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A Rapid, Green and Controllable Strategy to Fabricate Electrodeposition of Reduced Graphene Oxide Film as Sensing Materials for Determination of Taxifolin

Yanju Wu, Mingxiu Lv, Bei Li, Junda Ge and Lin Gao*
Department of Material and Chemistry Engineering
Henan Institute of Engineering
Zhengzhou 450007, P. R. China
**Glin2004@163.com*

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The electrodeposition of a film of reduced graphene oxide (ERGO) with well-dispersed on a glassy carbon electrode (GCE) was achieved using cyclic voltammetry (CV) in a graphene oxide (GO) colloidal solution. Using square wave adsorptive stripping voltammetry (SWASV), the ERGO film was applied for the first time, in developing a high-sensitive electrochemical sensor for detection of taxifolin. Compared with bare GCE, the resulting electrodes (ERGO/GCE) exhibited excellent response toward the oxidation of taxifolin by significantly enhancing the oxidation peak currents and the decreased peak-to-peak separation. Under selected conditions, the reduction peak currents had linear relationship with taxifolin concentration in the range of $5.0 \times 10^{-8} - 1.5 \times 10^{-6}$ mol L^{-1}, with detection limit of 4.0×10^{-9} mol L^{-1}. Besides, the method was successfully applied to the quantitative determination of taxifolin in the *Prince's-feather fruit* with satisfactory results.

Keywords: Electrodeposition of reduced graphene oxide; electrochemical sensor; voltammetric sensor; taxifolin.

1. Introduction

Flavonoids have aroused increasing awareness because of their potential health beneficial effect.[1] Taxifolin, a bioflavonoid found in the rind of Siberian larch and Dahurian larch, has been widely used in the treatment of cerebral infarction and sequelae, cerebral thrombus, coronary heart disease and angina pectoris.[2,3] Accordingly, accurate analytical method for taxifolin is necessary and some determination techniques have been developed, such as high-performance liquid chromatography (HPLC),[4–6] UV-Vis spectrophotometry,[7] thin layer chromatography (TLC)[8] and capillary zone electrophoresis (CZE).[9] However, some of these methods are time-consuming, expensive or involve a tedious extraction process before detection, which hampers their further application. In contrast, electrochemical method is simple, rapid, sensitive and inexpensive. Furthermore, the redox properties of drugs can provide insight into their metabolic fate, their *in vivo* redox processes and their pharmacological activity.[10,11] Recently, much effort has been devoted to the electrochemical behavior of taxifolin on modified electrode,[12] but very limited.

Graphene, a perfect two-dimensional (2D) carbon material found in 2004,[13,14] is an ideal material for electrochemistry[13] because of its very large 2D electrical conductivity, large surface area and low cost. Hence graphene-based modified electrodes prepared by various methods have been explored as electrochemical sensors platforms.[14–18] However, graphene films on electrodes in these researches are usually prepared by chemical reduction of graphene oxide (CRGO) sheets.[19–22] Such a preparation methodology involves some toxic chemicals. Recently, electrochemical reduction of graphene oxide (ERGO), which has been reported by several research groups,[14,23–25] has arisen more interest due to its fast and green nature. Generally, graphene oxide (GO) is first assembled on the electrodes as precursor by solution deposition methods, and then is subjected to electrochemical reduction. By using electrons as the reducing agent, this method is green, fast, simple and will not result in contamination of the synthesized material. Therefore, the electrochemical performances and applications of electrochemically reduced GO are promising and will be further developed.

In this work, the ERGO film was directly fabricated on glassy carbon electrode (GCE) by using cyclic voltammetry (CV) in a GO colloidal solution. The ERGO film was characterized by electrochemical methods and scanning electron microscopy (SEM). Using square wave adsorptive stripping voltammetry (SWASV), the ERGO film was applied for the first time, in developing a high-sensitive electrochemical sensor for detection of taxifolin. The electrochemical behaviors of taxifolin at the modified electrode were investigated in detail. Besides, the method was also applied successfully in the determination of the content of taxifolin in the *prince's-feather fruit*.

