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Gold nanoparticles/ethylenediamine/carbon nanotube modified glassy carbon electrode as the voltammetric sensor for selective determination of rutin in the presence of ascorbic acid

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ABSTRACT

In this paper, the electrochemical behavior of rutin on a gold nanoparticles/ethylenediamine/multi-wall carbon nanotubes modified glassy carbon electrode (AuNPs/en/MWNTs/GCE) was investigated and the electrochemical parameters of rutin were calculated. Rutin effectively accumulated on the AuNPs/en/MWNTs/GCE and caused a pair of redox peaks at around 487 mV and 432 mV (vs. SCE) in 0.1 M phosphate buffer solution (pH 3.5). Under optimized conditions, the anodic peak current was linear to the rutin concentration in the range of 4.8×10^{-8} M–9.6×10^{-7} M. The regression equation was: $i_{pa} = 2.3728C_{rutin} - 0.1782$ (i_{pa}: 10^{-5} A, C_{rutin}: μM, $r = 0.9973$). The detection limit of 3.2×10^{-8} M was obtained. The proposed method was successfully used to the determination of rutin content in tablet samples with satisfactory results.

1. Introduction

Rutin (3′,4′,5,7-tetrahydroxyflarone-3β-*d*-rutinoside), as a kind of the most abundant bioactive flavonoid called as vitamin p, is widely present in multivitamin preparations and more than 70 herbal remedies. As a natural flavone derivative, rutin has a wide range of physiological activities including anti-inflammatory, hemostat, antibacterial anti-tumor and anti-oxidant [1–3]. It is always used clinically as the therapeutical medicine [4,5]. For example, it can be applied to the treatment of diseases, such as capillary bleeding by diluting the blood, reducing capillary permeability and lower blood pressure [6]. Hence, it is necessary to develop simple, sensitive, economical and efficient techniques for the determination of rutin. Many methods have been employed for the analysis of rutin, such as capillary electrophoresis [7], adsorptive stripping voltammetry [8], chemiluminescence [9], high-performance liquid chromatography (HPLC) [10], sequential injection analysis [11] and spectrophotometry [12]. Nevertheless, some of these methods, such as the chromatographic methods are time-consuming, expensive, and need complicated preconcentration, multisolvent extraction as well as trained technicians. Compared with other methods, electrochemical methods are characterized by simplicity, high sensitivity, good stability, low-cost instrumentation, small dimensions and on-site monitoring [13]. Thus, different modified electrodes have been exploited for the determination of rutin because rutin is an electroactive compound [14–26]. The complicated electrochemical oxidation mechanism of rutin has been revealed by Ghica and Brett [14]. The comparison of different modified electrodes for rutin determination was displayed in Table 1. As can be seen from Table 1, the lower detection limits of rutin were achieved at the in situ plated lead film electrode as well as the hanging mercury drop electrode [24,25]. However, the toxicity of the lead and mercury was the greatest drawback in the practical application of these electrodes. The maximum contaminant levels in drinking water for lead 15 μg L^{-1} and mercury 2 μg L^{-1} were declared by EPA [27].

At present, scientists have paid increasing attention to nano-scaled materials and their application in analytical chemistry due to their physicochemical characteristics. Gold nanoparticles possess some good properties, such as quantized charging/discharging, conductivity and catalytic and photocatalytic activity [28–31]. Voltammetric sensors based on gold nanoparticles for determination of biological molecule have received much interesting due to their good stability and biocompatibility [32]. Carbon nanotubes (CNTs) are another novel nano-material, which have captured worldwide researchers' interests since its discovery in

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Table 1
Comparison of different modified electrodes for rutin determination.

Electrode	Linear range/M	Detection limit/M	References
GSR	5.0×10^{-8}–50.0×10^{-8}	1.8×10^{-8}	[15]
2-Aminoethanethiol/Au	8.0×10^{-6}–2.5×10^{-4}	3.2×10^{-6}	[16]
CeO_2/Au	5.0×10^{-7}–5.0×10^{-4}	2.0×10^{-7}	[17]
Copper(II)-resin electrode	9.90×10^{-7}–8.07×10^{-6}	2.65×10^{-8}	[18]
IL/CPE	5.0×10^{-7}–1.0×10^{-4}	3.58×10^{-7}	[19]
MWNTs/β-CD/GCE	4.0×10^{-7}–1.0×10^{-3}	2.0×10^{-7}	[20]
SWNTs/Au	2.0×10^{-8}–5.0×10^{-6}	1.0×10^{-8}	[21]
PVP/CPE	3.9×10^{-7}–1.3×10^{-5}	1.5×10^{-7}	[22]
IL/CPE	4.0×10^{-8}–1.0×10^{-5}	1.0×10^{-8}	[23]
LF/GCE	5×10^{-10}–1×10^{-8}	2.5×10^{-10}	[24]
HMDE	2.0×10^{-9}–85.0×10^{-9}	5.0×10^{-10}	[25]
MCM-41/CPE	2.0×10^{-8}–1.0×10^{-6}	1.5×10^{-8}	[26]
AuNPs/en/MWNTs/GCE	4.8×10^{-8}–9.6×10^{-7}	3.2×10^{-8}	This paper

