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ORIGINAL PAPER

# Sensitive voltammetric sensor of dihydromyricetin based on Nafion/SWNT-modified glassy carbon electrode

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**Abstract** A novel voltammetric sensor, based on single-walled carbon nanotubes (SWNT) dispersed in Nafion and modified glassy carbon electrode (GCE), was fabricated and used to determine the trace amounts of dihydromyricetin (DMY). The electrochemical behavior of DMY at this sensor was investigated in 0.1 mol $L^{-1}$ sulfuric acid solutions+0.1 mol $L^{-1}$ NaCl by cyclic voltammetry and squarewave voltammetry. Compared with bare GCE, the electrode presented an excellent response of DMY through an adsorption-controlled quasi-reversible process. Under the optimum conditions, the response peak currents were linear relationship with the DMY concentrations in the range of $1.0\times10^{-7}$–$1.0\times10^{-5}$ mol $L^{-1}$ with a detection limit of $9\times10^{-8}$ mol $L^{-1}$. Based on this voltammetric sensor, a simple and sensitive electroanalytical method for DMY was proposed and applied to quantitative determination of DMY in *Ampelopsis grossedentata* samples. In addition, the oxidation mechanism was proposed and discussed, which could be a reference for the pharmacological action of DMY in clinical study.

**Keywords** Dihydromyricetin · Squarewave voltammetry · SWNT · Voltammetric sensor

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## Introduction

*Ampelopsis grossedentata* distributes in southern China widely, and their leaves (Tengcha) have been used as a beverage herbal medicine for hundreds of years. Dihydromyricetin (DMY, 3, 3′, 4′, 5, 5′, 7-hexahydroxy-2,3-dihydroflavanol, Fig. 1) is the main bioactive component in the leaves of *A. grossedentata*. It is one kind of flavonoids which has many pharmacological functions on organism, such as relieving cough, removing sputum, inhibiting hypertension, protecting liver [1–3], absorbing ultraviolet radiation [4–6], antioxidation [7–9], antibacterial [10–12], antitumor properties [13]. Hence, the quantification of DMY and understanding of its biological activity are of considerable interest. At present, recognition and determination of DMY mainly depend on high-performance liquid chromatography (HPLC) [14, 15], LC–MS [9], and spectroscopic techniques [16, 17]. However, complicated preconcentrations, multisolvent extraction techniques, or expensive devices and maintenance are coupled with these techniques. To our knowledge, there has been no report regarding the electrochemistry and voltammetric determination of DMY so far. More inadequate, the pharmacological action and reaction mechanism of DMY are not observed using these methods. Electrochemical methods offer improved characteristics such as short time, little reagent consumption, easy operation, and environmental friendly. More importantly, the techniques also help for identifying the redox of compounds and provide important information about pharmacological actions.

Carbon nanotubes (CNT) are generated by rolling a single or several layers of graphite into a seamless and hollow cylinder and can be divided into multi-walled carbon nanotubes [18] and single-walled carbon nanotubes

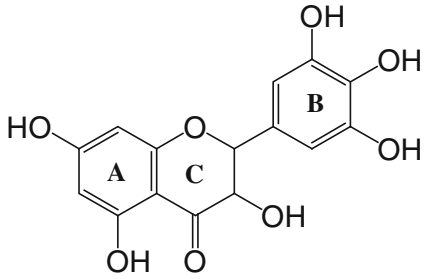



**Fig. 1** The chemical structure of DMY

(SWNTs) [19] based on the number of carbon atom layers. Because of the excellent electrical properties, the ultrahigh ratio of surface area to volume and the extreme sensitivity of its surface atoms to any surface adsorption reactions [20, 21], CNT has the ability to mediate electron-transfer reactions with an electroactive species in solution when used as electrodes [22–24].

In this approach, a Nafion/SWNT modified glassy carbon electrode (Nafion/SWNT/GCE) was fabricated and used as a voltammetric sensor to study the redox mechanism of DMY and determine it quantitatively. SWNT was acidized after purified to increase its solubility, and Nafion was employed to increase the immobilization stability of SWNT on GCE surface. The electrochemical behavior of DMY at this modified electrode was investigated in detail. The experimental results showed that this modified electrode displayed a significant voltammetric response to DMY with high sensitivity and stability, as well as a wider linear range.

## Experimental

### Apparatus and reagents

Model 650A electrochemical system (CHI Instrument Company, USA) was employed for electrochemical techniques. Transmission electron microscope (TEM; Tecnai $G^2$20 S-TWIN, FEI Company, Holland). A standard three-electrode electrochemical cell was used with GCE ($d$= 3 mm, Ai Daheng Sheng Tianjin S&T Ltd.) or modified GCE as working electrode, platinum (Pt) wire as auxiliary electrode, and an Ag/AgCl electrode as 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.

All reagents were of analytical grade and were used as received. DMY was purchased from Aladdin Chemistry Company (Shanghai, China). *A. grossedentata* was purchased from Beijing Jinxingchun Trade Center (Beijing, China). SWNT (95% purity) were obtained from Beijing Nachen S&T Ltd. Double distilled water was used for all preparations. Stock solutions ($2.0\times10^{-3}$ mol $L^{-1}$) of DMY were prepared with ethanol and stored at 4 °C darkly. Dilutions were done just before use. Each assay was performed at room temperature.