2. Experimental Methods

2.1. *Apparatus and reagents*

Model CHI 650A electrochemical system (CHI Instrumental, Shanghai, China) and RST5000 electrochemical workstation (Zhengzhou Shiruisi Instrument Co., Ltd., Zhengzhou, China) were employed for electrochemical techniques. Scanning electron microscopy (SEM) images were obtained with a Quonxe-2000 field emission scanning electron microscope (FEI Company, Holland). Atomic force microscopy (AFM) images were obtained with a BenYuan CSPM-5500 AFM (Guangzhou BenYuan nanometer Instrument Co., Ltd., Guangzhou, China). A standard three-electrode electrochemical cell was used with GCE ($d = 3$ mm) or modified GCE as a working electrode, platinum (Pt) wire as an auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode (the internal solution was saturated KCl solution). All the pH measurements were made with a PHS-3C precision pH meter (Leici Devices Factory of Shanghai, China), which was calibrated with standard buffer solution at 25 ± 0.1°C every day.

Taxifolin was purchased from Shanghai Jinsui Biological Technology Co., Ltd (Shanghai, China). Stock solution (1.0×10^{-3} mol L^{-1}) of taxifolin was prepared with absolute ethyl alcohol and stored at 4°C in the dark. Graphite was purchased from Nanjing Xfnano Materials Tech Co., Ltd (Nanjing, China). All reagents were of analytical grade and were used as received. Double distilled water was used for all preparations.

2.2. *Preparation of the modified electrode*

Firstly, GO was synthesized from graphite by the modified Hummers method.[26] The exfoliated GO was obtained by ultrasound of the GO dispersion, and centrifugation at 3000 rpm for 15 min. The resulting GO deposited on the mica were characterized by AFM. The results found that the GO sheets were almost single-layered, and the average thickness of single-layer GO sheets was approximately 1 nm, see Fig. 1.

Prior to modification, the bare GCE was polished successively with 0.3 μm and 0.05 μm Al_2O_3 power and rinsed thoroughly with doubly distilled water between each polishing step. After that, the GCE was sonicated in ethanol and doubly distilled water each for 2 min, and dried under N_2 blowing. After that, the bare GCE was immersed in pH 5.0 phosphate buffer solutions (PBS) containing 1.0 mg mL^{-1} GO, and then, the electrochemical reduction of GO was carried out by cyclic sweeping from 0.2 V to -1.6 V at 50 mV s^{-1} for 10 cycles. The obtained electrode was denoted as ERGO/GCE. The electrode was covered with an electrode cap to protect the electrode surface when not using it.

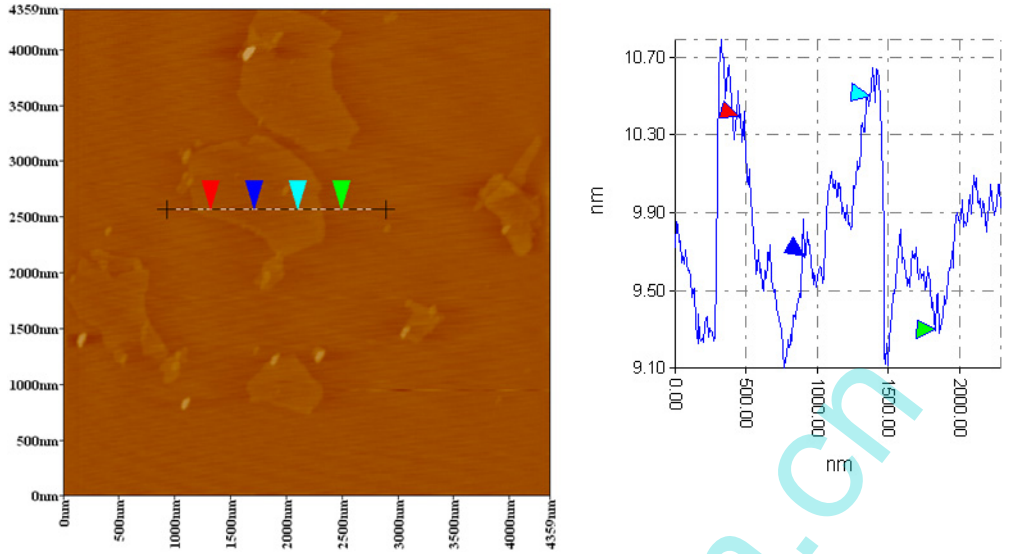


Fig. 1. AFM image of GO from its dilute aqueous dispersion on freshly cleaned mica.

