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Nafion/multi-wall carbon nanotubes composite film coated glassy carbon electrode for sensitive determination of caffeine

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ABSTRACT

A Nafion/multi-wall carbon nanotubes (MWNTs) composite film-modified electrode was fabricated and applied for the sensitive and selective determination of caffeine. Multi-wall carbon nanotubes (MWNTs) were easily dispersed homogeneously into methanol by ultrasonication in the presence of 0.1% Nafion. After evaporating the methanol, a Nafion/MWNTs composite film-modified electrode was achieved. Caffeine can be effectively accumulated at Nafion/MWNTs composite film-modified electrode and produce a sensitive anodic peak at around 1330 mV (vs. SCE) in a 0.01 mol L^{-1} H_2SO_4 medium (pH 2.0). Compared to the bare electrode and Nafion film-modified electrode, the Nafion/MWNTs film-modified electrode can remarkably increase the anodic peak current of caffeine. Under the suitable conditions, the anodic peak current was linear to caffeine concentration in the range of 6.0×10^{-7}–4.0×10^{-4} mol L^{-1}, and the limit of detection was 2.3×10^{-7} mol L^{-1}. The Nafion/MWNTs composite film-modified electrode can be renewed by repetitiously cycling in a blank solution for about three cycles. This newly exploited method was successfully used to determine caffeine in beverage samples.

1. Introduction

Caffeine (3,7-dihydro-1, 3,7-trimethyl-1H-purine-2, 6-dione) is an active alkaloid. It distributes widely in plants mainly including tea, coffee bean, cocoa and cola nuts, and always exists along with other N-methyl derivatives of xanthenes such as theophylline and theobromine [1,2]. Moreover, caffeine is a major ingredient of daily beverages including coffee, tea, coca-cola, et al, and it is one of the most widely used drugs in the world. Caffeine has many important pharmacological effects, such as the stimulant of central nervous system, diuresis and positive effect on cardiovascular system [3–5]. In addition, it is able to promote secretion of gastric acid and alleviate migraine. It also plays wide-range roles in other systems of the body. Therefore, the investigation and determination of caffeine not only have clinical significances, but also can give beneficial guidance to people's health and life. Thus different methods have been developed for the determination of caffeine and its analog currently [6], such as spectrophotometry [7–9], RP–TLC [10], LC–ESI–MS [11], gas chromatography [12], high performance liquid chromatography (HPLC) [13,14], capillary gas chromatography and capillary electrophoresis [15,16]. Nevertheless, some of these methods, such as the chromatographic methods are time-consuming, expensive, and need complicated preconcentration or multisolvent extraction as well as trained technicians. Instead, electrochemical methods are characterized by simplicity, high sensitivity, good stability, low-cost instrumentation and on-site monitoring [17]. In order to enhance the sensitivity and stability of the measurements, the electrodes modified with designable molecules have been used in electrochemical determination of caffeine, but electroanalysis of caffeine was seldom reported because the oxidation of caffeine occurs at a very high positive potential, except few literatures [18–23].

In recent years, carbon nanotubes (CNTs) have received increasing employment to prepare electrodes. Since being discovered by Lijima in 1991 [24], CNTs have obtained remarkable attention in chemical, physical and material fields due to their unique structure and extraordinary properties. CNTs are provided with excellent electronic properties, such as huge surface area and efficient catalytic activity, which indicate that they can promote charge transfer reaction when they are used as electrode materials [25–28]. At the present time, CNTs are widely used in electroanalytical chemistry.

Nafion, a perfluorinated sulphonated cation exchanger with properties of excellent antifouling capacity, chemical inertness and high permeability to cations, has been extensively employed as an electrode modifier. CNTs can be homogeneously dispersed in Nafion solution because of the hydrophobic side chains and

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polar head groups of Nafion. Nafion/CNTs composite thin film-modified electrodes have their attractive effects in electroanalytical applications. For example, they have been used as amperometric sensors for the trace detection of heavy metals [29–31] and dopamine [32], simultaneous determination of 2-nitrophenol and 4-nitrophenol [33], and the determination of clenbuterol [34]. Nafion has been used as the modifier coated on the electrode for the detection of caffeine [21], but no investigation has been reported on the electroanalysis of caffeine by Nafion/MWNTs composite film-modified electrodes.