1991 [33]. CNTs have the ability to hold the potential for wide applications in electrochemistry due to their small dimensions, high surface area, high electrical conductivity, unique structures, significant mechanical strength and good chemical stability [34]. Metal nanoparticles can be immobilized on the solid surface through covalently attached tether layers, and the nanoparticle size and density can be independently dominated by pre-synthesizing the nanoparticles and controlling the tether density or assembly conditions [35]. Cruickshank carried out electrostatic assembly of citrate-capped AuNPs on ethylenediamine (en) tether layers, which electrografted to glassy carbon, and found that the modified electrode showed a constant activity for the voltammetric reduction of H_2O_2 [36].

In this study, we reported a preparation and application of AuNPs/en/MWNTs composite film modified glassy carbon electrode (AuNPs/en/MWNTs/GCE). The AuNPs/en/MWNTs/GCE was applied to the research of electrochemical behavior of rutin. Experiments revealed that the redox peak currents of rutin could be remarkably enhanced on AuNPs/en/MWNTs/GCE, meaning good electrocatalytic activity for the oxidation of rutin. The electrochemical behavior of rutin on the AuNPs/en/MWNTs/GCE was studied with details in 0.1 M phosphate buffer solution (pH 3.5). In addition, The AuNPs/en/MWNTs/GCE separated the overlapping voltammetric response of rutin and ascorbic acid (AA) into two well-defined voltammetric peaks, which suggested that the AuNPs/en/MWNTs/GCE could be used to determine rutin in the presence of a certain concentration of AA.

2. Experimental

2.1. Reagents and solutions

Rutin and AA were purchased from National Institute for the Control of Pharmaceutical and Biological Products (China) and used as received. The stock solution of rutin (2.0×10^{-2} M) was prepared with ethanol, and diluted with 0.1 M phosphate medium (pH 3.5) before used. The Compound Rutin Tablets were purchased from Shanghai Zhaohui Pharmaceutical Co. Ltd. Rutin Tablets were purchased from Shanxi Fenhe Pharmaceutical Co. Ltd., respectively, with the specified amount of 20 mg per tablet. The multi-wall carbon nanotubes (diameter: 10–20 nm, length: 1–2 μm, purity >95%) were obtained from Shenzhen Nanotech Port Co., Ltd., China. Nafion (wt. 5%) was purchased from Sigma. All the other chemicals used were analytical grade without further purification and prepared with double-distilled water. All solutions used in the measurements were not deoxygenated with nitrogen bubbling.

2.2. Apparatus

RST3000 electrochemical system (Suzhou Risetech Instrument Co., Ltd. Suzhou, China) was employed for all the voltammetric measurement. A conventional three-electrode system was used, including a bare glassy carbon electrode (GCE) (d = 4 mm) or AuNPs/en/MWNTs film modified GCE as working electrode, a saturated calomel electrode as reference electrode and a platinum wire electrode as auxiliary electrode. All the pH values were measured with a PHS-3C precision pH meter (Leici Devices Factory of Shanghai,

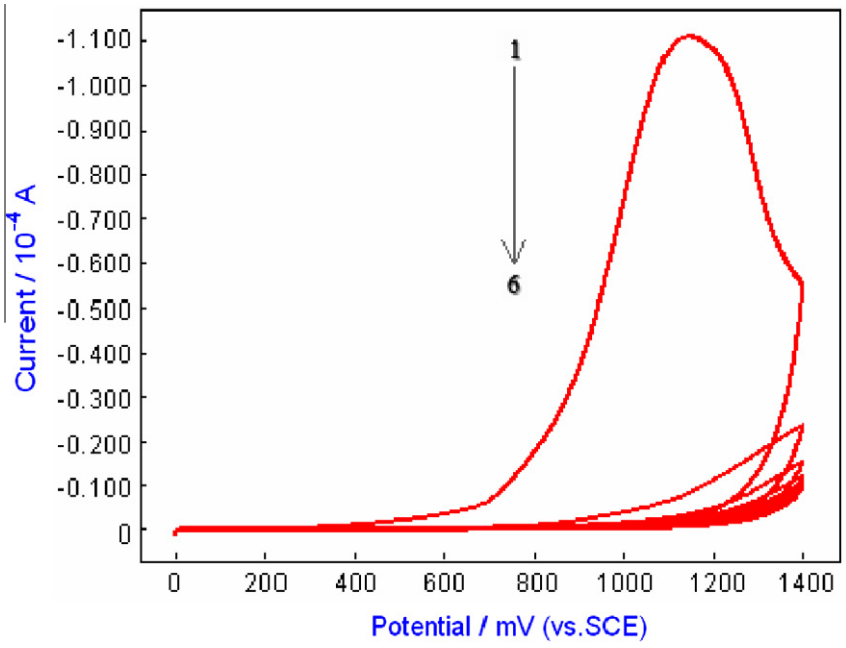

Fig. 1. Six times cyclic voltammetry scan between 0 mV and 1400 mV on the MWNTs/GCE in a solution of 0.1 M en-ethanol solution containing 0.1 M $LiClO_4$ as the electrolyte; scan rate 10 mV s^{-1}.