2.3. *Experimental procedure for electrochemical analysis*

A certain volume of stock solution of taxifolin and 10 mL $0.1\,\mathrm{mol\,L^{-1}}$ H_2SO_4 solutions (pH = 0.95) were added into an electrochemical cell, and then the electrode was immersed into the cell. The CV and square wave voltammetry (SWV) were performed to investigate the electrochemical behavior of taxifolin at ERGO/GCE.

2.4. *Real sample assay procedure*

The sample powder was obtained by grinding certain amount of dried *Prince's-feather fruit*. About 2 g of the powder was weighed and extracted with 50 mL 80% ethanol for 2 h in an ultrasonic bath. Then, the extractum was extracted with ethyl acetate. Finally, the sample was obtained by silica-gel column chromatography. The sample solution was stored in the dark. Just before each measurement, the sample solution was diluted quantitatively using the supporting electrolyte.

3. Results and Discussion

3.1. *Morphological characterization of the ERGO/GCE*

To obtain further information on the successful preparation of ERGO films, morphologies of bare GCE [Fig. 2(a)] and ERGO/GCE [Fig. 2(b)] were characterized by using SEM. Figure 2 shows the SEM images obtained from GCEs modified without/with ERGO films. Compared with the glazed surface of bare GCE, a close association with each other to form thin and crumpled sheets was displayed, and the edges of individual sheets were distinguishable with kinked and wrinkled areas, which is highly beneficial in maintaining a high surface area on the electrode and helpful in constructing an interface for the electrochemical sensors. Moreover, the films barely show aggregation, indicating that the assembly of ERGO films by CV on a solid substrate is a rapid and green way to fabricate well-dispersed ERGO films.

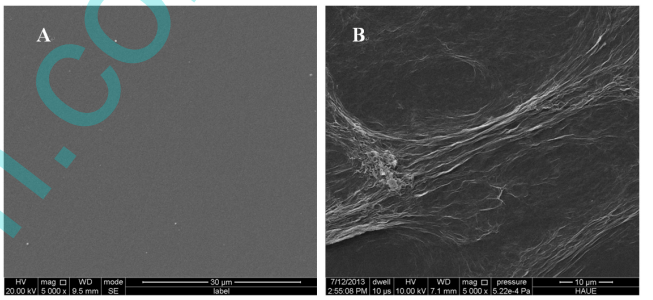


Fig. 2. The SEM images obtained from the bare GCE (a) and ERGO/GCE (b).

3.2. *Electrochemical characterization of ERGO/GCE*

In order to highlight the particular feature of the proposed electrode, its voltammetric response for redox probe $[Fe(CN)_6]^{3-/4-}$ was compared with bare GCE. Figure 3 shows the cyclic voltammograms

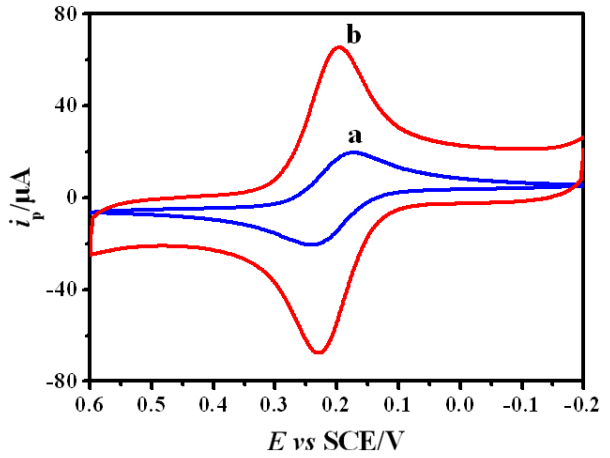


Fig. 3. CVs of a bare GCE (curve a) and ERGO/GCE (curve b) in 1.0×10^{-3} mol L^{-1} $K_3[Fe(CN)_6] + 0.1$ mol L^{-1} KCl solution.

