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

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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 (EMIMBF$_4$) 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.

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 filed 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-flammatory, anti-tumor and anticancer [22]. Many analytical methods such as capillary electrophoresis [23], chemiluminescence [24], HPLC [25] and spec-

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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 CeO_2 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 from a radical anion. The radical anion undergoes a second reversible 1e-oxidation to from 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 ($EMIMBF_4$) 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 ($EMIMBF_4$, Hangzhou Kemer Chemical Company), methyltrimethoxysilane (MTMOS, $\geq$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 $EMIMBF_4$ 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 $K_3[Fe(CN)_6]$ 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]: $\mathrm{Capp} = I/S\upsilon$. 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 υ is the scan rate. By exploring the slope of the straight line of I versus υ, the observed capacitance value of IL-CCE was found to be 29.79 μF/cm^2. By the same method the observed capacitance value of CCE was calculated as 3.35 μF/cm^2, 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.

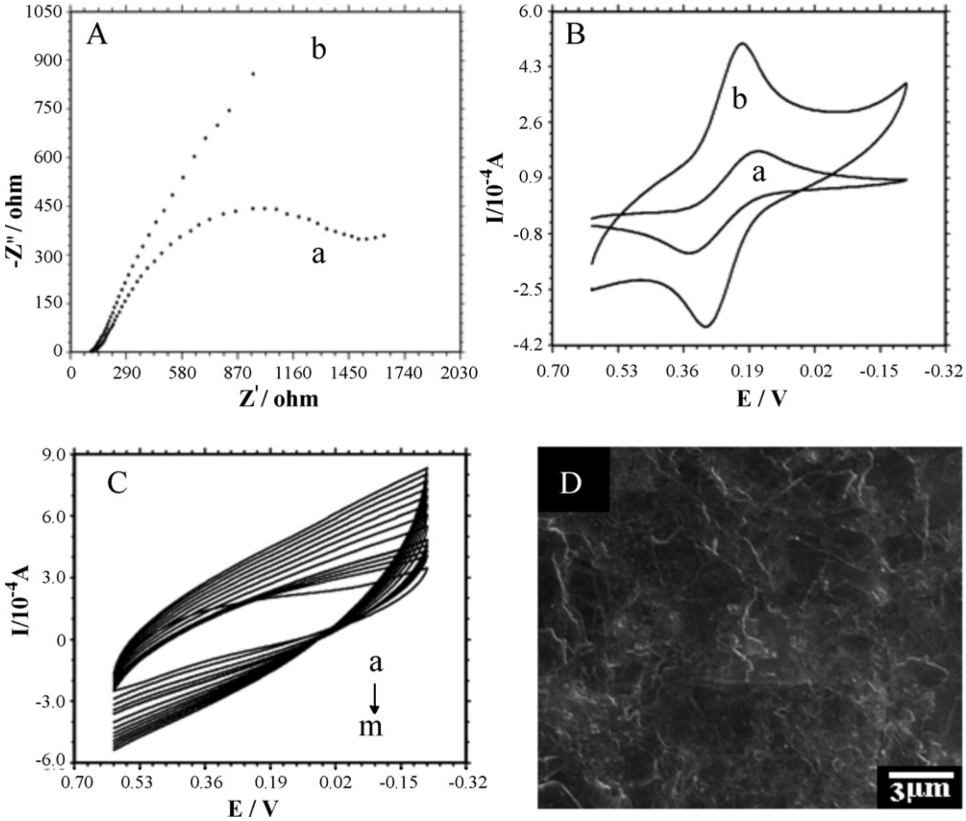

Fig. 1. (A) EIS of (a) CCE, (b) IL-CCE in the presence of 10.0 mmol/L $[Fe(CN)_6]^{-3/-4}$ and 0.1 mol/L KCl with the frequencies swept from 10^4 to 10^{-2} Hz. (B) Cyclic voltammograms of (a) CCE, (b) IL-CCE in pH 2.5 PBS with the scan rate of 20 mV/s. (C) Cyclic voltammograms of IL-CCE in 0.05 mol/L pH 7.4 phosphate buffer solution with different scan rates (from a to m: 10, 30, 50, 70, 100, 150, 200, 250, 300, 350, 400, 450, 500 mV/s, respectively). (D) SEM image of IL-CCE.

