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Research Article

Determination of salidroside and tyrosol in *Rhodiola* by capillary electrophoresis with graphene/poly(urea-formaldehyde) composite modified electrode

This report describes the fabrication and application of a novel graphene/poly(urea-formaldehyde) composite modified electrode as a sensitive amperometric detector of CE. The composite electrode was fabricated on the basis of the in situ polycondensation of a mixture of graphenes and urea–formaldehyde prepolymers on the surface of a platinum disc electrode. It was coupled with CE for the separation and detection of salidroside and tyrosol in *Rhodiola*, a traditional Chinese medicine, to demonstrate its feasibility and performance. Salidroside and tyrosol have been well separated within 6 min in a 40 cm long capillary at a separation voltage of 12 kV using a 50 mM borate buffer (pH 9.8). The prepared graphene-based CE detector offered significantly lower detection potential, yielded enhanced signal-to-noise characteristics, and exhibited high resistance to surface fouling and enhanced stability. It showed long-term stability and reproducibility with relative standard deviations of less than 5% for the peak current ($n = 15$).

Keywords:
Amperometric detection / Capillary electrophoresis / Graphene / Poly(urea-formaldehyde) / *Rhodiola*
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1 Introduction

Since Novoselov et al. successfully prepared graphene in 2004 [1], it has attracted much attention because of its unique nanostructure and properties [2, 3]. As an important two-dimension nanomaterial, graphene has been employed to fabricate electrochemical sensors and biosensors because of its excellent conductivity and electrocatalytic activity [4–6]. It was demonstrated that graphene showed strong electrocatalytic activity when it was employed to improve the electrochemical response of some important bioactive substances based on the fact that graphene-based electrodes reduce overpotential significantly [4–9]. The ability of graphene to promote the electron-transfer reactions suggests great promise for the amperometric detection (AD) of capillary electrophoresis (CE).

Since CE in its modern form was first described by Jorgenson and Lukacs in 1981 [10, 11], it has been applied in the separation and determination of a variety of samples because of its minimal sample volume requirements, short analysis time, and high separation efficiency. It holds considerable promise for biomedical and pharmaceutical analysis, clinical diagnostics, environmental monitoring, and forensic investigations [12–16]. AD offers great promise for CE, with features that include high sensitivity, inherent miniaturization of the detector and control instrumentation, low cost, low-power demands, and high compatibility with micromachining technologies [17]. The performance of CE-AD is strongly influenced by the detection-electrode material. Usually, the detection electrode should provide favorable sensitivity ad reproducibility. To date, a wide range of materials, including platinum, gold, graphite, carbon nanotube, and boron-doped diamond, have been used to fabricate the detection electrode for the AD of CE [17].

Traditional Chinese herbal medicine, *Rhodiola* (i.e. Roseroot) is the dried roots of *Rhodiola rosea* L. It has been widely used to treat fatigue, asthma, hemorrhage, anemia, impotence, and nervous system disorders [18]. Slidroside and tyrosol are the two major bioactive constituents in *Rhodiola*. Their contents are important parameters for evaluating the quality of the herbal drug. The Pharmacopoeia of China requires that the content of salidroside in *Rhodiola* should not be less than 0.5% [18]. Hence, it is necessary to establish some rapid, simple, and accurate approaches for the determination of the bioactive constitu-

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Abbreviations: AD, amperometric detection; **GO,** graphene oxide; **HDV,** hydrodynamic voltammogram; **PUF,** poly(urea-formaldehyde)

ents in *Rhodiola*. LC [19, 20] has been widely employed in the simultaneous determination of salidroside, tyrosol, and other coexistent constituents in *Rhodiola*. In addition, CE [21, 22] has also been employed for the quantitative determination of salidroside and tyrosol in *Rhodiola* using ultraviolet (UV) detectors. Because the absorbance path length of capillary (the typical id, 25–100 μm) is very short, the low sensitivity of the UV detector used results in poor detection limit. Usually, the content of the constituents in the herbal drugs is very low. Highly sensitive detection approaches are highly demanded. Because both salidroside and tyrosol a (their molecular structures are shown in Fig. 1) contain phenolic hydroxyl groups that are electroactive at modest oxidation potential, CE coupled with highly sensitive graphene-based detection electrode should be a useful technique for the constituent investigation of *Rhodiola*.