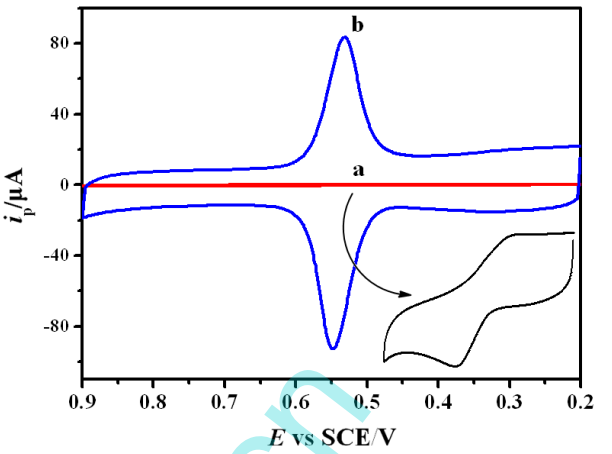


Fig. 4. CVs of taxifolin (4.0×10^{-5} mol L^{-1}) at bare GCE (a) and ERGO/GCE (b); Supporting electrolyte: 0.1 mol L^{-1} H_2SO_4 solutions (pH = 0.95), $v = 0.05$ V s^{-1}.

(CVs) of bare GCE (curve a) and ERGO/GCE (curve b) in 1.0×10^{-3} mol L^{-1} $K_3[Fe(CN)_6] + 0.1$ mol L^{-1} KCl solution. A pair of redox peaks of $[Fe(CN)_6]^{3-/4-}$ is showed on bare GCE with the peak-to-peak separation (ΔE_p) as 66 mV at the scan rate of 50 mV s^{-1}. While on the ERGO/GCE, both cathodic and anodic peak currents increase obviously with the ΔE_p value decreased to 34 mV. The larger peak currents and the smaller ΔE_p of redox probe $Fe(CN)_6^{3-/4-}$ is observed on the ERGO/GCE. The results suggested that the ERGO films could efficiently accelerate the electron transfer on the electrode surface to amplify the electrochemical signal due to its excellent electric conductivity and large specific surface area.

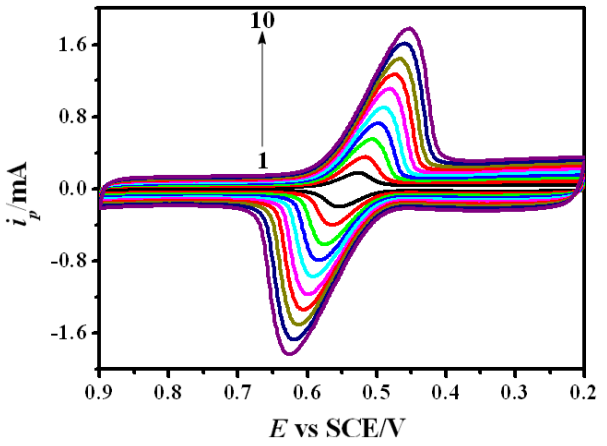
At the same time, according to Randles–Sevcik formula[27]: $i_{pa} = 2.69 \times 10^5 n^{3/2} A D_o^{1/2} c_o v^{1/2}$, where i_{pa} refers to the anodic peak current (A); n is the electron transfer number; A is the surface area of the electrode (cm^2); D_o is the diffusion coefficient (cm^2 s^{-1}); c_o is the concentration of $K_3[Fe(CN)_6]$ (mol L^{-1}) and v is the scan rate (V s^{-1}). By exploring the redox peak current with scan rate, the average electroactive area of bare GCE and ERGO/GCE was calculated as 0.044 cm^2 and 0.089 cm^2, respectively. The results further indicated that the preparation of the ERGO films could significantly improve the effective area of the electrode surface.