China), which was calibrated with standard buffer solution every day.

2.3. Modification of MWNTs/GCE, assembly of gold nanoparticles on en/MWNTs/GCE

According to our previous report [37], the pretreated GCE and the acidified MWNTs were carried out. MWNTs suspension was accomplished as follows: 5.0 mg of treated MWNTs was sonicated in 10.0 mL 0.1% (w/w) Nafion methanol solution for about 30 min, and then homogeneous suspension would be achieved. The pretreated GCE was coated with 12.0 μL MWNTs suspension evenly, and then allowed to evaporate methanol at room temperature. Finally, the MWNTs/GCE was obtained. Procedure for electrografting en films to MWNTs/GCE were described as followings: in brief, the potential was cycled six times between 0 mV and 1400 mV (vs. SCE) at 10 mV s^{-1} in a solution of 0.1 M en-ethanol containing 0.1 M $LiClO_4$ as the electrolyte (see Fig. 1). After modification, the surface was rinsed with ethanol, and then followed by double-distilled water and dried with N_2. To assemble gold nanoparticles, en/MWNTs/GCE was immersed in citrate-capped AuNPs for 2 h at 4 °C in the dark. After treatment, the modified electrode was rinsed with double-distilled water, dried with a gentle stream of N_2 and used immediately.

2.4. Analytical procedures

Except as otherwise stated, 0.1 M NaH_2PO_4–Na_2HPO_4 buffer solution (pH 3.5) was used as the supporting electrolyte for rutin determination. A stock solution of 2.0×10^{-2} M rutin was firstly prepared, and then an aliquot was diluted to the appropriate concentration before commencing the voltammetric scan. Before each measurement, the three-electrode system was installed in a blank solution, and the cyclic voltammetry scan from −200 to 800 mV (vs. SCE) was repeated successively for six times for the modified electrode. The quantitative determination of rutin was achieved by measuring the oxidation peak current after background subtraction using differential pulse anodic stripping voltammetry (DPASV). Two tablets of the Compound Rutin Tablets or one tablet of the Rutin Tablets were ground into powder in an agate mortar, and then dissolved in 10 mL ethanol, respectively. The mixtures were sonicated for an hour, and then filtrated. In order to fit into the linear range of the proposed method, some of the filtrate of the Compound Rutin Tablets or the Rutin Tablets was diluted by a factor of 1/10,000 (v/v) with phosphate buffer solution for the determination. The dilution process can actually help in reducing the matrix effect in real samples.

3. Results and discussion

3.1. Characteristics of the AuNPs/en/MWNTs/GCE

MWNTs were coated on GCE evenly and used to form pendant chains of ethylenediamine (en) through electrochemical graft. As

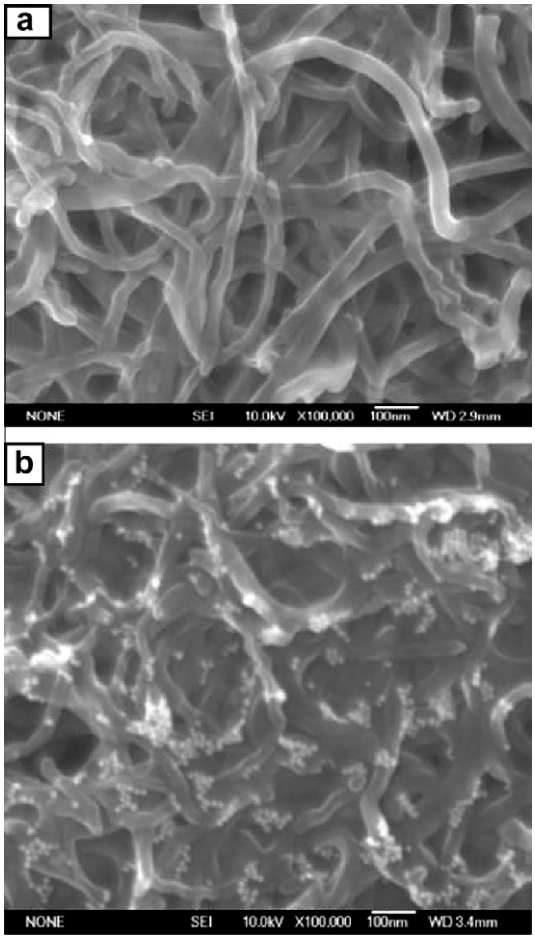

Fig. 3. SEM images of MWNTs film (a), and AuNPs/en/MWNTs films (b).

