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# Electrochemical behavior of polydatin and its highly-sensitive determination based on graphene modified electrode

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ABSTRACT

A voltammetric sensor for polydatin sensing was simply fabricated by in-situ electrochemically reducing graphene oxide at a glassy carbon electrode. The redox behavior of polydatin was investigated systematically. For the first time, the kinetics parameters of electrode reaction of polydatin were calculated using various electrochemical techniques. Significant electrochemical signal increases were achieved by the excellent conductivity and large surface area of reduced graphene oxide. Thereafter, a highly-sensitive electroanalytical method for polydatin was established with a good linear relationship from $4.0 \times 10^{-8}$ mol $L^{-1}$ to $3.5 \times 10^{-6}$ mol $L^{-1}$ and a detection limit of $4.0 \times 10^{-8}$ mol $L^{-1}$. In addition, the practical application of present method was demonstrated by determining the concentration of polydatin in real sample with satisfactory result.



## 1. Introduction

Polydatin (PDT), also named Piceid (3.4′,5-trihydroxystilbene-3-β-D-glucoside), is a polyphenol which occurs naturally in various families of plants, such as grape skin, nuts, pomegranate and so on [1,2]. Its chemical structure is shown in Scheme 1. Several works have reported the beneficial and biological effects of polydatin, including anti-cancer [3,4], anti-inflammatory [5], anti-allergy [6,7], antioxidant [8], prominent nephroprotective activities and low toxic effects [9], potential cardioprotective effects and protection of cardiac function [10,11]. Polydatin has also been verified that it could inhibit the platelet aggregation, lower the level of blood lipid, reduce lipid peroxidation, dilate blood vessels, protect from myocardial ischemia/reperfusion damage, and liver protective effect [12–15]. Recently, Qin et al. report that the lifespan-extension role of polydatin is mainly attributed to its antioxidative activity by regulating the aging-associated genes daf-16 and stress-resistance protein SOD-3 involved in insulin/IGF-1 signaling pathway, addressing the potential of polydatin to extend human average life expectancy and the significance of polydatin in drug development and invention therapy in the study of aging and aging-related diseases [16]. Consequently, based on its widely investigation in the field of clinical and pharmacological research, it is necessary and important to establish analytical methods for the determination of polydatin.

At present, some analytical techniques have been published for the determination of polydatin, such as liquid chromatography-tandem mass spectrometry (LC-MS/MS) [17], capillary electrophoresis (CE) [18], gas chromatography/mass spectrometry (GC/MS) [19,20], high performance liquid chromatography (HPLC) [21–23], fluorescence [24]. These methods mostly involved the separation process and usage of poisonous organic solvent, consuming a relatively long time. However, electrochemical techniques have some advantages such as simple, sensitive, rapid, inexpensive and convenient to study the redox mechanism. Moreover, the data obtained from electrochemical techniques are often correlated with molecular structures and pharmacological activities of drugs. Therefore, it is valuable to develop an electroanalytical method for polydatin assay. As far as we are aware of, only one research reported for determining the concentration of polydatin in Traditional Chinese Medicine based on MWNTs modified GCE with a detection limit of $4.57 \times 10^{-7}$ mol $L^{-1}$ [25]. And by our knowledge, there has no work for investigating the electrode reaction kinetics parameters of polydatin in details, including the above-mentioned reference.

Graphene (GR), a two dimensional monolayer sheet of $sp^2$ hybridized carbon [26], is now used extensively in fabrication of electrochemical sensors due to its perfect electric/thermo conductivity, high electrocatalytic activities, large specific surface areas and excellent electrochemical stability [27–29]. Graphene oxide (GO), the oxide form of GR, can be reduced to GR with different kind methods including chemical reduction [30], thermal reduction [31], photocatalytic reduction [32] and electrochemical reduction [33]. Chemical reduction method is often introducing some toxic chemicals and thermal reduction usually needs high temperature with multiple steps. Photocatalytic reduction is highly dependent on the activity of photoelectric material under UV condition, which limits its application. By contrast, the method of direct

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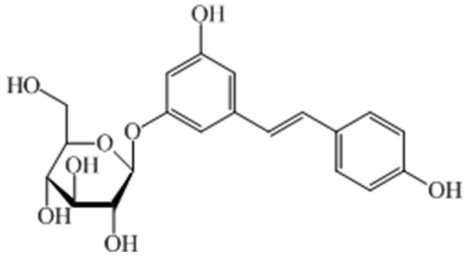


**Scheme 1.** The chemical structure of polydatin.

electrochemical reduction of GO into GR is a good choice because it is eco-friendly, fast and efficient. In addition, the reduction degree of GO can be controlled by changing the electrochemical parameters [34]. Therefore, the electrochemically reduced GO (ERGO) is showing the great application potential in many fields, such as sensors [35–36], supercapacitors [37], and fuel cells [38].

In this work, the ERGO was modified on the electrode surface in-situ by simple casting-drying and electrochemical reduction method (ERGO/GCE). In the whole process, the GO was without further functionalization or blending with other functional materials. So the fabrication of modified electrode was simple and convenient. Then, the electrochemical properties of polydatin were investigated systematically and the dynamic parameters of electrode process were obtained using various electrochemical techniques for the first time. Therefore, a simple, inexpensive and highly sensitive voltammetric method for determination of polydatin was proposed and used for determining polydatin content in *Polygonum cuspidatum* with satisfactory results.