3.2. Electrochemical behaviors of rutin on IL-CCE

Fig. 2 showed the cyclic voltammograms of 100 μmol/L rutin on different electrodes in pH 2.5 PBS. Both on CCE (curve a) and IL-CCE (curve b) a pair of well-defined redox peaks appeared, indicating the electrochemical reaction of rutin had took place on the working electrode. The electrochemical reaction mechanism of rutin on the solid electrodes had been clearly elucidated with a two electron and two proton oxidation processes that give a final product of 3′,4′-diquinone [27]. On the traditional CCE a pair of redox peaks appeared (curve a) with the redox peak potential as 530 mV (Epa) and 430 mV (Epc) (versus SCE). The anodic (Ipa) and cathodic (Ipc) peak current was recorded as −15.66 and 12.36 μA, respectively. The ΔE_p value was got as 100 mV and the ratio of Ipa/Ipc was 1.27. Curve b was the cyclic voltammogram of rutin on IL-CCE. A pair of well-defined redox peaks was observed with improved electrochemical behaviors. The redox peak potentials were located at 526 mV (Epa) and 448 mV (Epc). The anodic (Ipa) and cathodic peak current (Ipc) were recorded as −29.08 and 27.58 μA, which was about two times higher than that of CCE. The ratio of redox peak current (Ipa/Ipc) was calculated to be 1.05 with ΔE_p as 78 mV, indicating a more reversible electrode reaction. The results showed that the presence of IL in CCE exhibited the advantages such as high conductivity and inherent catalytic ability, which played an important role in improving the reversibility and enhancing the sensitivity. Based on the increase of redox peak current, a new electroanalytical method for rutin detection was further developed.

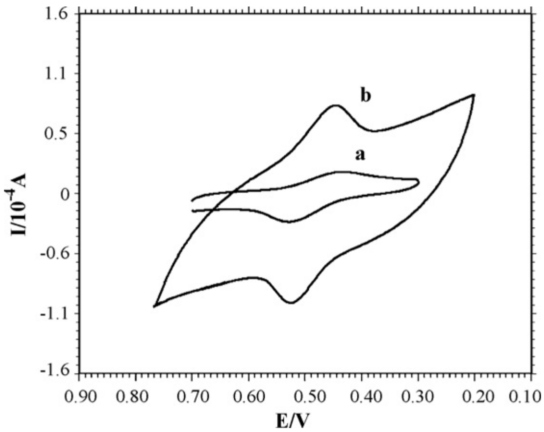

Fig. 2. Cyclic voltammograms of (a) CCE and (b) IL-CCE in pH 2.5 PBS containing 100.0 μmol/L rutin with the scan rate of 20 mV/s.

The influence of scan rate on the cyclic voltammetric responses of 100.0 μmol/L rutin was investigated in the range from 10 to 100 mV/s. As shown in Fig. 3, both the redox peak current increased gradually with the increase of scan rate. The redox peak currents exhibited a linear relationship with the square root of scan rate ($\upsilon^{1/2}$), which indicated a diffusional-controlled electrode process. Two linear regression equations were calculated as Ipc (μA) = 4.211$\upsilon^{1/2}$ (V/s) – 0.319 (γ = 0.998) and Ipa (μA) = –4.698$\upsilon^{1/2}$ (V/s) + 0.372 (γ = 0.997). With the increase of scan rate the redox peak potential also shifted with the increase of ΔE_p. The redox peak potential and logarithm of scan rate ($\ln \upsilon$) also exhibited a good linear relationship with the regression equations as Epc (V) = –0.041 $\ln \upsilon$ + 0.275 (γ = 0.999) and Epa (V) = 0.038 $\ln \upsilon$ + 0.613 (γ = 0.998). According to the Nicholson's equations [30], the electrochemical parameters such as the charge transfer coefficient (α), the number of electron transfer (n) and the electrode reaction rate constant (ks) of rutin on the IL-CCE were further calculated with the results as 0.481, 1.85 and 3.27 s^{-1}, respectively.

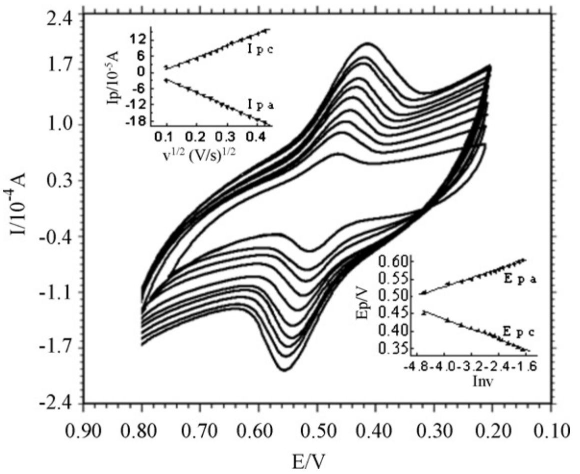

Fig. 3. Cyclic voltammograms of 100.0 μmol/L rutin with different scan rates (υ) on IL-CCE in pH 2.5 PBS (from the inner to the outer are 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mV/s, respectively). Insets are the linear relationship of redox peak current (Ip) versus $\upsilon^{1/2}$ and linear relationship between redox peak potentials (Ep) with ln υ.