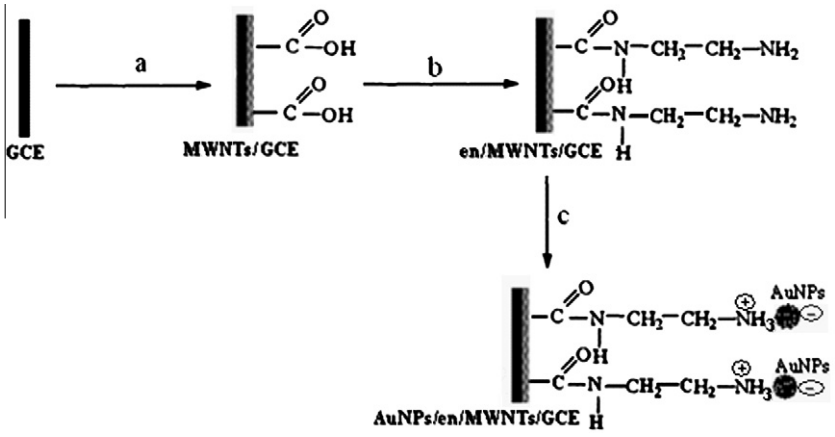

Fig. 2. Schematic illustration of the preparation procedure: coating MWNTs suspension on GCE (a), electrografting en films to MWNTs/GCE (b), and electrostatic assembly of citrate-capped AuNPs on ethylenediamine (c).

can be seen from Fig. 1, when en was electrografted using six cycles between 0 and 1400 mV (vs. SCE) at 10 mV s^{-1}, there was an anodic peak at about 1050 mV at the first cycle, and then the anodic peak almost disappeared after the first cycle. This phenomenon was very similar to the reported literature [38]. The final step was the electrostatic assembly of citrate-capped AuNPs on ethylenediamine (en) tether layers electrografted to MWNTs. The preparation procedure of the AuNPs/en/MWNTs/GCE was illustrated in Fig. 2.

SEM can effectively prove the surface morphologies of the modified electrode. The morphology of the MWNTs film (Fig. 3a) showed a network-like structure. Compared with the MWNTs film, the SEM image of AuNPs/en/MWNTs films (Fig. 3b) displayed many observable light dots which were due to the assembly of AuNPs. SEM image (Fig. 3b) confirmed that gold nanoparticles were typically bound on MWNTs with fairly even distribution, although a few aggregates were observed.

3.2. Electrochemical response of rutin on AuNPs/en/MWNTs/GCE

Fig. 4 showed the cyclic voltammograms of rutin on different modified electrodes. Rutin did not display any redox peaks at the bare GCE (a), which demonstrated the weaker adsorption and slower electrochemical reaction of rutin on the GCE surface. However, there were well-defined redox peaks on the en/MWNTs/GCE (b), MWNTs/GCE (c) and AuNPs/en/MWNTs/GCE (d) in 0.1 M phosphate buffer solution (pH 3.5). But the heights of the redox peaks were obvious higher on the AuNPs/en/MWNTs/GCE than that of the redox peaks on the en/MWNTs/GC or MWNTs/GCE. The anodic (E_{pa}) and cathodic peak potentials (E_{pc}) were at about 487 mV and 432 mV (vs. SCE), respectively, and the ratio of i_{pa}/i_{pc} was about 1.2, which showed that the electrode reaction was almost reversible. Nano-gold and MWNTs can enhance the electron-transfer rate and make more rutin participate in the electrochemical reaction due to their accumulation and catalytic ability.

3.3. Effect of scan rate

The effect of scan rate on the electrochemical response of 4.0×10^{-5} M rutin was shown in Fig. 5. In the range from 20 to 500 mV s^{-1}, the redox peak currents increased gradually along with the increase of the scan rate. There was a good linear relationship between the anodic peak current and the scan rate (v). The regression equation was $i_{pa} = 0.0175v + 0.7158$ (i_{pa}: 10^{-5} A, v: mV s^{-1}, $r = 0.9988$), which indicated that the electron-transfer reaction of rutin on the AuNPs/en/MWNTs/GCE was adsorption-controlled process. According to the equation: $i_{pa} = n^2F^2vA\Gamma_0^*/4RT = nFQv/4RT$ [39], n was calculated to be $1.95 \approx 2$, suggesting that two electrons were involved in the oxidation process. As shown in Fig. 5, when the scan rate rose, the redox peak potentials shifted with the increasing peak-to-peak separation, which demonstrated that the electrode reaction gradually became more irreversible. The peak potential was linear to $\ln v$. The regression equations were $E_{pa} = 0.017\ln v + 0.4097$ ($r = 0.9967$) and $E_{pc} = 0.514 - 0.0178\ln v$ ($r = 0.9973$) (E_p: V, v: mV s^{-1}). According to the equations [40]: $E_{pa} = E^{o'} + m[0.78 + \ln(D^{1/2}k_s^{-1}) - 0.5\ln m] + (m/2)\ln v(m = RT/[(1-\alpha)n_\alpha F])$ and $E_{pc} = E^{o'} - m[0.78 + \ln(D^{1/2}k_s^{-1}) - 0.5\ln m] - (m/2)\ln v(m = RT/(\alpha n_\alpha F))$, the electron-transfer coefficient α was estimated to be 0.62. The results were in accordance with the report [21].