In this paper, a convenient and rapid method was used to fabricate glassy carbon electrode modified with multi-wall carbon nanotubes (MWNTs) dispersed in 0.1% Nafion solutions. The voltammetric study of caffeine has been performed at the Nafion/MWNTs modified electrode. A very sensitive and well-defined anodic peak was observed. The Nafion/MWNTs modified electrode can intensively enhance the oxidation of caffeine and strongly improve its anodic peak current due to the attractive properties of Nafion/MWNTs. According to the oxidation peak currents of caffeine proportionably responding to the caffeine concentration, the Nafion/MWNTs modified electrode can be applied as the sensor to determine caffeine. The limit of detection was 2.3×10^{-7} mol L^{-1}. The method proposed was applied for the determination of caffeine in real samples, such as cola beverages, energy beverage and tea without any time-consuming extraction or separation steps prior to measurement, and the results were satisfactory.

2. Experimental

2.1. Apparatus and reagent

RST3000 electrochemical system (Suzhou Risetech Instrument Co. Ltd., Suzhou, China) was employed for all the voltammetric measurement. A conventional three-electrode system was used, including a bare glassy carbon electrode (GCE) (d = 4 mm) or Nafion/MWNTs film-modified GCE as working electrode, a saturated calomel electrode as reference electrode and a platinum wire electrode as auxiliary electrode. All the pH values were measured with a PHS-3C precision pH meter (Leici Devices Factory of Shanghai, China), which was calibrated with standard buffer solution every day. The scanning electron microscopy (SEM) was performed with a Hitachi X-650 microscope.

Caffeine was purchased from National Institute for the Control of Pharmaceutical and Biological Products (China) and used as received. The stock solution of caffeine (3.0×10^{-3} mol L^{-1}) was prepared with doubly distilled water, and diluted with 0.01 mol L^{-1} H_2SO_4 (pH 2.0) before use. The multi-wall carbon nanotubes (diameter: 10–20 nm, length: 1–2 μm, purity > 95%) were obtained from Shenzhen Nanotech Port Co. Ltd, China. Nafion (wt. 5%) was purchased from Sigma. All the other chemicals used were analytical grade without further purification and prepared with doubly distilled water. pH of the solutions was adjusted with 0.1mol L^{-1} H_2SO_4 and NaOH.

2.2. Preparation of Nafion/MWNTs composite film-modified GCE

The bare GCE was pretreated carefully with 0.05 μm alumina slurry on a polishing cloth, rinsed thoroughly with 1:1 HNO_3–H_2O (v/v), and then washed with pure ethanol and redistilled water, respectively. 10 mg of the untreated MWNTs was added to plentiful concentrated nitric acid (wt. 68%), and then sonicated for about 4 h. The mixture was filtrated and washed with doubly distilled water until the filtrate was litmusless. The treated MWNTs were dried under an infrared lamp. Nafion/MWNTs suspension was accomplished as follows: 5.0 mg of treated MWNTs was sonicated in 10.0 ml (wt. 0.1%) Nafion methanol solution for about 30 min, and then homogeneous suspension would be achieved. MWNTs suspension was obtained with the same procedure, but 0.1% Nafion solution was replaced with N,N-dimethylformamide (DMF). The pretreated GCE was coated evenly with 10.0 μL of Nafion/MWNTs suspension, and then methanol was evaporated at room temperature. For contrast, the Nafion/GCE was prepared with the same procedure without MWNTs. MWNTs/GCE was achieved after evaporating DMF under the ultraviolet lamp in this work. Before use, the modified electrodes were washed repeatedly with double-distilled water to remove the loosely combined modifiers.

