



# The novel voltammetric method for determination of hesperetin based on a sensitive electrochemical sensor



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## ABSTRACT

A highly sensitive voltammetric sensor, based on reduced graphene oxide on SWCNTs modified glassy carbon electrode (GCE), was constructed and used for sensitive detection of hesperetin. The electrochemical behavior of hesperetin at this sensor was investigated systematically and a novel voltammetric method for determination of hesperetin was proposed. The redox characters of hesperetin was discussed in detail and a reasonable reaction mechanism was proposed also. As the analytical method, the response currents were linear relationship with the hesperetin concentrations in the range of  $5.0 \times 10^{-8}$  to  $3.0 \times 10^{-6}$  mol L<sup>-1</sup>, with a detection limit of  $2.0 \times 10^{-8}$  mol L<sup>-1</sup> ( $S/N=3$ ). The method was also applied successfully to detect hesperetin in biological samples and Chinese herbal medicine Flos buddlejae with satisfactory results.

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## 1. Introduction

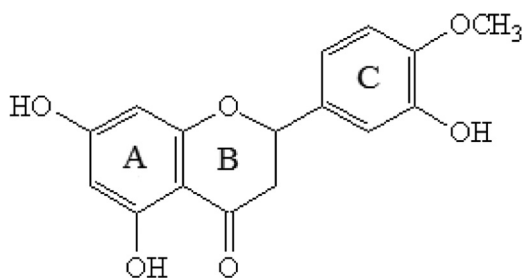
Hesperetin (3',5,7-trihydroxy-4-methoxy flavonone), one of the most abundant flavonoids, was found in citrus fruits and some Chinese herbal medicine in nature. Its chemical structure was shown in Scheme 1. It has been reported that hesperetin exhibits various pharmacological activities, such as anti-adipogenic, anti-inflammatory, anti-oxidative activity [1–5], and antimicrobial effect [6]. In addition, growing evidence on the possible therapeutic efficacy of hesperetin has been established in preclinical models, including lowering plasma cholesterol [7], antiplatelet activity [8], inhibiting vascular formation [9], preventing cardiovascular disease [10] and neuroprotective effects [11,12]. Most importantly, hesperetin has received considerable attention in cancer prevention [10,13]. In consideration of the critical pharmacological activities, a sensitive and reliable analytical method in determining hesperetin is necessary. To date, some determination techniques have been reported, such as high-performance liquid chromatography (HPLC) [14], high-performance liquid chromatography/tandem mass spectrometry (HPLC-MS) [15], ultra-high-performance liquid chromatography with ultraviolet detector (UHPLC-UV) [16], rapid reverse phase-high-performance liquid chromatographic, (RP-HPLC) [17], high-performance liquid chromatography and capillary electrophoresis (HPLC-CZE) [18], capillary zone electrophoresis with electrokinetic supercharging (CZE-EKS) [19],

high-performance liquid chromatography with electrochemical detection (HPLC-ECD) [20]. However, complicated preconcentrations, multisolvent extraction techniques or needs expensive devices and maintenance are coupled with these techniques due to the complexity of the real samples and the low concentration of the analyte. More inadequate, the pharmacological action and reaction mechanism of hesperetin can not be observed using these methods. So, electrochemical methods have attracted enormous attentions by virtue of fast response, low cost, easy operation, high sensitivity and selectivity. Nevertheless, only one literature on electrochemical means for hesperetin so far [21]. Volikakis and Efstathiou determined rutin and other flavonoids by flow-injection/adsorptive stripping voltammetry using nujol-graphite and diphenylether-graphite paste electrodes and obtained the analytical range and the reproducibility (RSD%) were  $10^{-5}$  to  $10^{-8}$  mol L<sup>-1</sup> and 2.5–10%, respectively. However, there was no electrochemical determination specifically aimed at hesperetin and the electrochemical reaction mechanism have not been researched due to complex reaction of hesperetin at the electrodes. In present work, a novel, sensitive and credible electroanalytical method was developed in determination of hesperetin.

Graphene, a two-dimensional graphitic carbon material, possesses excellent mechanical, thermal electrical, optical properties, highly electrical conductivity [22–24] and large surface area [25]. Thus, since the advent of graphene, it has been widely used for establishing various electrochemical sensors and biosensors [26–28]. Nevertheless, due to graphene generally tends to form irreversible agglomerates in water, the direct dispersion of graphene in water has been generally considered unattainable. Hence,

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**Scheme 1.** The chemical structure of hesperetin.

graphene is mostly obtained from graphene oxide (GO) which could dispersed in water by chemically [29,30] or electrochemical [31,32] reduction. The electrochemical reduction of GO is more efficient and environmentally friendly. Carbon nanotubes (CNTs) have also generated a great deal of interest as novel platforms for electrochemical sensors, because of their larger specific surface area, good electrical conductivity and electrocatalytic properties. Based on these properties of CNTs, many works in electrochemical sensing have been done [33,34]. It is worth mentioning that due to the synergistic effects from graphene and CNTs, their combination could exhibit much more excellent electrochemical performance compared with a single component of CNTs or graphene [35].

In this work, a sensitive voltammetric sensor, based on reduced GO and SWCNTs modified glassy carbon electrode (ERGO/SWCNTs/GCE), was fabricated and used in determination of hesperetin. The electrochemical behavior of hesperetin was studied in detail at the proposed sensor and a reasonable reaction mechanism was suggested. For the analytical method proposed, it had wider response linear range with hesperetin concentration from  $5.0 \times 10^{-8}$  to  $3.0 \times 10^{-6}$  mol L<sup>-1</sup> and a detection limit of  $2.0 \times 10^{-8}$  mol L<sup>-1</sup>. Finally, the proposed method was successfully applied to analyze real samples (human urine sample and Chinese herbal medicine of *Flos buddlejae*) with satisfactory results.