As an important thermosetting polymer, poly(urea-formaldehyde) (PUF) is made from urea and formaldehyde by polycondensation. A variety of PUF/inorganic material composites have been prepared for various purposes [23–26]. Recently, we prepared carbon nanotube/PUF composite for enhanced electrochemical sensing [27]. To prepare PUF, urea and formaldehyde are usually allowed to react in basic mediums under heat to produce water-soluble prepolymer solution that can further polycondense to form water-insoluble crosslinked polymeric network with the aid of curing catalysts such as ammonium chloride [28, 29]. As a reactive polymer mixture, urea–formaldehyde prepolymer solution offers great promise for the preparation of graphene-based functional materials and other PUF-containing composites because it is rigid and water-insoluble. However, we are not aware of early reports on the preparation of conductive graphene/PUF composite for the purposes of electrochemical sensing.

In this work, graphene/PUF composite modified electrode has been fabricated by in situ polycondensation as the end-column amperometric detector of a CE system. The fabrication details, characterization, feasibility, and performance of the novel graphene-based electrode have been demonstrated by determining salidroside and tyrosol in *Rhodiola* in connection with CE in the following sections.

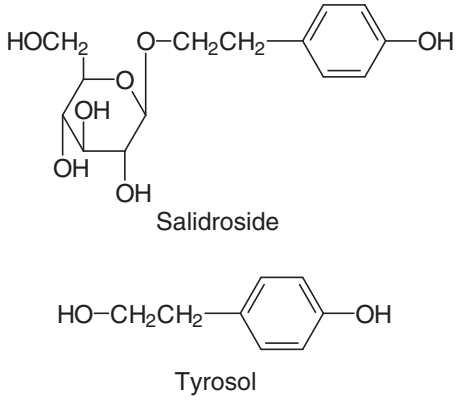

Figure 1. Molecular structures of salidroside and tyrosol.

2 Materials and methods

2.1 Reagent and solutions

Salidroside was supplied by National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China) while tyrosol was obtained from Aldrich (Wilwaukee, WI, USA). Urea, formaldehyde, concentrated ammonia (28%), ammonium chloride, borax, graphite powder, sodium nitrate, potassium permanganate, hydrogen peroxide solution (30%), hydrazine hydrate (85%), and sulfuric acid (98%) were all supplied by SinoPharm (Shanghai, China). All aqueous solutions were made up in doubly distilled water. Other chemicals were of analytical grade.

Stock solutions of salidroside and tyrosol (10 mM) were prepared in methanol and were kept at 4°C in a refrigerator. They were stable for at least 1 month. The running buffer for CE separation was 50 mM borate buffer (pH 9.8). The stock solutions were diluted to the desired concentration with the running buffer prior to use.

2.2 Fabrication of platinum disc electrode

A piece of platinum wire (5 cm long, 250 μm diameter) was inserted into a 3.0-cm-long fused-silica capillary (320 μm id × 450 μm od, Hebei Yongnian Ruipu Chromatogram Equipment, Hebei, China) until the length of the protruded part of the wire was ~1 mm. Subsequently, epoxy resin and hardener (Zhejian Cixi Tiandong Adhesive, Ningbo, China) were mixed thoroughly at a weight ratio of 2:1. The mixture was carefully applied to the protruded part of the wire until it permeated the interspaces between the inner wall of the capillary and the platinum for ~5 mm. After 3 h, the epoxy mixture cured and the protruded end of the wire was sealed in place. The sealed end of the capillary was then carefully polished with sand paper to form a platinum disc electrode.