3.4. Effect of pH

Fig. 6 displayed the effect of different pH on the response of 8.0×10^{-5} M rutin. When the pH changed from 2.0 to 9.0, the anodic peak moved to the negative direction. There was a linear relationship between the anodic peak potential and the pH value as follows: $E_{pa} = 0.6838 - 0.056$ pH ($r = 0.9984$). According to the slope of 56 mV pH^{-1}, it could be deduced that the numbers of electron and proton transferred were equal in the electrochemical reaction. With the increasing of pH, the peak current increased until at about pH 3.5, and then decreased. But when the pH was over

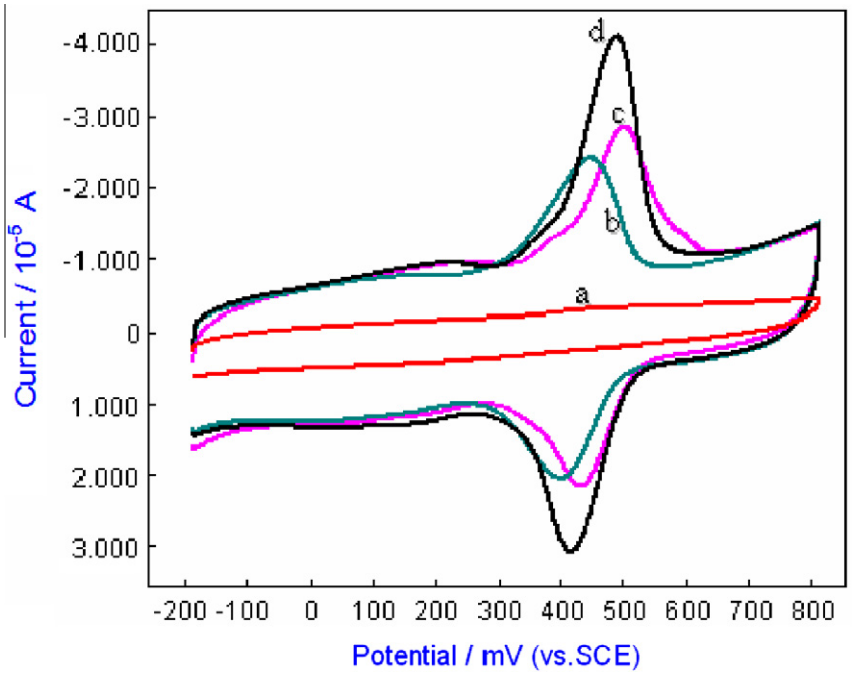

Fig. 4. Cyclic voltammograms of 8.0×10^{-5} M rutin in 0.1 M phosphate buffer (pH 3.5) on the different electrodes: the bare GCE (a), en/MWNTs /GCE (b), MWNTs/GCE (c) and AuNPs/en/MWNTs/GCE (d); scan rate 100 mV s^{-1}.

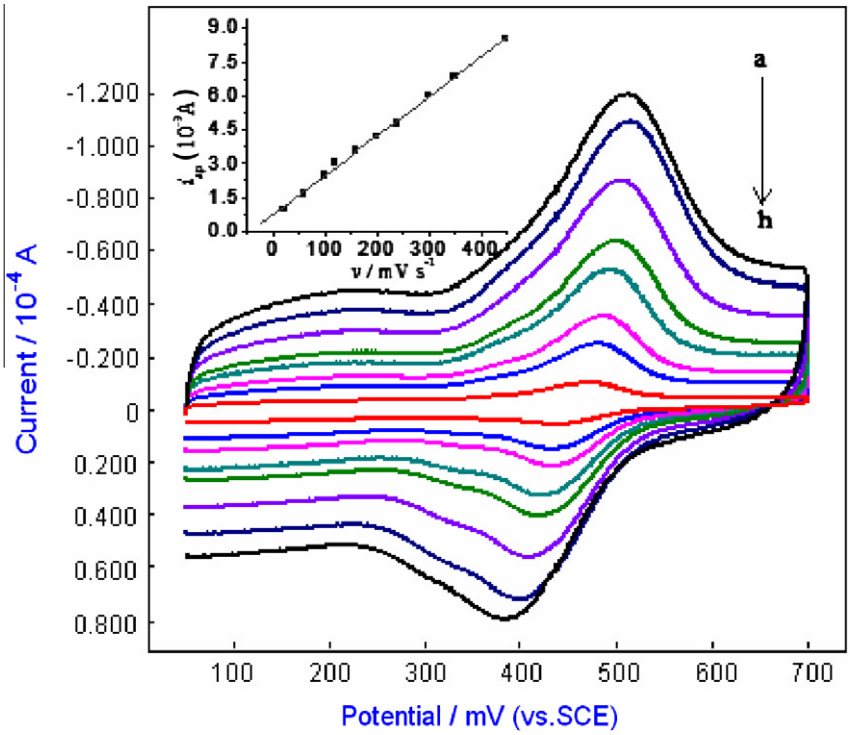

Fig. 5. Dependence of peak current on different scan rate (a → h): 500, 400, 300, 200, 160, 100, 60, 20 mV s $^{-1}$; other conditions as in Fig. 4; insert is the i_{pa} vs. v plot.