3.3. *Electrochemical behavior of taxifolin at ERGO/GCE*

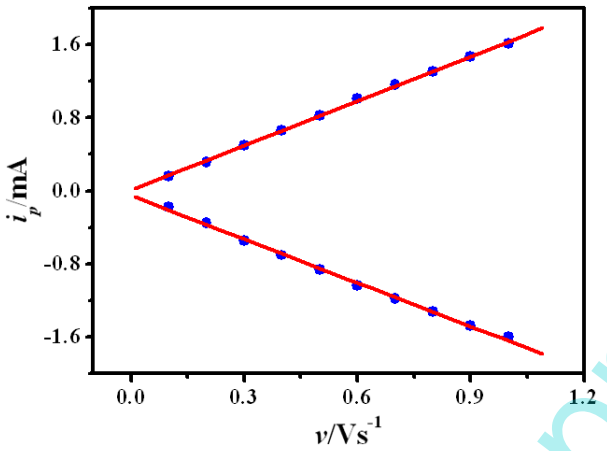
The electrochemical behavior of taxifolin on ERGO/GCE was investigated by CV. For comparison, the CVs of bare GCE were also conducted. At the bare GCE (Fig. 4, curve a), a pair of relatively weak redox peak currents corresponding to the electrochemical redox of taxifolin was observed at an anodic peak potential (E_{pa}) of 0.637 V and a cathodic peak potential (E_{pc}) of 0.425 V (inset of Fig. 4). When the ERGO films are deposited on GCE surface, as can be seen from curve c of Fig. 4, taxifolin exhibits a pair of well-defined redox waves on the ERGO/GCE with $E_{pa} = 0.548$ V and $E_{pc} = 0.532$ V under the same experimental condition, of which the peak current is about 146-fold higher than that of bare GCE, and the peak-to-peak separation (ΔE_p) is only 16 mV. This results might be attributed to the unique properties of ERGO film. Firstly, the ERGO film provides a large specific surface area to increase the loading amount of taxifolin. Secondly, thin, crumpled and the edges of individual sheets exhibit excellent conductivity, making the ERGO film as a promoter to accelerate electron transfer between the electrode and taxifolin in the solution. Besides, it can also be seen from Fig. 4 that the background current of ERGO/GCE is much larger than that of the bare GCE, indicating high specific capacitance of ERGO films on electrode.

3.3.1. *Effect of scan rate*

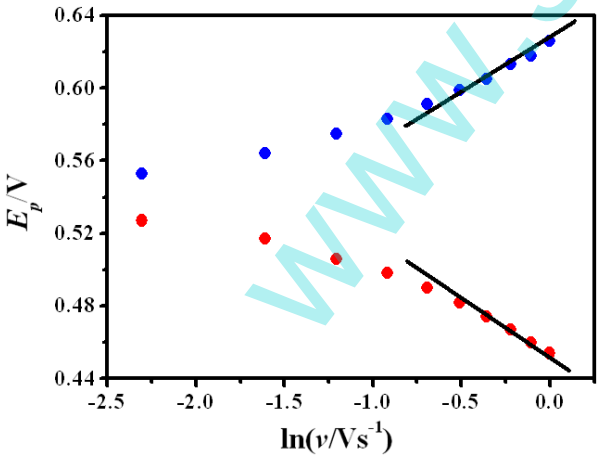
To further elucidate the electrode reaction of taxifolin at ERGO/GCE, the effect of scan rates (v) on the voltammetric response of taxifolin on ERGO/GCE was investigated. Figure 5(a) shows the CVs of 4.0×10^{-5} mol L^{-1} taxifolin in a 0.1 mol L^{-1}



(a)



(b)



(c)

Fig. 5. (a) CVs acquired on ERGO/GCE with 4.0×10^{-5} mol L^{-1} taxifolin in supporting electrolyte of 0.1 mol L^{-1} H_2SO_4 solutions (pH = 0.95) at different scan rates from 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.0 V s^{-1} (from 1 to 10); (b) The plot of the redox peak currents of taxifolin versus scan rate; (c) The relationship between E_p and ln v.