2.3 Preparation of graphene

Graphene oxide (GO) was synthesized from graphite by a modified Hummers method [30]. Briefly, 2 g graphite powder was dispersed in 46 mL of sulfuric acid (98 wt%) under agitation. Subsequently, 1.2 g sodium nitrate and 6 g potassium permanganate were successfully added into the mixture. Note that both compounds should be added slowly to prevent the temperature from exceeding 20°C. After the reaction was allowed to proceed in a 35°C water bath for 30 min, 92 mL of doubly distilled water was gradually added. And then, the temperature of the water bath was increased to 98°C and the reaction was maintained for 40 min in order to increase the oxidation degree of the GO product. After the volume of the resultant bright-yellow suspension was adjusted to 280 mL with doubly distilled water, 6 mL of hydrogen peroxide solution (30%) was added. The prepared

GO could be isolated from the solution by centrifugation. The acid and salt impurities in the crude GO were removed by careful washing with doubly distilled water with the aid of centrifugation. The wet GO was dewatered by vacuum drying (50°C).

To the prepared graphene, 50 mg GO powder was dispersed in 50 mL doubly distilled water and sonicated in an ultrasonic cleaner (SKQ-2200, frequency 56 kHz, output power 100 W) for 1 h. Reduction of GO was carried out by adding 0.3 mL hydrazine hydrate (85%) into the solution. The reduction reaction was allowed to take place at 95°C for 1 h. The obtained black graphene could be easily isolated form the solution by vacuum filtration and was purified by washing with copious amounts of doubly distilled water. Finally, it was dried in vacuum.

2.4 Preparation of urea–formaldehyde prepolymer solution

Concentrated ammonia (28% w/w, about 1.5 mL) was added to a volume of 35 mL of formaldehyde aqueous solution (37% w/w) to adjust pH to be 7.5−8.0. After 11.4 g urea was dissolved in the solution, the mixture was heated in a 60°C water bath for 15 min. Subsequently, 0.6 g additional urea was dissolved in the solution. The reaction was allowed to continue at 95°C for 1 h to obtain urea–formaldehyde prepolymer solution. The solid content in the solution was approximately 50% w/v.

2.5 Electrode modification

To prepare the modification solution, 5 mL doubly distilled water containing 20 mg graphene powder and 60 μL of urea–formaldehyde prepolymer solution were sonicated for 30 min. Prior to modification, the bare platinum disc electrode (250 μm diameter) was successively polished with emery paper and alumina powder, sonicated in doubly distilled water. After the surface of the disc electrode was allowed to touch the surface of the modification solution for 30 s, it was taken out and was allowed to dry in air for 10 min. The modification procedure was repeated twice. Subsequently, the modified electrode was dipped in 5% ammonium chloride aqueous solution for 10 min to convert urea–formaldehyde prepolymer to crosslink PUF that was water-insoluble. After the in situ polycondensation, a layer of graphene/PUF composite layer formed on the surface of the base electrode. Finally, the modified electrode was flushed with water and dried in air.

2.6 Apparatus

The CE-AD system used in this work has been described in our previous reports [31, 32]. A ±30 kV high-voltage dc power supply (Shanghai Institute of Nuclear Research, China) provided a separation voltage between the two ends of the capillary. The inlet of the capillary was held at a positive potential while the outlet of capillary was maintained at ground. The separations were carried out in a 40 cm length of 25 μm id and 360 μm od fused-silica capillary (Polymicro Technologies, Phoenix, AZ, USA).

As illustrated in Fig. 1 in Supporting Information, a three-electrode electrochemical cell consisting of a disc detection electrode, a platinum auxiliary electrode and an Ag/AgCl wire as the reference electrode, was used in combination with a BAS LC-4C amperometric detector (Bioanalytical Systems, West Lafayette, IN, USA). The detection electrode was positioned carefully opposite the outlet of the capillary with the aid of a high-integrated 3-D amperometric setup (Fig. 1 in Supporting Information) and arranged in a wall-jet configuration. The gap between the end of the capillary and the surface of the detection electrode was ~50 μm. The details and operation procedure of the 3-D adjustable alignment device can be found in Supporting Information. The electropherograms were recorded using a LKB · REC 1 chart record (Pharmacia, Sweden). The surface morphologies of the prepared materials were measured by using a scanning electron microscope (PHILIPS XL 30, Eindhoven, The Netherlands).