The determination of DMY by HPLC was carried out using an Agilent 1200 Series liquid chromatography with an Agilent C18 (4.6×150 mm) and an Ultraviolet-vis detector set at 290 nm. The mobile phase was a methanol/0.1% phosphate solution mixture (28:72, %$v$/$v$) at a flow rate of 1.0 mL $min^{-1}$, while the injection volume was 10 μL [25].

### Electrode pretreatment and SWNT-modified procedure

The GCE was polished with finer emery paper and 0.1 μm alumina slurry and successively rinsed thoroughly with acetone, ethanol, and distilled water in ultrasonic bath for 1 min.

The commercial samples of SWNT were pretreated according to the methods described elsewhere [26, 27]. Acidized SWNT (1 mg) was ultrasonically dispersed in a Nafion solution (0.1%) to give the final supernatant of 0.2 mg $mL^{-1}$. The Nafion/SWNT film was prepared by dropping the suspension of Nafion/SWNT (5 μL) on the polished GCE surface and then evaporating the solvent naturally. The prepared electrode was stored in 0.01 mol $L^{-1}$ PBS (pH 7.0) at 4 °C when not used. For comparison, a Nafion-modified GCE was prepared using the same way.

### Real sample assay procedure

Certain amount of *A. grossedentata* were added in certain double distilled water with solid–liquid ratio of 1:10, and boiling for 1 h, then filtered while hot. The filtrate was stored in refrigerators for 24 h; the crystals precipitating were dissolved in ethanol. The solution prepared as above was analyzed as the real sample.

## Results and discussion

### Transmission electron microscope image of Nafion/SWNT/GCE

TEM was employed to observe the morphology of Nafion/SWNT film. The distinct structure of SWNT was observed from Fig. 2. These data indicates that the Nafion/SWNT film was successfully immobilized on the substrate surface just as designed.

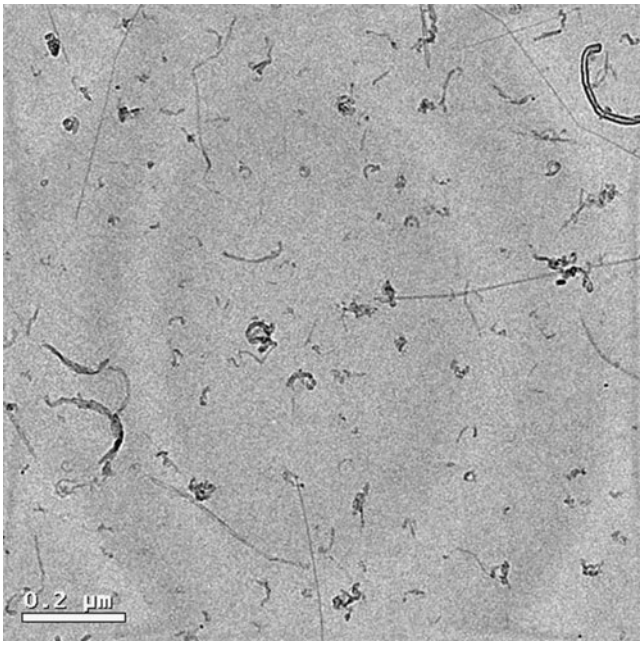



**Fig. 2** TEM image of Nafion/SWNT film (acceleration voltage, 200 kV; metallization of the surface, copper)

## Electrochemical impedance spectroscopy and cyclic voltammetry characterization of the modified electrodes

Electrochemical impedance spectroscopy (EIS) was used to further characterize the modified film on the electrode surface. The Nyquist plots of EIS consist of a linear semicircle part and a semicircle part. The first part, which is observed at lower frequencies, corresponds to the diffusing limited process. And the other part, which is observed at higher frequencies, corresponds to the electron transfer limited process. Besides, the electron transfer resistance ($R_{ct}$), which presents as the semicircle diameter of the plot, indicates the interface properties of electrodes [28]. $R_{ct}$ demonstrates the interfacial electron-transfer impedance of the probe at the electrode surface and the value varies with different substances which were modified on the electrodes [29]. Figure 3 showed the Nyquist plots of EIS using equimolar of $2.0\times10^{-3}$ mol $L^{-1}$ $Fe(CN)_6^{3-/4-}$ as electrochemical probe at different electrodes: curves a, b, and c comparing to bare GCE, Nafion/GCE, and Nafion/SWNT/GCE, respectively. After fitting suitable circle and calculation, $R_{ct}$ obtained was about 184.7, $3.092\times10^4$, $1.892\times10^4$ Ω for bare GCE, Nafion/GCE, Nafion/SWNT/GCE, respectively. The $R_{ct}$ value with Nafion/GCE is the maximum, because Nafion is a good cation exchanger and it presents as a blocking layer for electron exchange at the electrode-solution interface. For reasons described as the electrostatic repulsion between negatively charged Nafion and $Fe(CN)_6^{3-/4-}$. Nevertheless, after filling in SWNT, which is of good conductivity, the electron exchange becomes easier and the $R_{ct}$ value is remarkably decreased compared with pure Nafion. These data indicate the Nafion/SWNT film was successfully immobilized on the substrate surface just as design.

