DDMIMPF₆ composite electrode was calculated as 1.6 %, demonstrating the good reproducibility of the proposed electrode. The stability was also studied. After

Table 2 Determination of rutin in drug tablets by SWV ($n=5$)

Sample	Specified (mg/tablet)	Detected (mg/tablet)	RSD (%)	Added (mg L ⁻¹)	Found (mg L ⁻¹)	Average recovery (%)
1	20	19.9±0.2	1.01	0.122	0.117±0.03	95.7
2	20	20.1±0.5	2.05	0.122	0.125±0.02	102.5
3	20	20.0±0.5	2.16	0.122	0.126±0.04	103.3

Table 3 Determination of rutin in urine sample by SWV ($n=5$)

Sample	Added (μM)	Found (μM)	Average recovery (%)
1	0.5	0.49±0.06	98
2	0.6	0.62±0.02	103
3	0.7	0.67±0.03	96

the MWNTs/DDMIMPF₆ composite electrode was stored for 2 weeks, no apparent decrease of the electrochemical response to rutin was observed, which indicated the good stability of the electrode.

Interferences

The influence of some foreign compounds was examined. In some cases, their interference can be overcome by using the reduction peak for determination. The inorganic ions and organic compounds commonly existed in pharmaceuticals and biological samples. Ascorbic acid (AA) is the main coexisting substance in compound rutin tablet samples, so its effects on the determination of 1 μM rutin were studied. The reduction peak of AA and rutin was located at the different potential position (358 mV, 571 mV) by SWV and did not interfere with each other, while the oxidation peak on the traditional CPE could not be distinguishable due to the oxidation of AA and rutin simultaneously and their peak potentials were indistinguishable.

It was also observed that for 1 μM rutin, the 1,000 times of Cd²⁺, Pb²⁺, Ca²⁺, V_{B1}, Cu²⁺, Fe³⁺, Na⁺, K⁺, CO₃²⁻, PO₄³⁻, Cl⁻, NO₃⁻, aminoacetic acid, glucose, and citrate did not interfere with the determination of rutin (i.e., the variation of peak current was smaller than 10 %). The tolerance limit of additives to 1 μM rutin was 50 times for UA, ten times for dopamine and for epinephrine, and two times for quercetin. But quercetin is not the coexisting substance in drug tablets and urine sample, which is acceptable for rutin determination.

Real samples analysis

In order to fit into the linear range of the method, drug tablets and urine sample for the detection were accurately diluted with the supporting electrolyte. The determination of rutin was conducted by the proposed method. As shown in Table 2, the results obtained by the proposed method are in

good agreement with label amount. From Table 2, the recovery of five independent experiments varied from 95.9 to 103.3 %, and the content of rutin is calculated to be 20.12 mg per tablet (the declared content is 20 mg per tablet), demonstrating the accuracy of the proposed method. Meanwhile, as a preliminary evaluation of the validity of the new composite electrode, the recovery of rutin in urine sample was tested. Different contents of rutin standard solutions were added to the diluted (50-fold) urine sample, and the results were listed in Table 3. The experimental results demonstrated that the proposed methods could be efficiently used for the determination of rutin.

Conclusions

An MWNTs/DDMIMPF₆ composite electrode was fabricated and characterized by SEM and voltammetry. Since the mixture of the carbon nanotubes and the DDMIMPF₆ have the unique features and properties, the electrode shows excellent electrochemical behavior such as high conductivity, wide electrochemical windows, and good stability. The electrochemical behavior of rutin at the composite electrode was investigated in pH 2.09 B–R buffer solution. Compared with its response at MWNTs/OPFP composite electrode and DDMIMPF₆-CPE, the electrochemical sensitivity of rutin at the proposed electrode was improved dramatically. The presence of coexisting substances such as AA shows no interferences to the determinations. The proposed method was sensitive and simple for the determination of rutin, and it can be successfully applied to the determination of rutin in tablets and in urine samples which showed good electrochemical characteristics and analytical performance.

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