2.7 Sample preparation

Three samples of *Rhodiola* were obtained from Sun-Tian-Tang Traditional Chinese Medicine Store (Shanghai, China). They were all dried at 60°C for 2 h and then were pulverized. About 1.0 g of the powder was weighed accurately and dispersed in 10 mL of methanol. The mixture was kept in a 60°C water bath for 3 h. After cooling, it was sonicated for 30 min and filtered through a filter paper. The extract was diluted using 50 mM borate buffer (pH 9.8) at a ratio of 5 (1–5) just prior to CE analysis.

2.8 CE procedure

Prior to use, the capillary used for the separation was treated before use by flushing with 0.1 M NaOH and doubly distilled water for 10 min each. Subsequently, the capillary was filled with the running buffer and was conditioned with the running buffer for at least 10 min at the voltage of 12 kV between the two ends of the capillary. CE was performed at a separation voltage of 12 kV. The potential applied to the detection electrode was +0.80 V (versus Ag/AgCl wire). Samples were injected electrokinetically into the capillary at 12 kV for 6 s. The amperometric detector was on during the injection procedures. Moreover, sample solutions, standard solutions, and running buffer were all filtered through a polypropylene filter (0.22 μm, Shanghai Bandao Industry, Shanghai, China) prior to their use. Peak identification was performed by standard-addition method.

3 Results and discussion

In this work, a novel method based on the in situ polycondensation of urea–formaldehyde prepolymers was developed for the facile preparation of graphene/PUF composite modified electrode. Figure 2 in Supporting Information illustrates the reaction routes for the preparation of graphene/PUF composite. Addition and condensation reactions take place when urea reacts with formaldehyde. In the first stage, urea is hydroxymethylolated by the addition of formaldehyde to the amino groups in basic condition to form mono- and dimethylolureas. The second stage is the condensation of the methylolureas to low molecular weight urea–formaldehyde prepolymers. The reactions lead to the formation of methylene bridges between amido nitrogens via various reaction routes. To prepare the modified electrode, a mixture solution of the urea–formaldehyde prepolymers and graphenes was loaded on the surface of a platinum disc electrode by dip coating. After drying, it was treated with ammonium chloride aqueous solution to cross urea–formaldehyde prepolymers so that a layer of water-insoluble graphene/PUF composite layer was formed on the base electrode. The platinum disc electrode was directly fabricated in the inner bore of a piece of fused-silica capillary (320 μm id and 450 μm od) due to the size compatibility of the detection electrode and the orifice of the separation capillary (25 μm id, 360 od).

Figure 2 shows the SEM images of graphenes and the graphene/PUF composite modified on an electrode. It can be seen clearly from Fig. 2 that the surface morphology of graphene/PUF composite was much different from that of pristine graphenes because the PUF in the composite could