To provide further information about the electrochemical properties of Nafion/SWNT/GCE, potassium ferricyanide ($K_3[Fe(CN)_6]$) was selected as the electrochemical probe again to evaluate the performance of the modified electrodes by cyclic voltammetry (CV). Figure 4 showed the

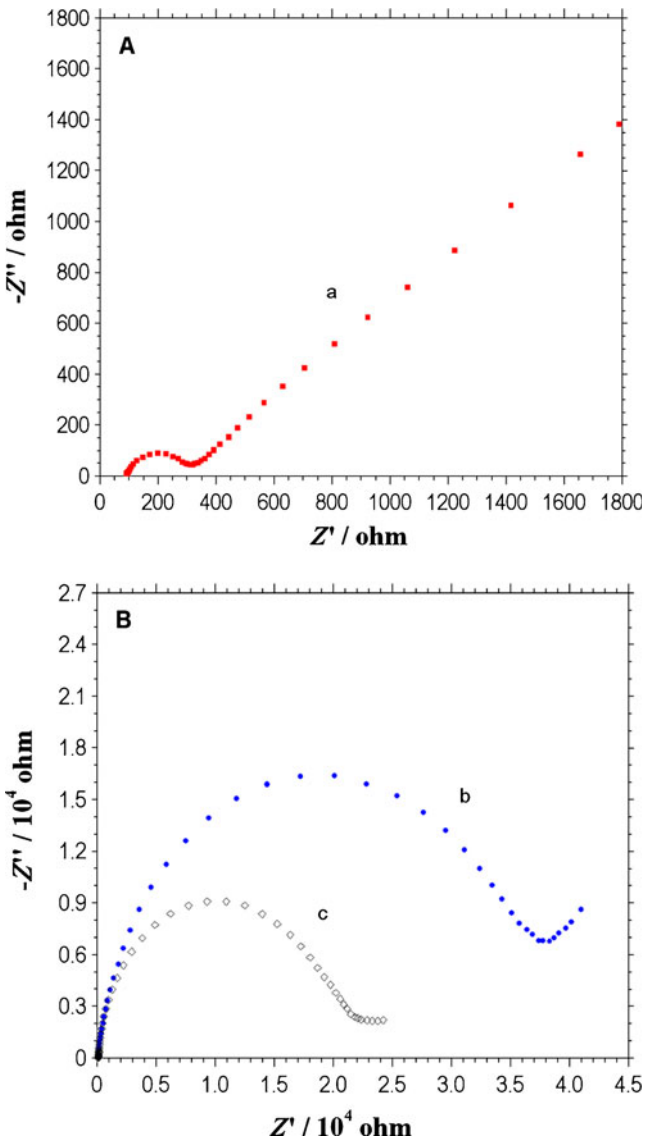



**Fig. 3** Nyquist of electrochemical impedance spectroscopies with different electrodes: **a** a clean, freshly polished bare GCE (*curve a*), **b** Nafion/GCE (*curve b*), Nafion/SWNT/GCE (*curve c*). Init E (V), *a–c* 0.255, 0.237, 0.25; high frequency (Hertz), 100,000; low frequency (Hertz), 0.01; amplitude (volts), 0.005; solution, $2\times10^{-3}$ mol $L^{-1}$ $Fe(CN)_6^{3-/4-}$+0.2 mol $L^{-1}$ KCl

voltammograms of the bare GCE, Nafion/GCE, and Nafion/SWNT/GCE in $2.0\times10^{-3}$ mol $L^{-1}$ $K_3[Fe(CN)_6]$+ 0.2 mol $L^{-1}$ KCl solution, respectively. Well-defined CV, characteristic of a diffusion-limited reversible redox process, was observed at the bare GCE (Fig. 4a). The anodic and cathodic peaks were disappeared at Nafion/GCE (Fig. 4b) due to the Nafion film which hinders the diffusion of ferricyanide toward the electrode surface. However, in spite of being very weak, the redox reaction appeared again when a little of SWNT was embedded in Nafion film (Fig. 4c), showing SWNT excellent electro-active character toward the rare ferricyanide-diffused electrode surface. On the basis of the EIS and CV results, we can conclude that Nafion/SWNT is successfully immobilized on the GCE surface as designed and the functions of SWNT and Nafion are clearly demonstrated.

## Cyclic voltammetric behavior of DMY at Nafion/SWNT/GCE

The electrochemical behavior of DMY at Nafion/SWNT/GCE was investigated in 0.1 mol $L^{-1}$ sulfuric acid solution+0.1 mol $L^{-1}$ NaCl by CV. As shown in Fig. 5a, no peaks were observed in blank solution (curve a); two oxidation peaks (marked as P1 and P3) and one less obvious reduction peak (marked as P2) were shown in DMY solution ($4.0\times10^{-5}$ mol $L^{-1}$) with $E_{p1}$=0.504 V, $E_{p2}$= 0.480 V, $E_{p3}$=1.245 V (curve b in Fig. 5a). Another character observed in Fig. 5a was that the two oxidation peaks almost disappeared in following cyclic scans (curve c, d), suggesting a rapid and efficient passivation of the Nafion/SWNT/GCE surface [30]. If scan potential was reversed just before P3 appearance, the passivation did not appear, and a reduction peak current obviously arose (Fig. 5b, curve b). These data demonstrate that the passivation of electrode surface come from the oxidation products of P3, which sullied the electrode surface and hindered the reduction of oxidation products from P1. Thus, the potential window of 0.10–0.80 V was performed in following discussion.