The Nafion/MWNTs modified electrode was stored in phosphate solution (pH 7.0) and can be used for 80 cyclic voltammetric cycles. According to the literatures [35], the microscopic area of the Nafion/MWNTs modified GCE was calculated to be 0.8668 cm^2, which was 6.9 times greater than the bare GCE (0.1256 cm^2).

2.3. Analytical procedures

Except as otherwise stated, 0.01 mol L^{-1} H_2SO_4 (pH 2.0) was used as supporting electrolyte for caffeine determination. A stock solution of 3.0×10^{-3} mol L^{-1} caffeine was firstly prepared, and then an aliquot was diluted to the appropriate concentration with 0.01 mol L^{-1} H_2SO_4 (pH 2.0) before commencing the voltammetric scan. Voltammograms were obtained by scanning the potential from 600 to 1500 mV (vs. SCE). After each measurement, the three-electrode system was installed in a blank solution, and then the cyclic voltammetry scan was repeated successively for three times for renewing the electrode. The quantitative determination of caffeine was achieved by measuring the oxidation peak current after background subtraction using differential pulse voltammetry (DPV). In order to fit into the linear range of the method, beverage samples employed for operation were accurately diluted by a factor of 1/100 (v/v) with the supporting electrolyte. Tea was prepared by infusion, using a tea-bag (2.0 g) immersed in 100 ml of boiling water for 3 min [18]. It was then diluted by a factor of 1/200 (v/v). The dilution process can actually help reducing the matrix effect of real samples.

3. Results and discussion

3.1. Characterization of Nafion/MWNTs modified electrode

Fig. 1 displays the characterization of the Nafion/MWNTs composite film on the GC electrode by using SEM method. It is obvious that the Nafion/MWNTs composite film was uniformly coated on the electrode surface and formed a spaghetti-like porous reticular formation. The special surface morphology offered a much larger real surface area than the apparent geometric area.

3.2. Electrochemical response of caffeine on Nafion/MWNTs modified electrode

Fig. 2 shows the cyclic voltammetric responses of the Nafion/MWNTs/GCE (Fig. 2a), MWNTs/GCE (Fig. 2b), Nafion/GCE (Fig. 2c) and bare GCE (Fig. 2d) in the presence of 3.0×10^{-5} mol L^{-1} caffeine in 0.01 mol L^{-1} H_2SO_4 (pH 2.0) medium at a scan rate of 80 mV s^{-1}. Under the same conditions, no anodic peak of caffeine was observed at the bare GCE, but an anodic peak of caffeine was observed at the modified electrodes. Especially at the Nafion/MWNTs nanocomposite modified electrode, the peak current was significantly higher than those at the MWNTs/GCE or the Nafion/GCE. The oxidation process of caffeine at Nafion/MWNTs/GCE, MWNTs/GCE or Nafion/GCE is irreversible, which is consistent with