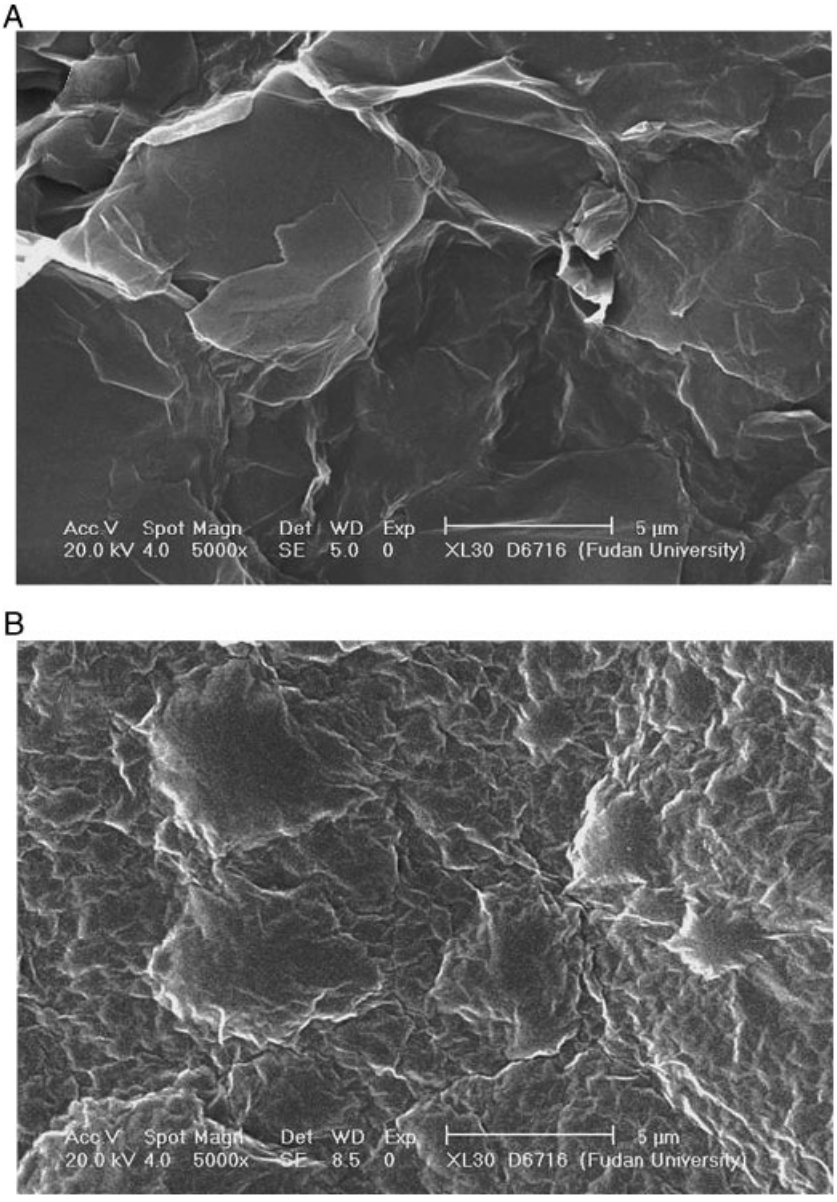

Figure 2. Scanning electron micrograph (SEM) images of pristine graphene (A) and graphene/PUF (B) composite. Conditions: accelerating voltage, 20 kV; magnification, × 5000.

adhere graphenes to form a layer of film. A great amount of small wrinkles and edges of graphenes were observed on the surface of graphene/PUF composite, indicating graphenes were well dispersed and connected throughout the composite and an interconnected graphene network formed on the electrode. This conductive graphene network may establish electric conduction pathways throughout the whole system, which is responsible for the electric conductivity and electrochemical sensing.

To demonstrate the feasibility and performance of the graphene/PUF composite modified electrode, it was coupled with a CE system as an end-column amperometric detector. The attractive performance of the electrode was indicated from the detection of salidroside and tyrosol, two naturally occurring phenolic compounds, offering enhanced sensitivity, lower noise levels, and well-resolved peaks. Figure 3 illustrates the representative electropherograms of a mixture containing 0.5 mM salidroside and 0.5 mM tyrosol recorded with a graphene/PUF composite modified electrode (A) and a bare platinum disc electrode (B). The two analytes can be well separated within 6 min. Figure 4A shows the typical hydrodynamic voltammograms (HDVs) for the electrochemical oxidation of 0.5 mM salidroside on the bare platinum disc electrode (a) and the graphene/PUF composite modified electrode (b). The curves were recorded point-wise by changing the applied potential by 0.1 V from +0.1 to + 1.1 V (versus Ag/AgCl wire). The current response of the graphene/PUF composite modified electrode is higher than that of the bare platinum detection electrode at the same potential. When the applied potential exceeds +0.56 V for the bare platinum electrode and +0.40 V for the graphene/PUF composite electrode, the peak currents of both electrodes raise rapidly. However, the current response increases much slowly upon increasing potential above +0.90 and +0.80 V for the platinum electrode and the graphene/PUF composite modified electrode, respectively. The detection potential of the graphene-based electrode was, therefore, maintained at +0.80 V, under which condition the background current was not too high and the S/N was the highest. The half-wave potentials of salidroside at the platinum electrode and the graphene/PUF composite modified electrode are +0.68 and +0.51 V, respectively. The electrocatalytic activity of graphenes toward salidroside is pronounced as the half-wave potential on the graphene/PUF composite electrode has decreased by 170 mV in comparison with that on the bare platinum electrode, indicating that the graphene-modified electrode allows AD with higher sensitivity and at significantly lower detection potentials.