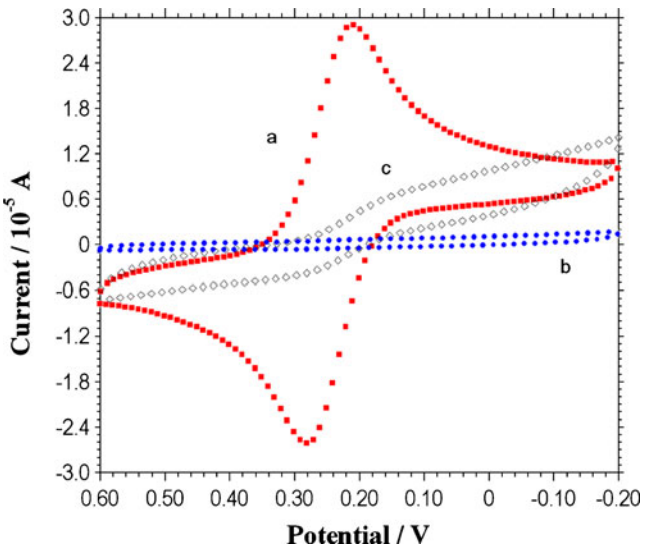



**Fig. 4** Cyclic voltammograms of $2.0\times10^{-3}$ mol $L^{-1}$ $K_3[Fe(CN)_6]$+ 0.2 mol $L^{-1}$ KCl solution at a clean, freshly polished bare GCE (*curve a*), Nafion/GCE (*curve b*), and Nafion/SWNT/GCE (*curve c*) with scan rate $v$=0.10 V $s^{-1}$

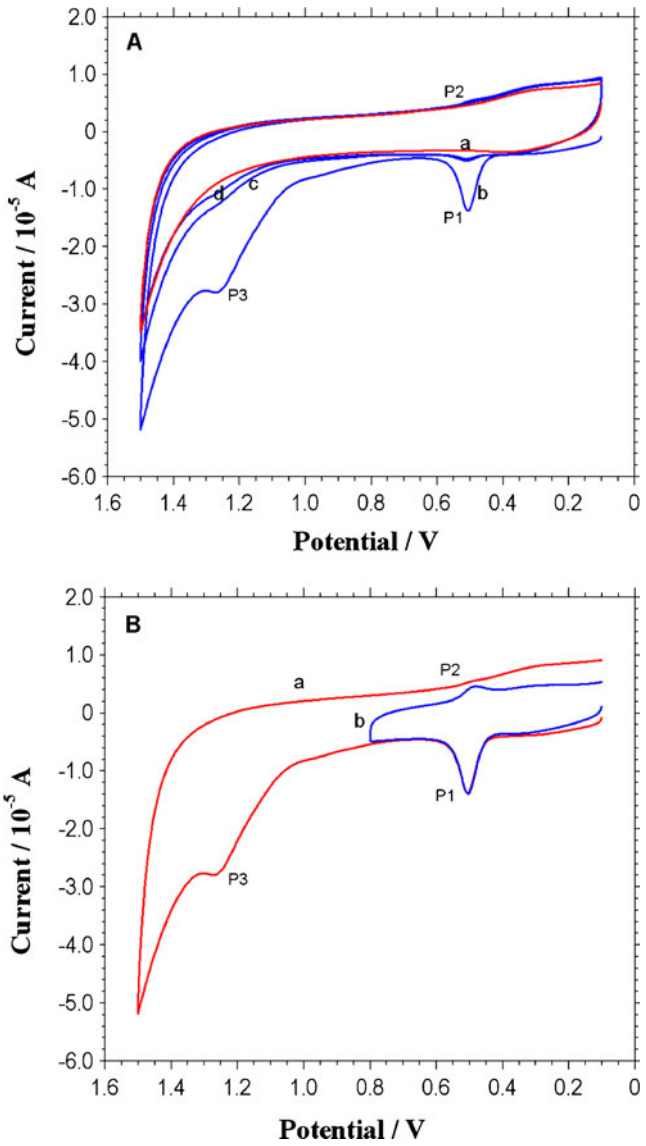



**Fig. 5** **a** Cyclic voltammograms of the background (*curve a*) and DMY ($4.0\times10^{-5}$ mol $L^{-1}$, *curve b, c, d*) in 0.1 mol $L^{-1}$ sulfuric acid solutions+0.1 mol $L^{-1}$ NaCl at Nafion/SWNT/GCE in the potential range of 0.10–1.50 V. **b** Cyclic voltammograms of DMY ($4.0\times10^{-5}$ mol $L^{-1}$) at Nafion/SWNT/GCE in the potential range of 0.10–1.50 V (*curve a*) and 0.10–0.80 V (*curve b*)