H_2SO_4 solution at the ERGO/GCE with v ranging from 0.10 V s^{-1} to 1.00 V s^{-1}. It is clear that both the redox peak currents were enhanced by increasing the potential scan rate. As can be seen in Fig. 5(b), the redox peak currents were found to be linearly proportional to the scan rate. The linear regression equations are $i_{pa} = -0.0524 - 1.586v$ ($R = 0.999$) and $i_{pc} = 0.00614 + 1.628v$ ($R = 0.999$). This indicates that the modified electrode reaction of taxifolin is an adsorption-controlled process.[28] Based on Laviron's theory of an adsorption-controlled process, the i_p–v relation can be described as follows[29]:

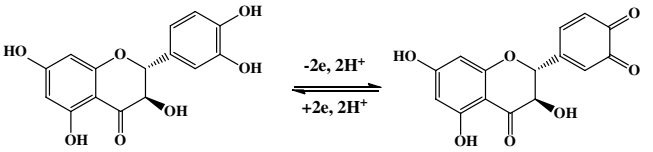
$$i_p = \frac{n^2F^2A\Gamma^*v}{4RT} = \frac{nFQv}{4RT}.$$

This means that the electron-transfer number, n, can be calculated as long as the CV peak area, Q, is obtained under a certain scan rate. As the scan rates varied from 0.10 V s^{-1} to 1.00 V s^{-1}, $n = 2$ was calculated as an average. Moreover, with the increase of v, the oxidation peak potential (E_{pa}) was positively shifted and the reduction peak potential (E_{pc}) was negatively shifted, indicating that the redox reversibility of taxifolin was impaired. When $v > 0.5$ V s^{-1}, the E_{pa} and E_{pc} were linearly dependent on the ln v with the regression equations of E_{pa} (V) $= 0.0523 \ln v + 0.625$ ($R = 0.994$) and E_{pc} (V) $= -0.0549 \ln v + 0.454$ ($R = 0.999$), see Fig. 5(c). Based on the Laviron's theory[30] with slopes of the lines $RT/[(1-\alpha)nF]$ and $-RT/\alpha nF$, the value of the electron transfer coefficient (α) were calculated as 0.49.

3.3.2. *Effect of supporting electrolyte and pH value*

The types of supporting electrolytes played a key role in the voltammetric responses of taxifolin. The current responses of 4.0×10^{-5} mol L^{-1} taxifolin were estimated in different supporting electrolytes such as H_2SO_4, NaOH, phosphate buffer, acetate buffer, Britton Robinson and borate buffer solutions. The results showed that higher peak current and the better peak shape could be obtained in a H_2SO_4 solution. Therefore, the H_2SO_4 buffer solution was adopted as priority for the following experiments.

To further investigate the mechanism of the electrochemical redox of taxifolin, the effect of the solution pH on the response of taxifolin was also studied by CV. The results shows that both the



Scheme 1. Redox mechanism of taxifolin at ERGO/GCE.

anodic peak potential (E_{pa}) and the cathodic potential (E_{pc}) shifted negatively with increasing the solution pH (0.5–3.0), indicating that the electrocatalytic oxidation of taxifolin at ERGO/GCE is a proton-involved reaction. The relationship between the formal peak potential ($E^{0'}$) and the pH could be fitted into the regression equation, $E^{0'} = 0.632 - 0.049\,\text{pH}$ ($R = 0.999$). From the slope value, which is very close to the theoretical value of -59 mV, it is indicated that the electrocatalytic redox of taxifolin at the ERGO/GCE is an equal electron-and proton-process. Since the redox of taxifolin is a two-electron process, the number of protons involved should also be two.

Based on these results, the electrochemical reaction mechanism was expressed as Scheme 1.