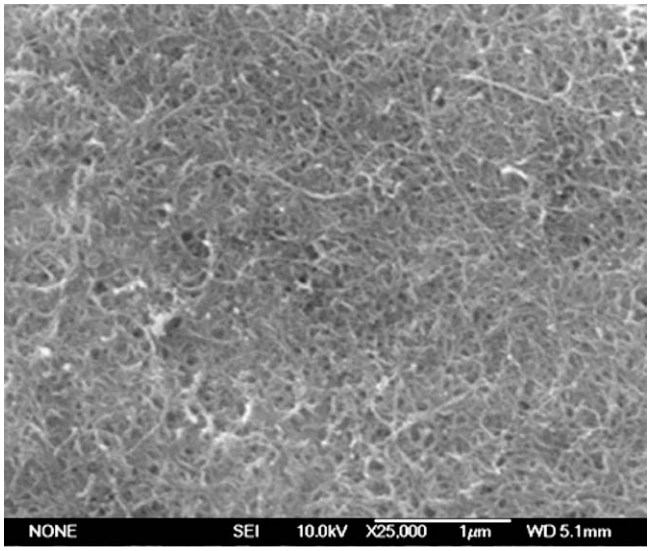

Fig. 1. SEM image of Nafion/MWNTs composite film on glassy carbon electrode

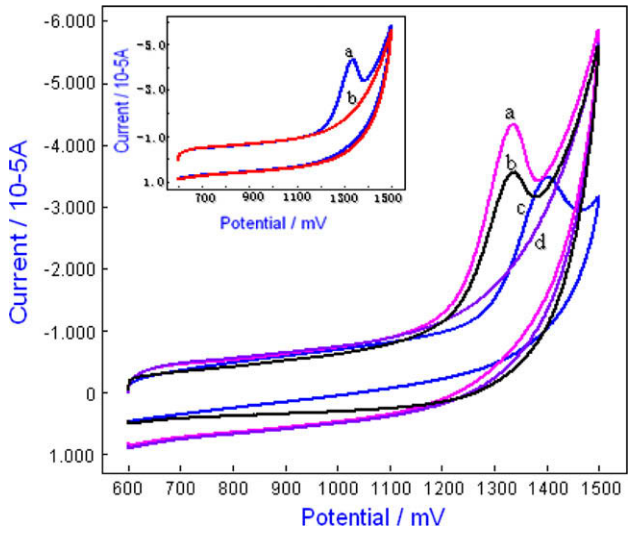

Fig. 2. Cyclic voltammograms of the Nafion/MWNTs modified GCE (a), MWNTs modified GCE (b), Nafion modified GCE (c), the bare GCE (d) containing 3.0×10^{-5} mol L^{-1} caffeine in 0.01 mol L^{-1} H_2SO_4 (pH 2.0) medium; scan rate 80 mV s^{-1}; insert is the cyclic voltammograms of the Nafion/MWNTs modified GCE with 3.0×10^{-5} mol L^{-1} caffeine (a) and without caffeine (b).

the reported [23]. The oxidation mechanism of caffeine has been revealed by Dryhurst et al. [36]. Moreover, compared with the Nafion/GCE, the oxidation potential at the MWNTs/GCE or Nafion/MWNTs/GCE was negatively shifted from 1401 to 1330 mV. This phenomenon may be an evidence of catalytic effect of MWNTs toward caffeine oxidation. The reasons for the notable sensitivity of the caffeine determination at the Nafion/MWNTs/GCE may be summarized as follows: (1) the Nafion/MWNTs/GCE contains the cation exchanger of Nafion which has selective cation exchange enriched ability due to the electrostatic interaction. (2) MWNTs display attractive characteristics, such as much larger specific surface area, excellent adsorptive ability and catalytic ability. Without a doubt, the synergetic functions of Nafion and MWNTs make contributions to the higher current response of caffeine [29–34].

3.3. Influence of supporting electrolyte and pH on the peak currents and peak potentials

Different electrolyte solutions can influence the electrochemical behavior of caffeine. So various types of 0.01 mol L^{-1} acids including HNO_3, HCl, H_2SO_4, CH_3COOH were tested as possible supporting electrolytes, as shown in Fig. 3. The 0.01 mol/L sulfate buffer solution was chosen as the most suitable medium due to the excellent peak response separated from the background currents and the lower oxidation potential (Fig. 3c).

The peak potentials and currents are closely related to the pH of sulfate buffer solution. As can be seen from Fig. 4, the peak potential decreases with the increasing of pH, but the peak current decreases slightly from pH 0.7 to pH 2.0 and decreases obviously in a higher pH range. Therefore, pH 2.0 (Fig. 4d) was used as the optimal value for subsequent determination.