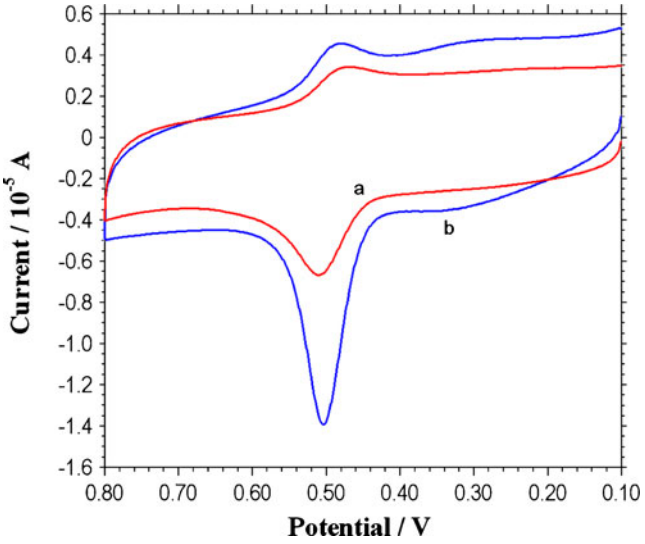



**Fig. 6** Cyclic voltammograms of DMY ($4.0\times10^{-5}$ mol $L^{-1}$) at bare GCE (*curve a*), Nafion/SWNT/GCE (*curve b*) with scan rate $v$= 0.10 V $s^{-1}$; the other experimental conditions are the same as those described in Fig. 5

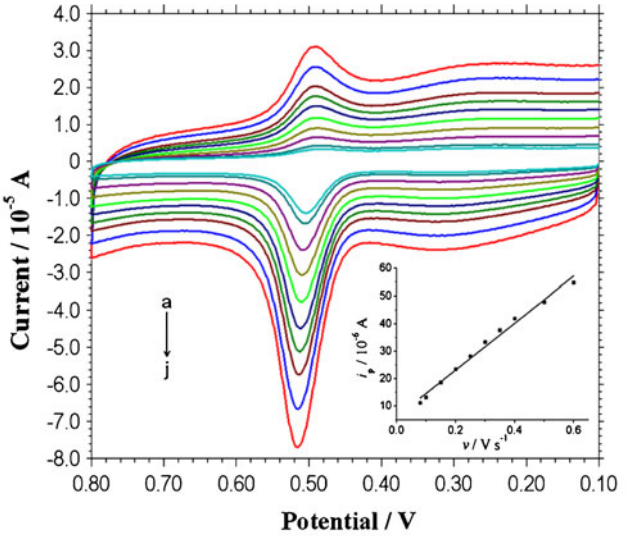



**Fig. 7** CV curves of DMY ($4.0\times10^{-5}$ mol $L^{-1}$) at Nafion/SWNT/GCE at different scan rate (from *a to j*: 80, 100, 150, 200, 250, 300, 350, 400, 500, 600 mV $s^{-1}$); *inset* shows the relationship of the peak potential $i_{p1}$ against $v$; the other experimental conditions are the same as those described in Fig. 5

The electrochemical responses of $4.0\times10^{-5}$ mol $L^{-1}$ DMY at bare GCE and Nafion/SWNT/GCE were compared and shown in Fig. 6. Clearly, the Nafion/SWNT/GCE exhibited better response, which benefitted from the porous structure of Nafion/SWNT.

*Influence of scan rates*

The reaction characters of DMY on the Nafion/SWNT/GCE were further investigated by the influence of scan rate ($v$) on peak current ($i_{p1}$). The superposition voltammograms were shown in Fig. 7. With the scan rates increasing, the anodic peak (P1) potential shifted in gradually positive direction and a good linear relationship was presented between $i_{p1}$ and $v$ (inset), indicating that the electrode reaction of DMY at Nafion/SWNT/GCE was a quasi-reversible process driven by adsorption. Based on Laviron's theory of adsorption-controlled process, the $i_p$–$v$ relation can be described as the following equation [31]:

$$i_p = \frac{nFQv}{4RT} \quad (Q = nFA\Gamma^*) \tag{1}$$

This means that the electron transfer number $n$ can be calculated as long as the CV peak area $Q$ obtained under certain scan rate. As scan rates varied between 80 and 600 mV/s, $n$=2 was calculated at average.

Based on literature [31], we know that if the charge transfer coefficient $\alpha$ is presumed as 0.5 for a quasi-reversible reaction dominated by adsorption, the calculated error for other kinetic parameters is not larger than 6%. Based on this idea, the following equation can be used to calculate the appearance rate constant ($k_s$) of electrode reaction:

$$\log k_s = \alpha\log(1-\alpha) + (1-\alpha)\log\alpha - \log\frac{RT}{nFv} - \alpha(1-\alpha)\frac{nF\Delta E_p}{2.3RT} \tag{2}$$

For this system, the value of $k_s$ was further calculated to be 1.13 $s^{-1}$.

*Influence of supporting electrolyte and pH*

The types of supporting electrolytes played a key role in the voltammetric responses of DMY. A series of supporting electrolytes were tested (phosphate buffer, Britton–Robinson, acetate buffer, ammonium–hydrochloric buffer, sulfuric acid). Both higher peak current and better peak shape were obtained in 0.1 mol $L^{-1}$ sulfuric acid+ 0.1 mol $L^{-1}$ NaCl. In addition, no response appeared when pH was greater than 5. Therefore, sulfuric acid buffer solution was adopted.

Figure 8 showed the effect of different pH on the response of DMY ($4.0\times10^{-5}$ mol $L^{-1}$) in the pH range of 0.94–2.70. As shown in Fig. 8, the value of formal peak potential ($E^{0'}$) shifted to the negative direction with the increase of solution pH. A linear regression equation was obtained as $E^{0'}(V)$=−0.0543pH+0.5558 ($\gamma$=0.999), which indicated that the number of electrons and protons involved in the reaction mechanisms was the same.