3.4. *SWV investigations*

To overcome the influence of the blank current for the detection sensitivity, we chose the reduction peak as the object to investigate. Moreover, we found that the peak corresponding to the differential pulse waveform is more distant from the background discharge, but the square wave waveform is preferable because of its highest sensitivity and its high scan rate, which is time efficient. So the SWV was employed in the determination of taxifolin. The optimum instrumental parameters (pulse-amplitude E_{sw}, frequency f) were studied for a $1.0 \times 10^{-6}\,\text{mol L}^{-1}$ taxifolin solution. The results indicated that the i_{pa} increased by increasing E_{sw} from 10 mV to 50 mV or f in the range of 10–50 Hz (see Fig. 6), but the peak potential shifted to more positive values, and the peak changed unshapely. So 30 mV was chosen as the optimum amplitude and 25 Hz was chosen as the optimum frequency.

3.5. *Analytical applications and methods validation*

3.5.1. *Accumulation conditions*

For consideration of the adsorption of taxifolin on the ERGO/GCE surface, SWV technique coupled with accumulation procedure was used in the study. With an increase in the accumulation time (t_{acc}), the i_{pc} increased. When t_{acc} was 300 s, i_{pc} achieved a maximum value in the taxifolin solution of $5.0 \times 10^{-7}\,\text{mol L}^{-1}$. A plateau appeared for prolonging the t_{acc} afterward, and the accumulation potential had a small effect on the peak current. So the t_{acc} of 300 s under open circuit was used for further studies.

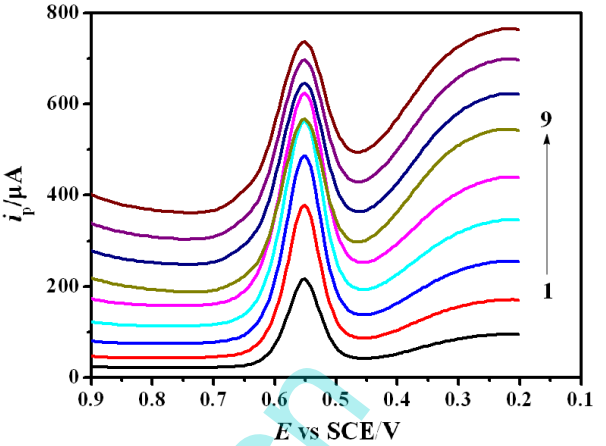


Fig. 6. Square wave anodic stripping voltammograms of $1.0 \times 10^{-6}\,\text{mol L}^{-1}$ taxifolin at different frequencies: (1–9) 10, 15, 20, 25, 30, 35, 40, 45 and 50 Hz; scan increment of 4 mV and pulse amplitude of 30 mV; the other experimental conditions are the same as those described in Fig. 4.

3.5.2. *Calibration curve, detection limit, repeatability and stability*

Series concentrations of taxifolin standard solutions were detected under the optimized working conditions described above. Figure 7 displayed the response of different concentrations of taxifolin by SWASV. A linear relationship could be established between i_{pa} and the concentration of taxifolin in the range of 5.0×10^{-8}–$1.5 \times 10^{-6}\,\text{mol L}^{-1}$ (the inset of Fig. 7). The linear regression equation and correlation coefficient are:

$$i_{pc} = 8.89 + 495.4c \quad (R = 0.999)$$

where i_{pc} is the reduction peak current in μA and c is the concentration of taxifolin in $\mu\text{mol L}^{-1}$. Standard deviations (SD) for the slope and intercept of the calibration curve were 4.94 and 6.53, respectively. Based on the signal-to-noise ratio of 3 (S/N),[31] the detection limit was obtained as $4.0 \times 10^{-9}\,\text{mol L}^{-1}$. These values confirmed the sensitivity of the proposed method for the determination