3.4. Effect of scan rate on the peak currents and peak potentials

The effect of scan rate (in the range of 30–400 mV s^{-1}) on the peak currents and peak potentials at the Nafion/MWNTs/GCE in 0.01 mol L^{-1} sulfate buffer solution (pH 2.0) containing 3.0×10^{-5} mol L^{-1} caffeine was investigated by cyclic voltammetry. As shown in Fig. 5, the peak potential at the Nafion/MWNTs / GCE shifts positively with the increasing of the scan rate. The anodic peak current is found to be directly proportional to the square root of the scan rate ($r = 0.9969$), indicating a diffusion controlled oxidation process occurring at the Nafion/MWNTs modified GCE, which is in good agreement with the previous report on the transport characteristics of caffeine on a chemically modified electrode [18].

3.5. Chosen parameters of differential pulse voltammetry

Differential pulse voltammetry (DPV) was used due to its high sensitivity and excellent separation from background current. Since the anodic peak currents are dependent on the various DPV parameters such as pulse amplitude, pulse increment, pulse width, pulse period, the preliminary experiments were employed to choose the best parameters. It was found that the peak currents increased with the increasing of pulse amplitude in the range of 10−60 mV, accompanied by the broadening peak width at the

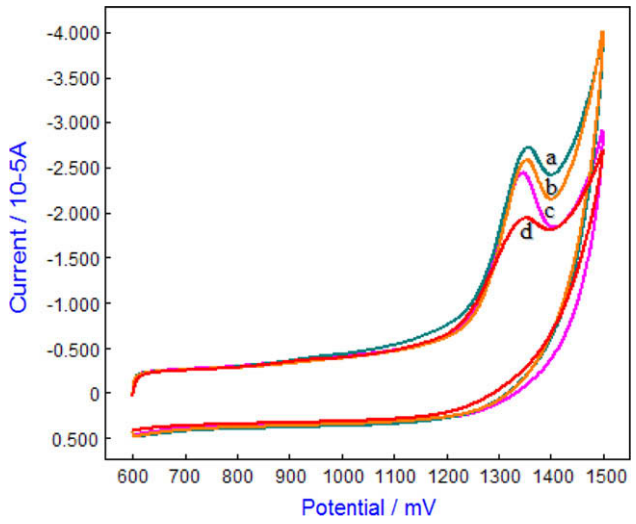

Fig. 3. Cyclic voltammograms of the Nafion/MWCNTs modified GCE in the presence of 3.0×10^{-5} mol L^{-1} caffeine in 0.01 mol L^{-1} different supporting electrolytes (a → d): HNO_3, HCl, H_2SO_4, CH_3COOH; scan rate 80 mV s^{-1}.

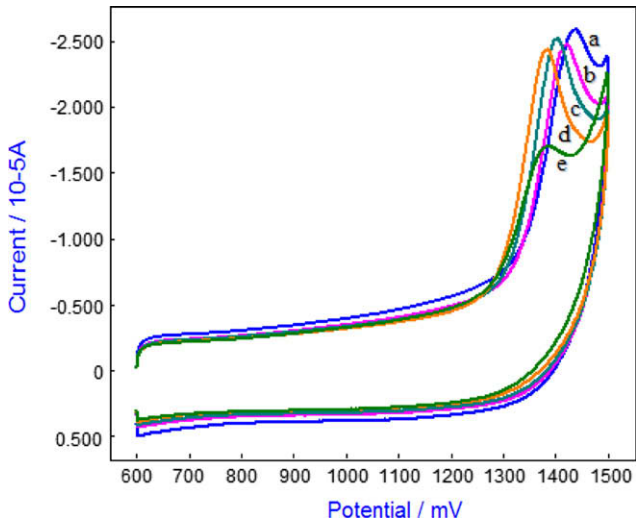

Fig. 4. Cyclic voltammograms of the Nafion/MWNTs/GCE in the presence of 3.0×10^{-5} mol L^{-1} caffeine with different pH of 0.01 mol L^{-1} H_2SO_4 mediums ($a \rightarrow e$): 0.7, 1.0, 1.5, 2.0, 2.5; scan rate 80 mV s^{-1}.