It was reported that the ability of graphene to promote electron-transfer reactions on the electrode could be attributed to their special electronic structure and high electric conductivity [6, 7]. As shown in Fig. 2B, the wrinkles and edges of graphenes on the surface of the graphene/PUF composite work like thousands upon thousands

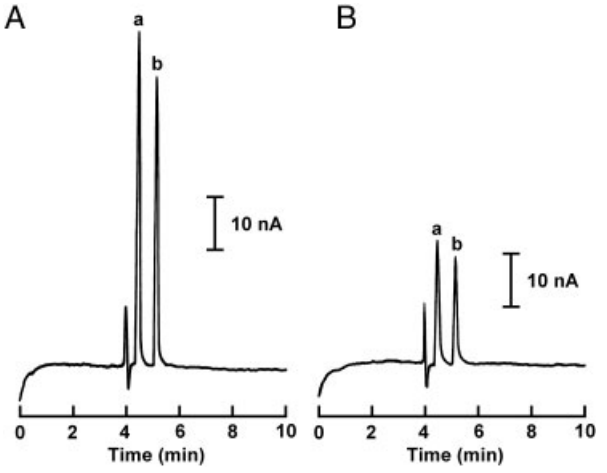

Figure 3. Electropherogram for a mixture containing 0.5 mM salidroside (a) and 0.5 mM tyrosol (b) at a bare platinum electrode (A) and a graphene/PUF composite modified electrode (B). Fused-silica capillary, 25 μm id × 40 cm length; detection electrode, 320 μm diameter composite disc electrode; running buffer, 50 mM borate buffer (pH 9.8); separation and injection voltage, 12 kV; injection time, 6 s; detection potential, +0.8 V (versus Ag/AgCl wire).