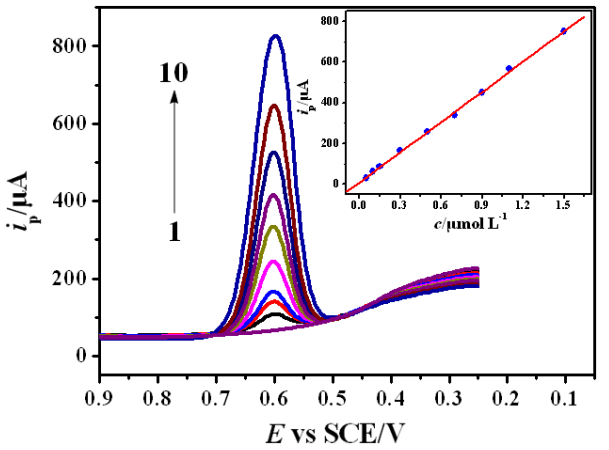


Fig. 7. Square wave anodic stripping voltammograms and their associated calibration plot (inset) for increasing concentrations of taxifolin at ERGO/GCE under optimum conditions; taxifolin concentration: (1) 0.0 mol L^{-1}, (2) 5.0×10^{-8} mol L^{-1}, (3) 1.0×10^{-7} mol L^{-1}, (4) 1.5×10^{-7} mol L^{-1}, (5) 3.0×10^{-7} mol L^{-1}, (6) 5.0×10^{-7} mol L^{-1}, (7) 7.0×10^{-7} mol L^{-1}, (8) 9.0×10^{-7} mol L^{-1}, (9) 1.1×10^{-6} mol L^{-1} and (10) 1.5×10^{-6} mol L^{-1}.

of taxifolin. To estimate the repeatability of the proposed electrode, the R.S.D. of five times successful measurement the peak current of 1.0×10^{-6} mol L^{-1} taxifolin was calculated to be 4.7%, which demonstrated a good repeatability of the proposed electrode. The ERGO/GCE can be stored for about 2 weeks and the decrease of the response was obtained as 2.9%, which indicated that ERGO/GCE had good stability.

3.5.3. *Interference studies*

For the possible analytical application of the proposed method, various possible interfering species were evaluated, with a fixed taxifolin concentration of 1.0×10^{-6} mol L^{-1}. The tolerance limit for a foreign species was taken as the largest amount yielding a relative error $< \pm 5\%$ for the determination of taxifolin. The experiment results showed that no interference could be observed for the following organic compounds: glucose (60), citric acid (30), glutamic acid (30), oxalic acid (50), ascorbic acid (10), uric acid (3), quercetin (5) and norepinephrine (3), where the data in brackets denote the molar ratio of interfering compound to taxifolin. At the same time, the inorganic species, such as Ca^{2+}, Zn^{2+}, Cu^{2+}, Mg^{2+}, NH_4^+, Cl^-, PO_4^{3-} and Ac^- did not interfere. The results indicate that the present method was adequate for the determination of taxifolin in real samples.

Table 1. Determination results of taxifolin in the *prince's-feather fruit* sample by SWASV.

Sample	Amount found (mg g^{-1})	RSD (%)	Stand added (mg g^{-1})	Total found (mg g^{-1})	Recovery (%)
1	4.764	2.7	2.104	6.814	97.4
2	4.567	4.1	2.104	6.707	101.7
3	4.674	3.4	2.104	6.697	96.2

3.6. *Determination of taxifolin in the real sample*

In order to evaluate the validity of the proposed method, it was employed in the determination of the content of taxifolin in the *prince's-feather fruit*. The standard addition method was used to determine the content of taxifolin. All the samples were determined for three times under the same conditions. The results are listed in Table 1. The recoveries of taxifolin at ERGO/GCE are in the range from 96.2% to 101.7%, declaring that this method is effective and reliable.

4. Conclusions

We have successfully employed an electrochemically reduced grapheme oxide-modified electrode for the sensitive detection of taxifolin. The proposed modified electrode showed enhanced electron transfer properties and high resolution capacity to the taxifolin. The method was also applied successfully in the determination of the content of taxifolin in the *prince's-feather fruit*. Compared with other methods, it is a simple, but highly sensitive, green and promising method for determination of taxifolin.

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