## 2. Experimental

### 2.1. Instruments and reagents

RST5000 electrochemical workstation (Zhengzhou Shiruisi Instrument Co. Ltd., Zhengzhou, China) was employed for electrochemical experiments. A conventional three-electrode electrochemical system consisting of a bare (3 mm diameter) or modified GCE as working electrode, an Ag/AgCl as reference electrode and a platinum (Pt) wire as auxiliary were used. The type of pH meter was pHs-3C (Shanghai Techcomp Jingke Scientific Instruments Co., Ltd.). High performance liquid chromatographic (HPLC) was performed on 1260 Infinity Quaternary LC System (Agilent Technologies Inc., Santa Clara, America).

SWCNTs (95% purity) was purchased from Beijing Nachen S&T Ltd., China. Graphite (powder < 20 μm) was obtained from Sino-pharm Chemical Reagent Co., Ltd. Hesperetin (≥ 98%) was purchased from Aladdin. The standard stock solution of hesperetin ( $1.0 \times 10^{-3}$  mol L<sup>-1</sup>) was prepared in ethanol and kept in refrigerator at 4 °C. PBS (0.1 mol L<sup>-1</sup>) was used as supporting electrolyte. All other reagents were of analytical reagent grade without further purification. Double-distilled water was used throughout and all experiments were performed at room temperature.

### 2.2. Preparation of modified GCE

Prior to modification, purification and carboxylation of the SWCNTs was performed according to the literature [36]. Then, 1.0 mg mL<sup>-1</sup> SWCNTs/DMF solution and 1.0 mg mL<sup>-1</sup> GO aqueous

solution were obtained according to literatures [37,38]. Before modification, the bare GCE was polished to a mirrorlike state with 0.3 and 0.05 μm alumina slurry, then washed successively with double-distilled water, anhydrous alcohol and double-distilled water in an ultrasonic bath and dried in air naturally. Next, the SWCNTs modified GCE (named as SWCNTs/GCE) was established by dropping 2 μL of SWCNTs/DMF solution on the fresh GCE surface and dried under IR-lamp. Then, 5 μL GO aqueous solution was dropped on the surface of SWCNTs/GCE and dried under IR-lamp (named as GO/SWCNTs/GCE). Finally, the dried electrode was immersed in PBS (pH 5.0, N<sub>2</sub>-saturated) and performed the cyclic scan between 0.0 V and -1.5 V for 10 cycles to reduce the GO. After the treatment, the modified electrode was donated as ERGO/SWCNTs/GCE. In order to better contrast, GO modified GCE (GO/GCE) was prepared by dropping 5 μL GO aqueous solution on the surface of GCE. Additionally, ERGO modified GCE (ERGO/GCE) was obtained by reducing the GO/GCE according to above procedure.

### 2.3. Analytical measurements

The prepared ERGO/SWCNTs/GCE was treated in pH 2.0 PBS (blank) by cyclic voltammetry scanning in the potential range of 0.2 and 0.9 V with rate of 0.1 V s<sup>-1</sup> until a stable background was obtained. Then, a certain hesperetin standard solution or sample were added to the electrolytic cell and a preconcentration step was performed under open-circuit along with solution agitation for 90 s. Linear sweep voltammetry (LSV) was employed to establish the analytical method and current-potential curves were recorded in potential range between 0.2 V and 0.7 V. Due to the adsorption characteristics of hesperetin at the electrode surface, it was need to renew the ERGO/SWCNTs/GCE surface by three successive CV scanning between 0.2 and 0.9 V in 0.1 mol L<sup>-1</sup> PBS (pH 10.0).

## 3. Results and discussion

### 3.1. Electrochemical characterization of ERGO/SWCNTs/GCE

Cyclic voltammetry (CV) was employed to probe the surface feature of different electrodes. Fig. 1A displayed cyclic voltammograms of the six electrodes in [Fe(CN)<sub>6</sub>]<sup>3-</sup> solution ( $1 \times 10^{-3}$  mol L<sup>-1</sup> containing 0.1 mol L<sup>-1</sup> KCl). Fig. 1B was the enlarged view of curves a to d in Fig. 1A. Well-defined CV, characteristic of diffusion-controlled reversible redox process, was observed at bare GCE (Fig. 1A curve a). The redox peak currents remarkably increased at SWCNTs/GCE (Fig. 1A curve c) or ERGO/GCE (Fig. 1A curve e), demonstrating that SWCNTs or ERGO could effectively accelerate the electron transfer rate. When GO was immobilized on the surface of GCE (Fig. 1A curve b) and SWCNTs/GCE (Fig. 1A curve d), the redox peak currents decreased obviously and the redox peak potential differences increased. The reason of these phenomena can attribute to a large number of oxygen containing functional groups on GO surface, which reduced the redox rate of [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup>. What's more, in the case of ERGO/SWCNTs/GCE used (Fig. 1A curve f), the response currents reached the maximum among the six electrodes, which benefited from combination effect of both SWCNTs and ERGO.

For further characterizing the fabricated electrode, electrochemical impedance spectroscopy (EIS) was carried out in the electrolyte containing  $5 \times 10^{-3}$  mol L<sup>-1</sup> [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> and 0.1 mol L<sup>-1</sup> KCl. The Nyquist plot of EIS has two parts (linear segment and semicircle part): the linear segment at lower frequencies shows a controlled diffusion process; the semicircle part at higher frequencies corresponds to the electron transfer limited process and the diameter of the semicircle presents the electron transfer resistance ( $R_{ct}$ ). Fig. 2 shows the Nyquist plots using different electrodes. After fitting a suitable circuit (inset in Fig. 2) and calculation, the  $R_{ct}$  obtained were

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