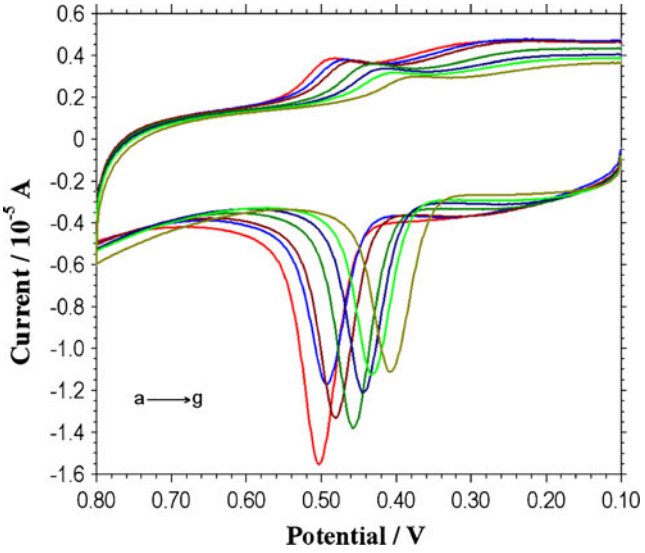



**Fig. 8** Cyclic voltammograms of DMY ($4.0\times10^{-5}$ mol $L^{-1}$) at different solution pH of sulfuric acid solutions+0.1 mol $L^{-1}$ NaCl. pH (*curves a to g*) 0.94, 1.20, 1.39, 1.80, 2.07, 2.26, 2.70

Structure-activity relationship studies of flavonoids have shown that the o-dihydroxy structure in the ring B is essential for effective free radical scavenging activity [32]. Based on above results, a possible electrode reaction mechanism of DMY at the Nafion/SWNT/GCE was proposed and expressed as scheme 1.

*Determination of saturating absorption capacity*

The chronocoulometry method is suitable for the determination of the saturating absorption capacity for this kind of electrode reaction. The Nafion/SWNT/GCE was immerged in a DMY solution ($8.0\times10^{-5}$ mol $L^{-1}$) for several minutes to achieve saturated absorption. And then, a step potential from 0.1 to 0.8 V was applied (Fig. 9, curve b). For control, $Q \sim t$ curve was recorded in blank sulfuric acid solution, too (Fig. 9, curve a). The corresponding $Q \sim t^{1/2}$ plots were also performed and shown as an inset in Fig. 9. As shown in Fig. 9, the control and DMY plots have same slope values, meaning no DMY diffusion occurred at the electrode surface. According to the formula given by Anson [33]:

$$Q = \frac{2nFAc(Dt)^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads} \quad (3)$$

Here, $Q_{dl}$ is double-layer charge; $Q_{ads}$ is the Faradaic charge due to the oxidation of adsorbed DMY. Using Laviron's theory of ($Q = nFA\Gamma^*$) and intercepts for curves a and b, the $\Gamma^*$ value of $6.0\times10^{-12}$ mol $mm^{-2}$ was obtained.

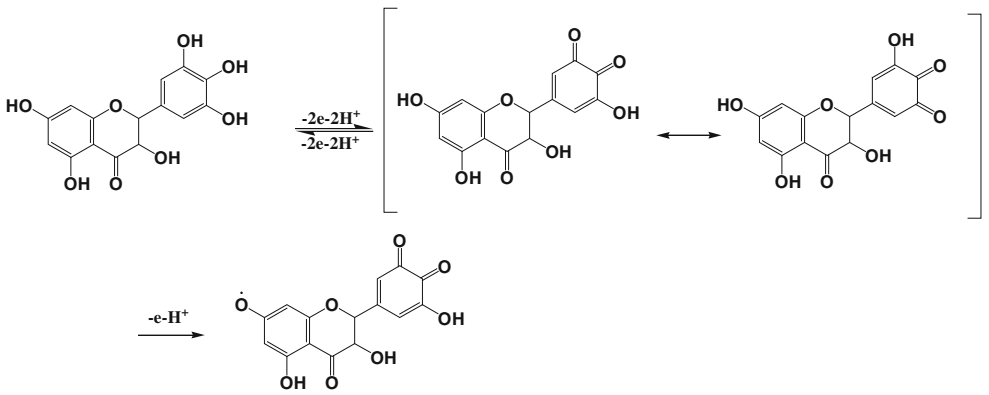
Analytical applications and methods validation

*Influence of accumulation time and potential*

In consideration of the detection sensitivity and adsorption of DMY on the Nafion/SWNT/GCE surface, squarewave voltammetry (SWV) technique, coupled with accumulation procedure, was adopted for researching the analytical method. For a DMY solution ($1.0\times10^{-5}$ mol $L^{-1}$), the peak currents increased with increasing accumulation time ($t_{acc}$), and it reached a maximum value when $t_{acc}$ was 200 s. However, for getting a better detection limit, $t_{acc}$ of 240 s was selected as the accumulation time in following study. After investigation, accumulation potential ($E_{acc}$) had little effect on peak currents, so accumulation of DMY was carried out under open circuit for further studies.