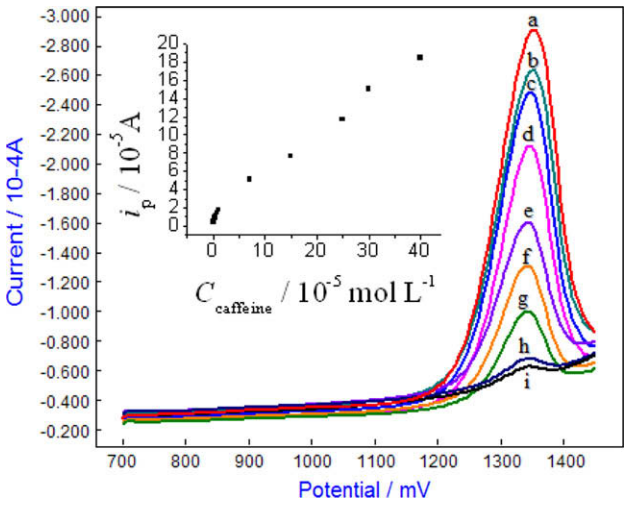

Fig. 6. Differential pulse voltammograms of Nafion/MWNTs/GCE in different of caffeine ($a \rightarrow i$): 6.0×10^{-4}, 3.5×10^{-4}, 4.0×10^{-4}, 3.0×10^{-4}, 1.5×10^{-4}, 9.0×10^{-5}, 7.0×10^{-5}, 1.0×10^{-5}, 8.0×10^{-6} mol L^{-1}; insert is the i_p vs. $C_{caffeine}$ plot. Instrument parameters: pulse amplitude: 50 mV, pulse increment: 6 mV, pulse width: 20 ms, pulse period: 60 ms.

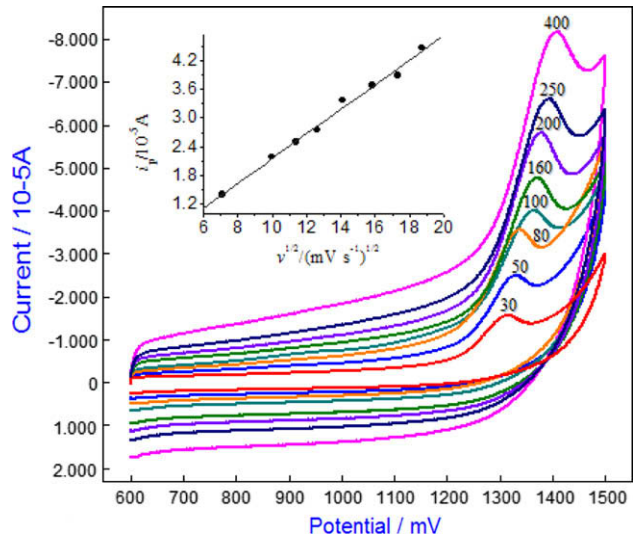

Fig. 5. Cyclic voltammograms of the Nafion/MWNTs/GCE in the presence of 3.0×10^{-5} mol L^{-1}caffeine at different scan rates from 30 to 400 mV s^{-1} in 0.01 mol L^{-1} H_2SO_4 medium (pH 2.0); insert is the i_p vs. $v^{1/2}$ plot.