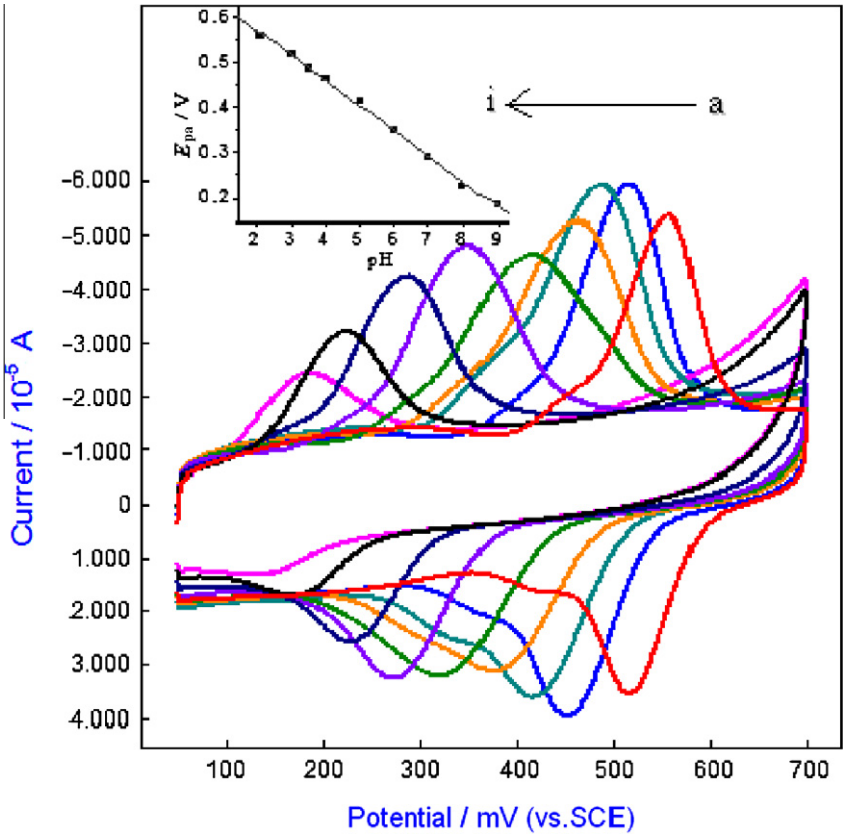

Fig. 6. Influence of solution pH on voltammograms of 8.0×10^{-5} M rutin. 0.1 M phosphate buffer solution pH (a → i): 2.0, 3.0, 3.5, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0; other conditions as in Fig. 4; insert is the E_{pa} vs. pH plot.

8.0, the anodic peak became very small. These experimental phenomena were related to the proton involved in the electrochemical reaction. When pH was exceeded 7.0, the electrostatic repulsion occurred between the nano-gold and rutin with negative charges.

Therefore, acidic solution of pH 3.5 was selected for the determination of rutin.

3.5. Influence of accumulation time and accumulation potential

When the accumulation time was changed from 0 s to 100 s, the anodic peak current of 2.0×10^{-5} M rutin increased gradually from 0 s to 70 s, and then the peak current was almost constant, which indicated that the accumulation of rutin at the electrode surface nearly reached a saturation state after 70 s. So 70 s was generally chosen as the accumulation time. When accumulation potential changed from −100 mV to 400 mV, the peak current increased first until it was up to 300 mV, and then decreased. Therefore, 300 mV was selected as the accumulation potential.

3.6. Calibration curve

In order to test the feasibility of the exploited method for the quantitative analysis of rutin, the relationship between the anodic peak current and the concentration of rutin was studied using differential pulse anodic stripping voltammetry (DPASV). Some experimental parameters were optimized, and the results were listed in Table 2. Under the optimum instrumental conditions (accumulation time: 70 s, accumulation potential: 300 mV, pulse amplitude: 50 mV, pulse increment: 1 mV, pulse width: 40 ms and pulse period: 100 ms), when the concentration of rutin changed from 4.8×10^{-8} M to 9.6×10^{-7} M, the anodic peak current and rutin concentration declared linear relationship (Fig. 7). The regression equation was: $i_{pa} = 2.3728C_{rutin} - 0.1782$ (i_{pa}: 10^{-5}A, C_{rutin}: μM, $r = 0.9973$). Based on the signal to noise ratio of 3, the detection limit of 3.2×10^{-8} M was obtained.