## 2. Experimental

### 2.1. Instruments and reagents

Electrochemical experiments were performed on RST5000 electrochemical workstation (Zhengzhou Shiruisi Instrument Co. Ltd., Zhengzhou, China), utilizing standard three-electrode electrochemical cell with bare or modified glassy carbon electrode (d = 3 mm) as working electrode, platinum (Pt) wire auxiliary electrode and Ag/AgCl reference electrode. All potentials referred in this paper are measured vs. Ag/AgCl electrode.

Polydatin was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). The standard solution of Polydatin ($1 \times 10^{-3}$ mol $L^{-1}$) was prepared with methanol and stored under 4 °C darkly to avoid oxidative degradation and isomerization of the *trans*-piceid to the *cis*-one. Specpure graphite powder (particle size < 50 μm) was obtained from Sinopharm Chemical Reagent Co., Ltd. 0.1 mol $L^{-1}$ phosphate buffer solutions (PBS) were prepared by mixing the stock solutions of 0.1 mol $L^{-1}$ $NaH_2PO_4$ and $Na_2HPO_4$. The low pH value of PBS was adjusted with 0.1 mol $L^{-1}$ $H_3PO_4$. All other reagents were of analytical grade without further purification and all solutions used in this work were prepared with doubly distilled water. Each assay was performed at room temperature. *P. cuspidatum* was obtained from local pharmacy and treated by methanol extraction before determination.

### 2.2. Preparation of modified electrode

Firstly, the graphite oxide was synthesized based on the modified Hummers method [39]. Then, exfoliation of graphite oxide to GO was achieved by ultrasonication of the dispersion for 3 h. The mass concentration of the brown-yellow GO dispersion was estimated to be 1.1 mg $mL^{-1}$.

Prior to modification, the GCE was polished with 0.3 μm aluminum slurry, rinsed thoroughly with redistilled water and sonicated successively in ethanol and redistilled water respectively. The cleaned GCE was dried under IR-lamp for the next modification. The GO film modified GCE was prepared by dropping GO dispersion solution (6 μL) onto the fresh GCE surface and dried under IR-lamp for 10 min (GO/GCE). Then the GO/GCE was immersed in $N_2$-saturated PBS (pH 5.0) and performed the cyclic scan between 0.0 and −1.5 V for 10 cycles to accomplish the in situ-electrochemical reduction of GO at the GCE surface. After the treatment, the modified electrode was denoted as ERGO/GCE.

### 2.3. Analytical measurements

Before analytical measurement, the new prepared ERGO/GCE was pretreated by successive cyclic voltammetric sweeps between 0.35 V and 0.85 V for 10 cycles in blank PBS (pH 2.5). Then the appropriate volume of polydatin standard solution was added into the electrochemical cell and the cyclic voltammetry (CV) or linear sweep voltammetry (LSV) were performed after an accumulation step (open-circuit along with agitation for 180 s). After each measurement, the ERGO/GCE was put in blank PBS (pH 8.0) for 2 cyclic sweeps between potentials of 0.35 and 0.85 V to renew electrode surface. For establishing the analytical method, LSV was employed for obtaining calibration curve and the potential window was from 0.55 to 0.85 V.

## 3. Results and discussion

### 3.1. Electrochemical reduction of GO

Fig. 1A displayed the cyclic voltammetric curves of electrochemical reduction of GO. As can be seen that a huge reduction peak appeared at −1.18 V in the first sweep from 0 V to −1.5 V direction, which may be attributed to the reduction of oxygen containing functional groups of GO. In the successive scanning process, reductive peak current disappeared, suggesting that the electrochemical reduction of GO was rapid and irreversible. The reduction of GO can also be seen from the color of GO film, which changed from yellow (before reduction) to black (after reduction). Fig. 1B showed the digital camera image of GO (a) and ERGO (b). This phenomenon was consistent with the existing literatures [33,34].

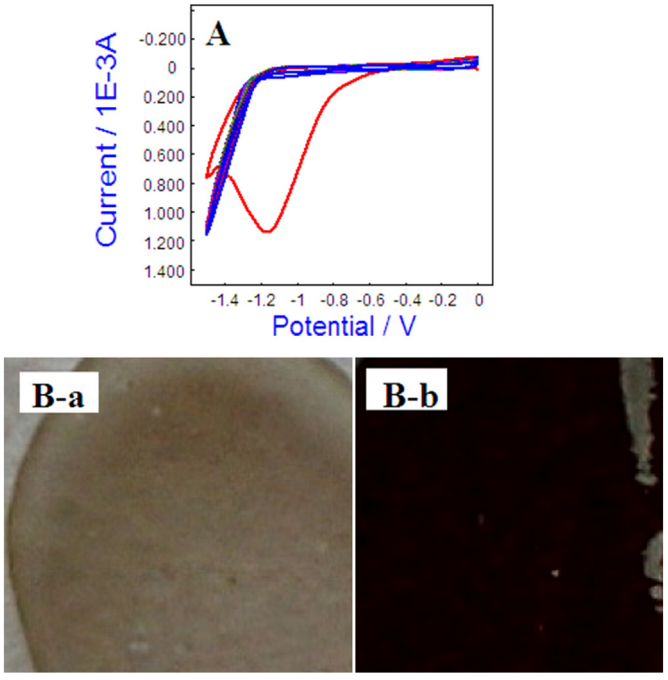


**Fig. 1.** (A) Cyclic voltammograms of GO/GCE in 0.1 mol $L^{-1}$ PBS (pH 5.0), Scan rate: 50 mV $s^{-1}$; (B) Digital camera image of GO (a) and ERGO (b) casted on ITO.