*Calibration curve*

The relationship between peak current and the concentration of DMY was investigated by SWV in the optimized conditions. A good relationship between peak current ($i_p$) and different concentration of DMY could be exhibited in the range of $1.0\times10^{-7}$–$1.0\times10^{-5}$ mol $L^{-1}$ (Fig. 10 and




**Scheme 1** Redox mechanism of DMY at Nafion/SWNT/GCE

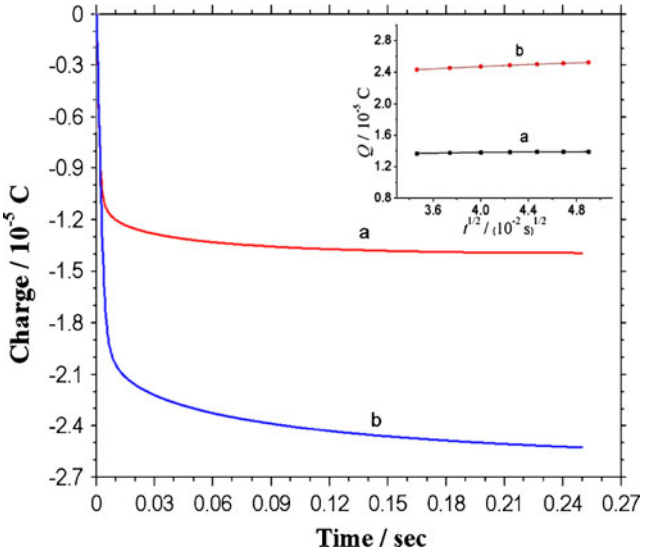



**Fig. 9** Chronocoulometric curves of the background (*curve a*) and DMY ($8.0\times10^{-5}$ mol $L^{-1}$) (*curve b*) in 0.1 mol $L^{-1}$ sulfuric acid solutions+0.1 mol $L^{-1}$ NaCl at Nafion/SWNT/GCE. *Inset*, the corresponding $Q \sim t^{1/2}$ plots

inset). The linear regression equation and correlation coefficient are:

$$i_p(\mu A) = -0.299 + 2.944 \times 10^6 C \ (\gamma = 0.9978)$$

Where $i_p$ was the oxidation peak current in $\mu$A and C was the concentration of DMY in moles per liter. The detection limit was obtained as $9.0\times10^{-8}$ mol $L^{-1}$.

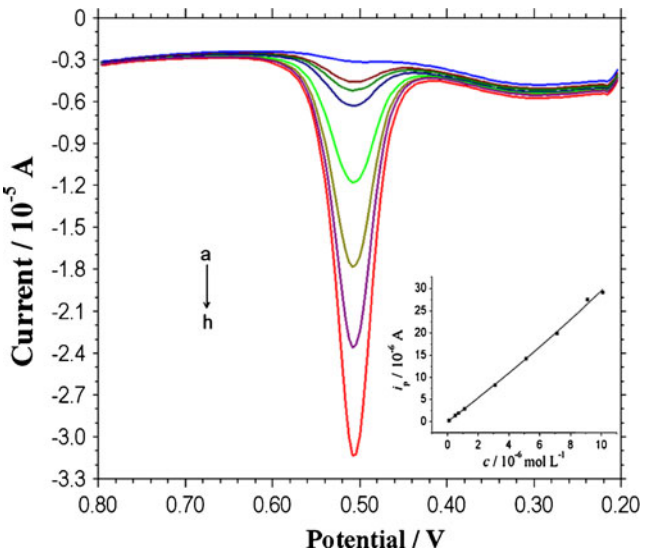



**Fig. 10** Squarewave voltammograms and their associated calibration plot (*inset*) for increasing concentrations of DMY at Nafion/SWNT/GCE under optimum conditions; DMY concentration: **a** $1.0\times10^{-7}$ mol $L^{-1}$, **b** $3.0\times10^{-7}$ mol $L^{-1}$, **c** $5.0\times10^{-7}$ mol $L^{-1}$, **d** $1.1\times10^{-6}$ mol $L^{-1}$, **e** $3.1\times10^{-6}$ mol $L^{-1}$, **f** $5.1\times10^{-6}$ mol $L^{-1}$, **g** $7.1\times10^{-6}$ mol $L^{-1}$, **h** $1.0\times10^{-5}$ mol $L^{-1}$

*Stability and reproducibility of the modified electrode*

To check the stability of the Nafion/SWNT/GCE, five successive CV in DMY solution were recorded (Nafion/SWNT/GCE was stirring in 0.2 mol $L^{-1}$ NaOH for 300 s between twice scans of CV to renew the modified electrode surface). The relative standard deviation (R.S.D.) of five successive measurements was calculated to be 3%. And the Nafion/SWNT/GCE can be stored about 1 week and the decrease of the response was gotten as 4.9%, which indicated that the Nafion/SWNT/GCE has good reproducibility.

*Interference studies*

The influence of some foreign species on the determination of DMY was evaluated in detail. A fixed amount of $1.0\times10^{-5}$ mol $L^{-1}$ DMY spiked with various foreign species was evaluated under the same experimental conditions. The following organic compounds: 10-fold of folic acid, 10-fold of caffeine, 10-fold of theophylline, and 10-fold of glucose, and the following inorganic compounds: 50-fold excess of Fe(III), Cu(II), and 100-fold excess of Ca(II), Mg(II) had no interference (signal change below 5%). All these indicated that the proposed method had good selectivity for the determination of DMY.