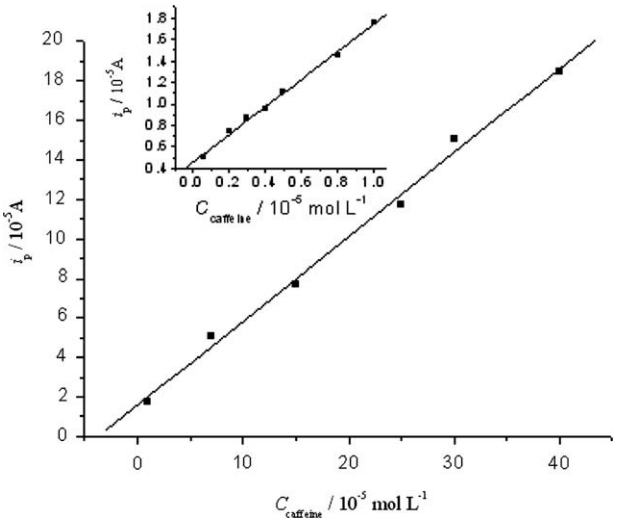

Fig. 7. The linear relationship between the peak current and concentration of caffeine in the range of 1.0×10^{-5}–4.0×10^{-4} mol L^{-1}; insert is the i_p vs. $C_{caffeine}$ in the range of 6.0×10^{-7}–1.0×10^{-5} mol L^{-1}.

same time. When the pulse amplitude was higher than 50 mV, the peak width became much wider. Therefore, 50 mV was chosen as the best pulse amplitude. Pulse increment was tested in the range of 1–14 mV. Experiments showed that the peak height increased with the pulse increment increasing. When the pulse increment was greater than 6 mV, the peak shape became much wider as well as not smooth. Thus 6 mV was selected as the optimal pulse increment. Any increase with either the pulse width or the pulse period resulted in the decrease of the peak current. The response for caffeine decreased with the increasing of pulse width and the pulse period. When the pulse width and the pulse period were up to 20 ms and 60 ms, respectively, the peak current was unstable and difficult to separate from the large background current. It was discovered that the change of these parameters had slight effect on the peak potential. To sum up, the optimal parameters were chosen as follows: pulse amplitude, 50 mV; pulse increment, 6 mV; pulse width, 20 ms; pulse period, 60 ms.

Table 1
Interference study for determination of 3.0×10^{-5} mol L^{-1} caffeine

Species	Tolerance limits ($C_{species}/C_{caffeine}$)
Glucose, sucrose, citric acid	200
Cu^{2+}, Zn^{2+}, Fe^{3+}, Mg^{2+}	200
K^+, Na^+, CO_3^{2-}, Cl^-, PO_4^{3-}, NO_3^-	>500
Hypoxanthine	3
Aminoacetic acid	50
Ascorbic acid	33

3.6. Calibration curve

In order to validate the accuracy of this method for caffeine quantitative analysis, the variation of peak current with different concentration caffeine was studied using differential pulse voltammetry (DPV) under the optimum instrumental conditions (pulse

Table 2
Results obtained in determination of caffeine in beverage samples and tea using the DPV (proposed) and UV–vis spectroscopic methods ($n = 5$).

Sample	DPV value	UV–vis spectroscopic value
Cola beverage 1	$6.2 \pm 0.53 \times 10^{-4}$ mol L^{-1}	$6.1 \pm 0.29 \times 10^{-4}$ mol L^{-1}
Cola beverage 2	$5.3 \pm 0.16 \times 10^{-4}$ mol L^{-1}	$5.2 \pm 0.53 \times 10^{-4}$ mol L^{-1}
Energy drinking water	200 ± 10 mg L^{-1}	198 ± 14 mg L^{-1}
Green tea	28.9 ± 0.42 mg g^{-1}	29.6 ± 0.25 mg g^{-1}

Table 3
Application of DPV method to the determination of caffeine in spiked cola beverage ($n = 5$).