Regeneration and reproducibility are two important characteristics for the modified electrode, which should be investigated. The same modified GCE was used for six times successive measurements of 2.0×10^{-5} M rutin. After each measurement, the surface of the AuNPs/en/MWNTs/GCE was regenerated by successively cycling between −200 mV and 800 mV (vs. SCE) in 0.1 M phosphate buffer solution (pH 3.5) for six cycles. The relative standard deviation (RSD) of the anodic peak current was 4.3%, which suggested good regeneration and reproducibility of the modified electrode.

Table 2
Experimental results of the optimized parameters containing 2.0×10^{-5} M rutin.

i_{pa} (10^{-5} A)	Parameters							
pH	2	3	3.5	4	5	6	7	8
i_{pa} (10^{-5} A)	8.57	8.8	9.67	7.93	6.5	4.88	3.18	2.59
Accumulation time (s)	10	20	30	40	50	60	70	80
i_{pa} (10^{-5} A)	6.24	5.5	6.57	6.55	6.33	6.5	6.49	6.48
Accumulation potential (mV)	−100	0	100	200	300	400	–	–
i_{pa} (10^{-5} A)	4.56	4.83	5.3	6.72	6.9	5.98	–	–
Pulse amplitude (mV)	10	20	30	40	50	60	70	80
i_{pa} (10^{-5} A)	1.28	2.66	4.05	5.98	7.31	7.21	7	6.98
Pulse increment (mV)	1	2	3	4	5	6	7	8
i_{pa} (10^{-5} A)	9.99	7.18	6.93	6.86	6.24	5.32	4.89	3.8
Pulse width (ms)	20	30	40	50	60	70	80	90
i_{pa} (10^{-5} A)	3.9	7.44	7.92	7.34	7.21	7.03	6.89	7.01
Pulse period (ms)	80	90	100	110	120	130	140	150
i_{pa} (10^{-5} A)	8.44	6.84	7.68	5.91	7.6	7.01	7.48	6.87

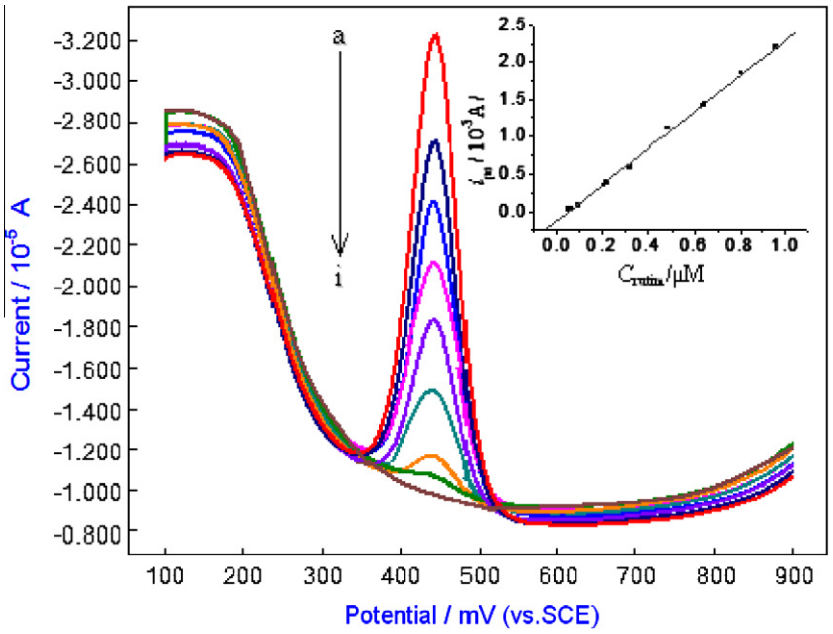

Fig. 7. Differential pulse anodic stripping voltammograms of different concentrations of rutin in 0.1 M phosphate buffer solution (pH 3.5) (a → i): 9.6×10^{-7}, 8.0×10^{-7}, 6.4×10^{-7}, 4.8×10^{-7}, 3.2×10^{-7}, 9.6×10^{-8}, 6.4×10^{-8}, 4.8×10^{-8}, 0 M; insert is the i_{pa} vs. C_{rutin} plot.