Since the electrode process was diffusional-controlled, the chronocoulometric experiment was carried out to calculate the diffusion coefficient (D) of rutin. Fig. 4 exhibited the typical chronocoulometric curves under the selected conditions. The relationship between Q and $t^{1/2}$ was constructed with the linear regression equation as Q (mC) = $0.671t^{1/2} + 0.087$ ($\gamma = 0.999$). According to Anson's equation [31]: $Q = 2nFAD^{1/2}ct^{1/2}/\pi^{1/2} + Q_{dl} + nF\tau$, the diffusion coefficient (D) was calculated as 2.95×10^{-3} cm^2/s, which was larger than a previous reported value of 2.0×10^{-5} cm^2/s [32] and the result indicated a fast electron transfer process of rutin on the IL-CCE.

3.3. Influence of buffer pH

The influence of buffer pH on the electrochemical responses of 100.0 μmol/L rutin was further investigated in the pH range from 1.6 to 4.5 with cyclic voltammograms shown in Fig. 5A. The relationships of the oxidation peak current and peak potential with buffer pH were also plotted. With the increase of buffer pH the peak potential shifted to the negative direction, indicating that protons took part in the electrode reaction. The relationship between the formal peak potential ($E^{0\prime}$) and pH was calculated with the results as $E^{0\prime}$ (V) = -0.058 pH + 0.587 ($\gamma = 0.998$). The slope value of 58 mV/pH was close to the theoretical value of 59 mV/pH. Based on the equation: $-0.058x/n = -0.059$, so the ratio of electron (x) and proton (n) taking part in the electrode reaction was 1 and the value of electron (x) was close to 2. From Fig. 5A it can also be seen that the oxidation peak current decreased with the oxidation peak potential was less positive if the pH of buffer was increasing, which exhibited the higher antioxidation properties of the rutin. The maximum value of oxidation peak current was got at the pH value of 2.5 and decreased gradually with the further increase of buffer pH (Fig. 5B). This is related to the proton taking part in the electrode reaction, which becomes more difficult in basic solutions due to the shortage of proton. Therefore, pH 2.5 buffer solution was selected for rutin detection.

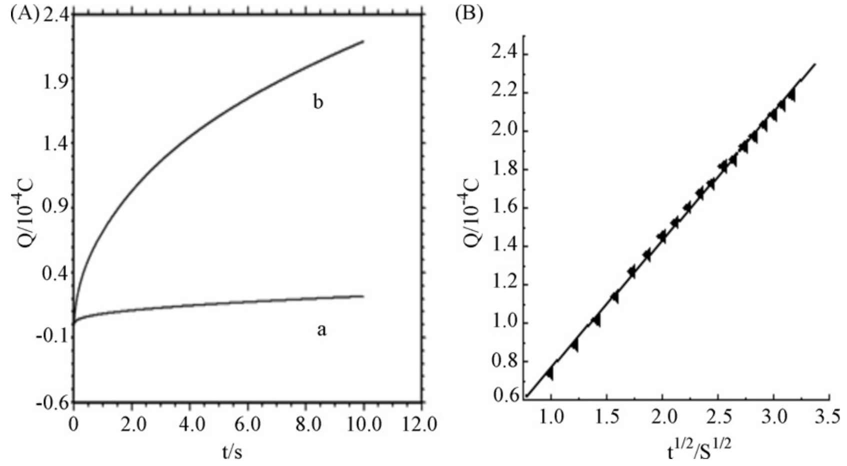

Fig. 4. (A) Chronocoulometric curve of IL-CCE in (a) pH 2.5 PBS and (b) pH 2.5 PBS containing 100.0 μmol/L rutin. (B) Linear relationship of Q and $t^{1/2}$.

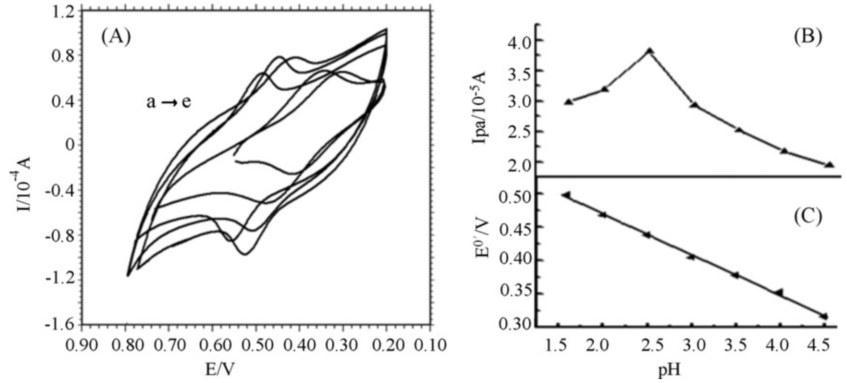

Fig. 5. (A) Cyclic voltammograms of 100.0 μmol/L rutin on IL-CCE with different pH PBS (from a to e are 1.6, 2.5, 3.0, 4.0, 4.5, respectively) with the scan rate of 20 mV/s. (B) The relationship between the anodic peak current (Ipa) and pH. (C) The relationship between the formal potential ($E^{0\prime}$) and pH.