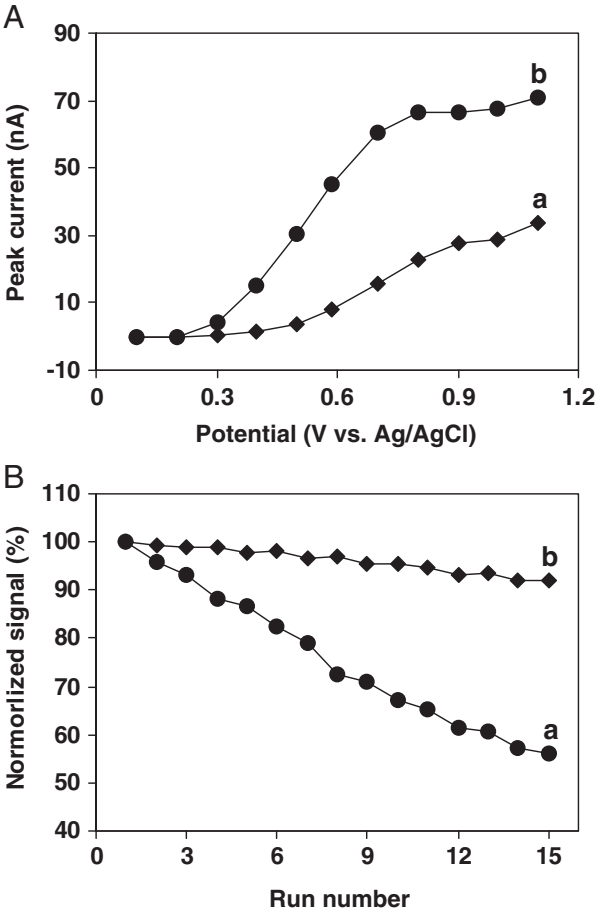

Figure 4. (A) HDVs for 0.5 mM salidroside at a bare platinum electrode (a) and a graphene/PUF composite modified electrode (b) and (B) stability of the response for the repetitive measurements of 0.1 mM salidroside both electrodes. Other conditions, as in Fig. 3.

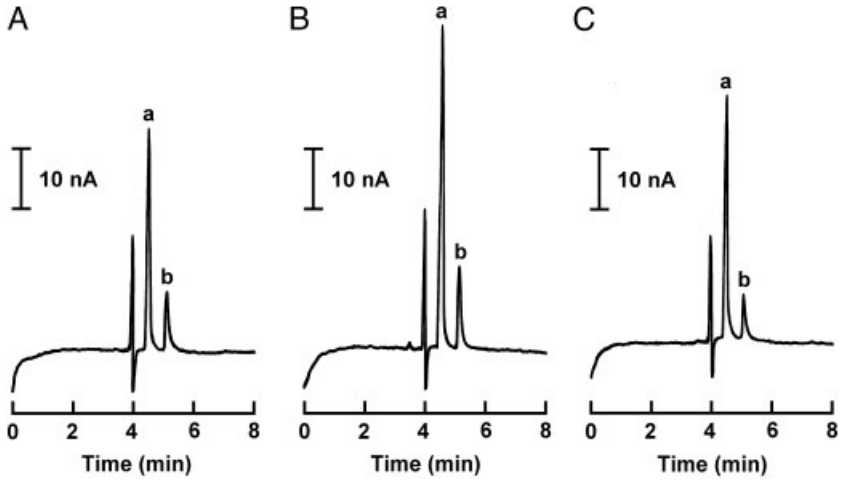

Figure 5. Typical electropherograms for the diluted extracts from three samples of *Rhodiola* (A, Sample 1; B, Sample 2; C, Sample 3). Detection electrode, graphene/PUF composite modified electrode; detection potential, +0.80 V (versus. Ag/AgCl wire); other conditions as in Fig. 3.

microelectrodes. The mass transfer on the graphene conducting network on the electrode is much faster than that on the bare platinum electrode so that the current response was enhanced to some extent. As shown in Fig. 3, the peak currents of salidroside and tyrosol at the graphene/PUF composite modified electrode are much higher than those at the bare platinum electrode. The higher sensitivity of the graphene-based detector is in agreement with the HDV data and leads to lower detection limits compared to the bare platinum electrode [0.24 versus 0.65 (salidroside) and 0.28 versus 0.75 μM (tyrosol), respectively (based on S/N = 3)]. The sensitivity and detection limits of the graphene/PUF composite modified electrode are comparable with those of graphene/PUF composite electrode [27]. Overall, the results indicate that graphene/PUF composite is a promising material for electrochemical sensing.

The stability of the detection electrode is crucially important for the AD of CE. Usually, some analytes tend to be adsorbed on the surface of the electrode. Sometimes, nonconducting polymers may form on the electrode. Such surface fouling usually results in decreased signal. The electrocatalytic detection on the graphene/PUF composite modified electrode is coupled to resistance to surface fouling and hence good stability. Such improvements were illustrated by the capillary electrophoretic measurements of salidroside. Figure 4B displays the response of the bare platinum electrode (a) and the graphene/PUF composite modified electrode (b) to 15 repetitive CE measurements of 0.1 mM salidroside. The time for each run was 20 min. The initial response was found to drop off gradually at the bare platinum detector, with a decrease of 43.9% (RSD 19.4%, $n = 15$). In contrast, a stable response (RSD of 3.2%, $n = 15$), with a very slow decrease of the response (up to 8.1%) was observed over the entire operation for the graphene-based detector. Such good repeatability reflects the reduced surface fouling of the graphene/PUF composite electrode, indicating that this approach is suitable for the analysis of real samples. The higher anti-passivation capability of the graphene/PUF composite can be attributed to the electrocatalytic activity of the composite.