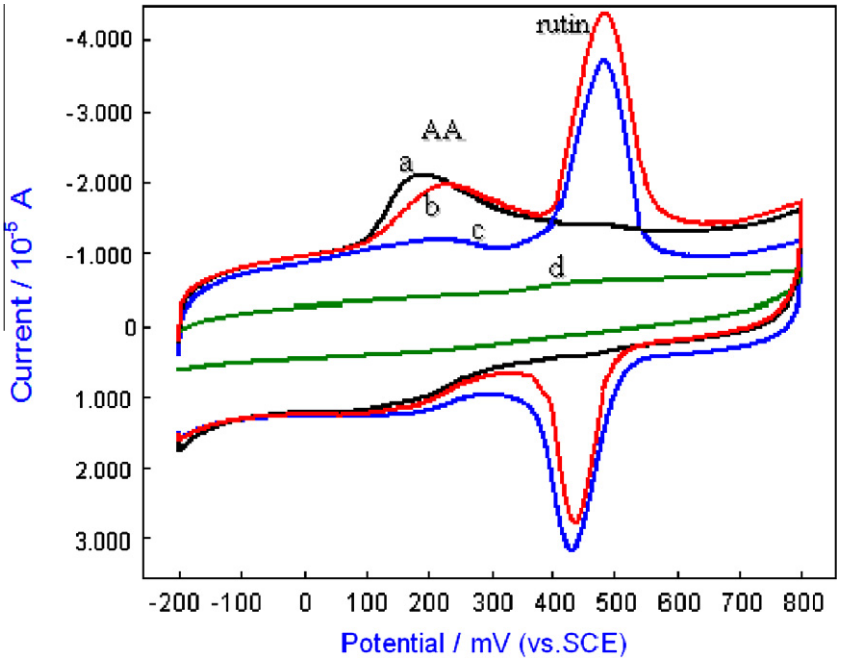

Fig. 8. Cyclic voltammograms of 1.0×10^{-4} M AA (a), the mixed solution of 1.0×10^{-4} M AA and 2.0×10^{-5} M rutin (b), 2.0×10^{-5} M rutin (c) and 0.1 M phosphate buffer solution (pH 3.5) (d) on the AuNPs/en/MWNTs/GCE; other conditions as in Fig. 4.

Table 3
Determination results for rutin in Compound Rutin Tablets[b] and Rutin Tablets.[b]

Sample	Detected (mg/tablet)	Spiked (10^{-7} M)	Found (10^{-7} M)	Average recovery (%)	RSD of recovery (%)
Compound Rutin Tablets[a]	20.0 ± 0.87	1.6	1.54 ± 0.31	96.3	2.7
		4.8	4.66 ± 0.24	98.8	3.0
Rutin Tablets[a]	19.4 ± 0.54	1.6	1.62 ± 0.40	101.3	1.9
		4.8	4.65 ± 0.18	96.9	2.5

[a] Dilution factor: 1/10,000.
[b] Number of samples assayed: 5.

3.7. Interference studies

The influence of some coexistent interference substances was examined in the presence of 2.0×10^{-5} M rutin. The results showed that when the concentration of K^+, Na^+, Cl^-, SO_4^{2-}, PO_4^{3-} and glucose were 500 times more than that of rutin, aminoacetic acid and citric acid 200 times, Zn^{2+}, Ca^{2+} 100 times as well as Mg^{2+} 60 times, no observable interference was observed in the determination of rutin according to the relative error <±10%.

Generally, as the electroactive substance, ascorbic acid (AA) always coexists in the Compound Rutin Tablets. The oxidation peak potential of AA is very close to that of rutin, which results in poor selectivity determination of AA or rutin in real samples on conventional electrodes. Therefore, it is essential to exploit more sensitive, selective and simple methods for the segregative determination of AA and rutin. Fig. 8 demonstrated the cyclic voltammetry (CV) curves of 1.0×10^{-4} M AA (a), the mixture of 2.0×10^{-5} M rutin and 1.0×10^{-4} M AA (b), 2.0×10^{-5} M rutin (c) and without AA and rutin (d) in 0.1 M phosphate buffer solution (pH 3.5) on AuNPs/en/MWNTs/GCE. Fig. 8b showed two anodic peaks at around 186 mV and 487 mV, which were attributed to the oxidation of AA and rutin with a 301 mV separation of both peaks, indicating broad enough separation for the simultaneous electrochemical determinations of rutin and AA in the mixed solution.

3.8. Application

This method was used for the determination of rutin in the Compound Rutin Tablets and Rutin Tablets. The contents of rutin in the Compound Rutin Tablets and Rutin Tablets were calculated to be 20.0 ± 0.87 mg and 19.4 ± 0.54 mg per tablet, respectively (the declared content of rutin was 20 mg per tablet). A standard addition method was employed to evaluate the determination results. The analytical results were listed in Table 3 and the recovery was 96.3–101.3%. In order to test the accuracy of the proposed method, the conventional method of HPLC was employed to determine the contents of rutin in the Compound Rutin Tablets and Rutin Tablets (the contents of rutin in the Compound Rutin Tablets and Rutin Tablets were 18.9 ± 0.47 mg and 18.1 ± 0.57 mg per tablet, respectively). The quantitative results obtained by HPLC were in agreement with the data determined by the proposed electrochemical method, indicating that the method was selective and suitable for rutin determination in real samples.

4. Conclusions

In this study, the electrochemical behavior of rutin was investigated on the AuNPs/en/MWNTs/GCE in a 0.1 M phosphate buffer solution of pH 3.5, and the electrochemical parameters were

calculated. Under the optimized conditions, the anodic peak current was proportional to the rutin concentration in the range from 4.8×10^{-8} to 9.6×10^{-7} M with the detection limit of 3.2×10^{-8} M. The coexisting substance of AA declared no interference to the determination of rutin. The proposed method was further applied to the determination of rutin in the Compound Rutin Tablet and Rutin Tablet samples with satisfactory results.

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