Added (mol L^{-1})	Expected (mol L^{-1})	Found (mol L^{-1})	Average recovery (%)	RSD of recovery (%)
9.0×10^{-5}	9.35×10^{-5}	9.10×10^{-5}	97.3	3.0
3.0×10^{-5}	3.35×10^{-5}	3.21×10^{-5}	95.8	1.6
9.0×10^{-6}	12.50×10^{-6}	12.22×10^{-6}	97.8	2.4
6.0×10^{-6}	9.50×10^{-6}	9.73×10^{-6}	103.6	2.6

amplitude: 50 mV, pulse increment: 6 mV, pulse width: 20 ms, pulse period: 60 ms) (Fig. 6). When the concentration of caffeine changes from 4.0×10^{-4} mol L^{-1} to 6.0×10^{-7} mol L^{-1}, the anodic peak current and caffeine concentration show linear relationship in the ranges of 4.0×10^{-4}–1.0×10^{-5} mol L^{-1} and 1.0×10^{-5}–6.0×10^{-7} mol L^{-1}, respectively (Fig. 7). The regression equations are: $i_p = 1.5725 + 0.4264C$ (i_p in 10^{-5} A, C in 10^{-5} mol L^{-1}, $r = 0.9971$) for the range of 1.0×10^{-5}–4.0×10^{-4} mol L^{-1} (Fig. 7) and $i_p = 0.4581 + 1.2857$ C (i_p in 10^{-5} A, C in 10^{-5} mol L^{-1}, $r = 0.9979$) for the range of 6.0×10^{-7}–1.0×10^{-5} mol L^{-1} (Fig. 7 insert). The different accumulation efficiency at different concentrations results in the different slopes of the two calibration curve. According to the following equation [37]: LOD = 3.3 ($s_{y/x}$/b), where $s_{y/x}$ is the residual standard deviation, b the slope of the calibration plot. This method usually implies a decision about controlling both false positive and false negative errors ($\alpha = \beta = 0.05$). The limit of detection was calculated to be 2.3×10^{-7} mol L^{-1}.

Regeneration and reproducibility are two vital characteristics for the modified electrode, which should be investigated for analytical determination. The same modified GCE was used for five times successive measurement of 3.0×10^{-5} mol L^{-1} caffeine. After each measurement, the surface of the Nafion/MWNTs/GCE was regenerated by successively scanning three cycles between 600 and 1500 mV in 0.01 mol L^{-1} H_2SO_4 medium solution. The electrode showed preferable regeneration and reproducibility, and the relative standard deviation (RSD) of the peak current was 2.3% ($n = 5$). Moreover, under the same preparing conditions, for five Nafion /MWNTs modified-GCEs, the RSD of the peak current was 6.5%, revealing good reproducibility.

3.7. Interference studies

The influence of potential coexistent interference compounds should be studied for the possible analytical application of the proposed method. A fixed amount of 3.0×10^{-5} mol L^{-1} caffeine spiked with various foreign species was evaluated under the same experimental conditions. According to the relative error < ±5% for the determination of caffeine, the results are shown in Table 1, which clearly prove the reasonable selectivity for the proposed method.

3.8. Analysis of real samples

In order to fit into the linear range of the method, beverage samples employed for operation were accurately diluted with the supporting electrolyte. The detected results are shown in Table 2. The results are in agreement with the value obtained employing UV–vis spectroscopic method [38] as well as the regulation of the American Beverage Association [39] in the range of 4.3×10^{-4}–8.7×10^{-4} mol L^{-1}. Caffeine concentration of energy drinking water is in agreement with the declared content (i.e., 200 mg L^{-1}). In order to test the correctness of the results the standard addition method was used to determine the cola beverage sample spiked with suitable caffeine. The experimental results are listed in Table 3. The recoveries of the caffeine standards added are 95.8% to 102.6%, which reveal good accuracy of the proposed method.

4. Conclusions

This study demonstrated that the Nafion/MWNTs/GCE can be applied to the detection of caffeine in beverages. Nafion-MWNTs composite was used to modify GCE and exhibited high sensitivity and good selectivity for caffeine detection. The proposed method displayed excellent characteristics, such as simplicity, economy, good sensitivity, selectivity, rapid analysis procedures and a large determination range, which offers a good possibility of using the Nafion/MWNTs/GCE as a sensor for routine analysis of caffeine in beverages without pre-treatment of the samples.

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