Table 1. Determined contents of salidroside and tyrosol in *Rhodiola* ($n = 3$, mg/g)[a)]

Sample	Salidroside	Tyrosol
1	4.395 (3.1)[b)]	1.178 (3.7)
2	6.411 (2.4)	1.631 (3.5)
3	4.825 (2.7)	0.9042 (4.0)

a) Detection potential is +0.80 V (versus Ag/AgCl wire). Other conditions are the same as in Fig. 3.
b) The data in the brackets are the RSDs (%).

A series of the standard mixture solutions of salidroside and tyrosol with concentrations ranging from 1 μM to 1 mM were analyzed by CE in connection with the graphene/PUF composite modified electrode to determine the linearity. The graphene/PUF composite electrode detector offers a well-defined concentration dependence. The calibration curves exhibit satisfactory linear behavior over the concentration range from 1 6M to 1 mM for both analytes. The linear equations were $y = 0.1176 + 125.839x$ ($R = 0.9997$, salidroside), $y = 0.1423 + 107.453x$ ($R = 0.9991$, tyrosol), where y is the peak current (nA), x is the concentration of the analytes (mM), and R is the correlation coefficient.

In addition, the suitability of the graphene-based detector to real plant samples was demonstrated by detecting salidroside and tyrosol in *Rhodiola* after CE separation. The typical electropherograms of the diluted extracts from three samples of *Rhodiola* are shown in Fig. 5A–C. The assay results are summarized in Table 1. By carefully comparing the electropherograms, it was found that all samples had similar profiles and constituent fingerprints based on the migration times and the heights of the peaks. Because both salidroside and tyrosol were found presented in all the three samples, they can be defined as characteristic markers in the fingerprint of *Rhodiola* under the selected conditions. The determined contents of salidroside and tyrosol in *Rhodiola* are in well agreement with a previous report (4.19–6.12 mg/g for salidroside and 0.86–1.28 mg/g for tyrosol, respectively) [21, 22].

Recovery experiments were performed by adding accurate amounts of salidroside and tyrosol to the diluted extract of *Rhodiola* in the running buffer. Subsequently, the standard-spiked sample solution was analyzed by CE coupled with graphene/PUF composite detection electrode under the selected conditions. The average recoveries and the corresponding RSD were 97.6 and 3.6% for salidroside and 95.4 and 3.3% for tyrosol, respectively ($n = 3$). The results demonstrated that this method had both high recovery and good precision for salidroside and tyrosol.

4 Concluding remarks

A new approach based on the in situ polycondensation of urea–formaldehyde prepolymer has been developed for the fabrication of graphene/PUF composite electrode as the end-column amperometric detector of CE. The performance, utility, and advantages of the novel detection electrode have been demonstrated in combination with the CE separation and determination of salidroside and tyrosol in *Rhodiola*. It is characterized by its higher resolution and sensitivity, lower expense of operation, and less amount of sample. The novel graphene-based CE detector offers favorable signal-to-background characteristics, strong electrocatalytic activity, sharp peaks for the analytes, good resistance to surface fouling, and simple fabrication, indicating great promise for a wide range of applications. It can be concluded that CE coupled with the graphene/PUF composite amperometric detector is an efficient approach for the constituent investigation of herbal drugs due to its special attributes. The simplicity and significant performance exhibited by the graphene/PUF composite electrode also indicate great promise for microchip CE, flow injection analysis, and other microfluidic analysis systems.

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The authors have declared no conflict of interest.

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