Table 1
Determination results of rutin in tablet samples ($n = 3$).

Sample	Specified (μmol/L)	Detected (μmol/L)	Added (μmol/L)	Detected (μmol/L)	RSD (%)	Recovery (%)	Standard method (μmol/L)
B080302	60.2	60.1	30.1	30.3	1.29	100.66 ± 0.24	60.3 ± 0.1
090904	60.2	59.9	30.1	30.2	2.47	100.33 ± 0.37	60.2 ± 0.2
H37023126	60.2	60.0	30.1	29.9	1.65	99.00 ± 0.56	59.9 ± 0.1

3.4. *DPV of rutin on the modified electrode*

Differential pulse voltammetry (DPV) was used for the rutin detection with high sensitivity and the typical differential pulse voltammograms were shown in Fig. 6. Under the selected conditions the DPV oxidation peak currents increased linearly with rutin concentration in the range from 0.3 to 100.0 μmol/L with the linear regression equation as Ipa (μA) = −0.156*C* (μmol/L) − 0.134 ($\gamma = 0.995$) and the detection limit as 0.09 μmol/L (3σ). The relative standard deviation (RSD) of seven successive detections of 100.0 μmol/L rutin with the same electrode gave a result of 2.4%, indicating the good reproducibility of the IL-CCE. The modified electrode was stored in a refrigerator at 4 °C for 15 days with the peak current decreased for 4.1% and 30 days with the peak current decreased for 9.2%. The results showed good storage stability for the IL-CCE. Six electrodes were made by the same procedure independently and the RSD value for the determination of 100.0 μmol/L rutin was calculated as 3.7%, which indicated the electrode had good repeatability.

3.5. *Samples determination*

The fabricated electrode was further applied to the rutin determination in compound rutin tablet samples, which were obtained from Shanxi Yunpeng Pharmaceutical Co. Ltd. (B080302), Shanghai Zhaohui Pharmaceutical Co. Ltd. (090904), Qingdao Huanghai Pharmaceutical Co. Ltd. (H37023126). The rutin sample solutions were prepared by grinding two pieces of rutin tablets (20 mg/tablets) in the agar, then transferred to a 10 mL calibration tube and diluted to the scale with ethanol. A 100 μL solution was taken and further diluted with pH 2.5 PBS in a 10 mL calibration tube. Table 1 presented the three parallel determinations of rutin ($n = 3$) in pharmaceutical formulations by the IL-CCE with standard addition method and the results of same samples detected by the official methods of analysis proposed by AOAC International [33]. It can be seen that the results were satisfactory with the recovery in the range from 99.00 to 100.66%. Also no significant difference appeared between the results obtained by the two different methods. So the proposed electrode could be efficiently applied to rutin detection in the commercial drug samples.

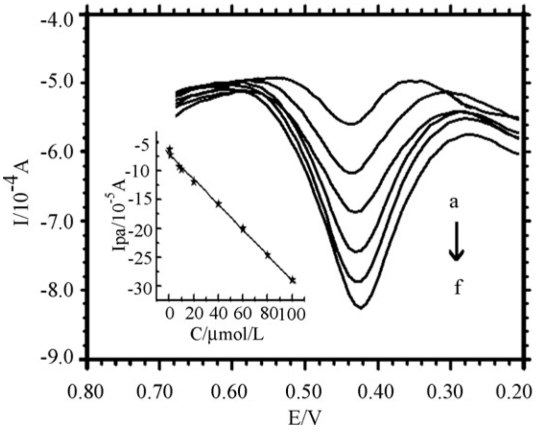

Fig. 6. Differential pulse voltammograms of various concentrations rutin on IL-CCE (from a to g: 0.3, 1.0, 5.0, 10.0, 80.0, 100.0 μmol/L, respectively). Inset is the relationship of the anodic peak current with the rutin concentration.

4. Conclusion

In this paper ionic liquid (IL) EMIMBF$_4$ was used in the preparation of a new kind of modified carbon ceramic electrode (CCE). The electrochemical performance of IL-CCE was greatly increased with good reversibility and increased sensitivity due to the presence of IL in the electrode. Electrochemical behaviors of rutin on the IL-CCE were carefully investigated with the electrochemical parameters calculated. Based on the oxidation peak current rutin can be detected in the concentration range from 0.3 to 100.0 μmol/L with the detection limit as 0.09 μmol/L (3σ). The proposed electrode showed the advantages including high sensitivity, wide linear calibration range, good reproducibility and stability, which was further used for rutin tablet samples determination with good recovery.

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