*Determination of DMY in the real sample*

DMY in *A. grossedentata* sample was detected to evaluate the practical applicability of the proposed method using freshly prepared electrodes. The standard addition method was employed to detect three parallel samples and the results were listed in Table 1. The R.S.D. was calculated to be 2.0% for three parallel samples determination. For demonstrating the detected accuracy, recovery was detected for each sample by adding some standard DMY in solution and HPLC method was employed for same samples (Table 1). The analytical results from the HPLC method (R.S.D. 4.56%) and proposed method were compared statistically by Student's *t* test at the 95% confidence level.

**Table 1** Determination results of DMY in the *Ampelopsis* sample by SWV and HPLC

| | SWV | | | | | HPLC |
|---|---|---|---|---|---|---|
| | Original found (mg $L^{-1}$) | Standard added (mg $L^{-1}$) | Total found (mg $L^{-1}$) | Recovery | Amount found (mg $L^{-1}$) | Amount found (mg $L^{-1}$) |
| 1 | 2.99 | 2.56 | 5.62 | 102.78% | | |
| 2 | 2.91 | 2.56 | 5.39 | 97.13% | 2.85 | 2.75 |
| 3 | 2.74 | 2.56 | 5.68 | 103.21% | | |

The results indicated that there was no significant difference between them. Because the proposed method was simpler and more time-saving than the HPLC method, it can be recommended for the DMY analysis.

## Conclusion

In this paper, an electrochemical sensor Nafion/SWNT/GCE was fabricated for the detection of trace amounts of DMY. The existence of SWNT significantly enhanced the response of DMY. Thus, the modified electrode exhibited good sensitivity of DMY with the detection limit of $9.0\times 10^{-8}$ mol $L^{-1}$ by SWV under accumulation time of 240 s. The proposed method was further applied for the detection of DMY in real *A. grossedentata* sample with satisfactory results. More importantly, the reaction mechanism of DMY was investigated using the method, which could provide a valuable reference for the pharmacological action of DMY in clinical study.

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## References

1. Yabe N, Matsui H (1997) J Ethnopharmacol 56:31
2. Yabe N, Tanaka K, Matsui H (1998) J Ethnopharmacol 59:147
3. Murakami T, Miyakoshi M, Araho D, Mizutani K, Kambara T, Ikeda T (2004) Biofactors 21:175–178
4. Towatari K, Yoshida K, Mori N, Shimizu K, Kondo R, Sakai K (2002) Planta Med 68:995
5. Anu L, Pedro AJ, Markku L, Riitta JT (2003) Environ Exp Bot 49:49–60
6. Riitta T, Timo V, Pedro JA, Riitta JT (2003) Basic Appl Ecol 4:219–228
7. Zhang YS, Ning ZX, Yang SZ, Wu H (2003) Acta Pharmacol Sin 38:241–244
8. Ma J, Luo XD, Protiva P, Yang H, Ma CY, Basile MJ (2003) J Nat Prod 66:983
9. Ma J, Yang H, Basile MJ, Kennelly EJ (2004) J Agric Food Chem 52:5873–5878
10. Matsumoto T, Tahara S (2001) Nippon Nogeik Kaishi 75:659–667
11. Liu DY, Ye JT, Yang WH, Yan J, Zeng CH, Zeng S (2004) Biomed Environ Sci 17:153
12. Tamano H, Satoshi T, Takayuki O (2005) Biochem Systemat Ecol 33:27–68
13. Ohyama M, Tanaka T, Ito T (1999) Bioorg Med Chem Lett 9:3057
14. Zhang YS, Zhang QY, Li LY, Wang B, Zhao YY, Guo DA (2007) J Chromatogr B 860:4–9
15. Lee KH, Kim JH (2008) Biotechnol Bioprocess Eng 13:274–278
16. Liu BG, Du JQ, Zeng J, Chen CG, Niu SY (2009) Eur Food Res Tech 230:325–331
17. Yu XY, Liu RH, Yang FX, Ji DH, Li XF (2011) J Mol Struct 985:407–412
18. Sumio I (1991) Nature 354:56–58
19. Sumio I, Toshinari I (1993) Nature 363:603–605
20. Cella Cella, Chen W, Myung NV, Mulchandani A (2010) J Am Chem Soc 132:5024–5026
21. Baughman RH, Zakhidov AA, Heer WA (2002) Science 297:787–789
22. Hiura H, Ebbesen TW, Tanigaki K (1995) Adv Mater 7:275–276
23. Li QW, Luo GA (1999) Sensor Actuator B Chem 59:42–47
24. Liu CY, Bard AJ, Wudl F, Weitz I, Heath JR (1999) Electrochem Solid State Lett 2:577–578
25. Tian SL, Zhang YS, Yang YX, Yang WL, Gong YX (2002) J Hunan Agriculture University 28:32–34
26. Lawrenee NS, Deo RP, Wang J (2005) Electroanalysis 17:65–72
27. Lawrence NS, Deo RP, Wang J (2004) Anal Chim Acta 517:131–137
28. Pei RJ, Cheng ZL, Wang EK, Yang XR (2001) Biosens Bioelectron 16:355
29. Liu YJ, Yin F, Long YM, Zhang ZH, Yao SZ (2003) J Colloid Interface Sci 258:7
30. Wang F, Zhao FY, Zhang YF, Yang HG, Ye BX (2011) Talanta 84:160–168
31. Laviron E (1979) J Electroanal Chem 101:19–28
32. Jovanovic SV, Steenken S, Hara Y, Simic MG (1996) J Chem Soc Perkin Trans 2:2497
33. Anson FC (1964) Anal Chem 36:932–934