

# Voltammetric sensor for caffeine based on a glassy carbon electrode modified with Nafion and graphene oxide

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**Abstract** We report on a voltammetric sensor for caffeine that is based on a glassy carbon electrode modified with Nafion and graphene oxide (GO). It exhibits a good affinity for caffeine (resulting from the presence of Nafion), and excellent electrochemical response (resulting from the presence of GO) for the oxidation of caffeine. The electrode enables the determination of caffeine in the range from  $4.0 \times 10^{-7}$  to  $8.0 \times 10^{-5}$  mol L<sup>-1</sup>, with a detection limit of  $2.0 \times 10^{-7}$  mol L<sup>-1</sup>. The sensor displays good stability, reproducibility, and high sensitivity. It was successfully applied to the quantitative determination of caffeine in beverages.

**Keywords** Caffeine · Nafion · Graphene oxide · Modified electrode · Voltammetry

## Introduction

Caffeine (1,3,7-trimethylxanthine) is a natural alkaloid, which is found in various kinds of food and beverage that we consume in daily life. It plays an important role in various physiological effects such as relaxation of bronchial muscle, stimulation of the central nervous system, gastric acid secretion and diuresis [1]. However, it can have some adverse effects on health if consumed in excess [2–4]. And

it is also considered to be a risk factor for cardiovascular diseases, asthma, kidney malfunction and may also cause depression and hyperactivity [5, 6]. That's why there have been numerous studies with the target to develop reliable methods for determining caffeine, such as spectrophotometry, chromatography and biosensing [7]. Nevertheless, these methods are generally more expensive, time-consuming and complicated than electroanalytical techniques [7]. Accordingly, interest in electrochemical methods has increased for its simplicity, high sensitivity, good stability, low-cost instrumentation and onsite monitoring [8]. However, the electrochemical determination of caffeine at the more common electrode materials (e.g., metals, glassy carbon) is generally not feasible because the oxidation of caffeine occurs at a very positive potential, thus overlapping with the discharge of the background medium [9]. So various modified electrodes have been developed for the determination of caffeine recently [7, 8, 10].

Nanomaterials have been widely used in analytical chemistry as chemical sensor and biosensor materials [11]. Graphene, a kind of nanomaterial, has attracted attention increasingly since it was discovered in 2004 [12]. It shows promising applications in scientific and technological fields owing to its novel properties such as exceptional thermal and mechanical properties, high electrical conductivity [13–15]. Graphene oxide (GO), the oxidation form of graphene, bears two-dimensional plane and lots of electroactive oxygen containing functional groups and disorder on the basal planes and edges [16–18]. It possesses the properties of large surface area and good chemical stability, too. However, the conductivity of it decreased remarkably compared to graphene. But the excellent solubility and the convenience of preparation and fabrication can make it a nice material for the modification of electrodes.

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In this paper, a novel voltammetric sensor of caffeine was fabricated based on GO combined with Nafion modified on glassy carbon electrode (Nafion/GO/GCE). The employment of Nafion has two functions: one intention is the immobilization of GO on GCE surface and the other is its good affinity towards caffeine [19], which would enhance the sensitivity toward caffeine. The characterizations of self-synthesized GO was investigated using spectrum of FT-IR and an atomic force microscopy (AFM), and the fabricated Nafion/GO/GCE were characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques respectively. The experimental results demonstrated that the Nafion/GO/GCE can improve the oxidation of caffeine intensively. Based on this voltammetric sensor, a sensitive voltammetry of determining caffeine was used in detecting caffeine content in beverages successfully. The analytical results were then compared with that of high performance liquid chromatography (HPLC).

## Experimental

### Chemicals and reagents

Nafion 117 (5%, w/v in alcoholic solution) was purchased from Alfa (<http://www.alfa.com/zh/gh100w.pgm>) and was diluted to 0.5% (w/v) with ethanol before use. Caffeine was purchased from Biological and Chemical Reagent Store (Shanghai, China) and used as received. Standard stock solution of caffeine ( $2.0 \times 10^{-2} \text{ mol L}^{-1}$ ) was prepared using doubly distilled water and stored at 4 °C. All reagents used for HPLC were of chromatographic pure. Graphite powder (chemically pure) was purchased from Tianjin Yong Da Chemical Reagent Development Center (Tianjin, China <Http://www.tjyongda.net>). It was grinded in the agate mortar and then was sieved in the sieve with 320 mesh. All other reagents were of analytical reagent grade and used without further purification. The experimental water used was double-distilled.

### Apparatus

All the voltammetric measurements were performed using a RST3000 electrochemical system (Zhengzhou Shiruisi Instrument Co. Ltd., Zhengzhou, China <http://www.srs666.com>) and a CHI650A electrochemical workstation (CHI Instrumental, Shanghai, China <http://www.chinstruments.com/schi.html>) was used for the EIS measurements. The three-electrode cell consisted of an Ag/AgCl reference electrode, a platinum wire auxiliary electrode and either a bare glassy carbon electrode (GCE) ( $d=3 \text{ mm}$ ) or Nafion/GO/GCE working electrode. All potentials in this paper were given against the Ag/AgCl ( $3 \text{ mol L}^{-1} \text{ KCl}$ ). All the

pH values were measured with a PHS-3C precision pH meter (Leici Devices Factory of Shanghai, China <http://www.lei-ci.com>), which was calibrated with standard buffer solution (pH 4.00 and 6.86) at  $25 \pm 0.1 \text{ }^\circ\text{C}$  every day.

The determination of Caffeine by HPLC was carried out using an Agilent 1200 Series liquid chromatograph with an Agilent C18 (4.6 mm $\times$ 150 mm) and an Ultraviolet–Vis detector set at 270 nm. The mobile phase was a methanol/water mixture (30:70, %v/v) at a flow rate of  $1.0 \text{ mL min}^{-1}$ , while the injection volume was 20  $\mu\text{L}$ . The standard solution of caffeine for linear calibration curve was made using methanol.

### Preparation of film-modified GCE

First of all, graphite oxide was synthesized using graphite power mainly according to literatures [20, 21]. Then exfoliation of graphite oxide to GO was achieved by ultrasonication of the dispersion for 40 min (1000 W, 20% amplitude) generally referring to literature [22]. A homogeneous aqueous dispersion of GO ( $2.3 \text{ mg mL}^{-1}$ ) was obtained as a result.

The bare GCE was polished carefully with  $0.05 \text{ }\mu\text{m}$  alumina slurry, and sonicated in absolute ethanol and water, respectively. Finally, the GC electrode was thoroughly rinsed with water and dried in air naturally.

Nafion/GO composite solution was prepared by mixing 0.5% Nafion and GO (the ratio was 10:1 ,v:v) and sonicated for 30 min to get a homogeneous turbid liquid. The Nafion/GO modified GCE was prepared by casting 5  $\mu\text{L}$  Nafion/GO turbid liquid evenly on the GCE surface with a microsyringe and dried at room temperature. For comparison, a Nafion modified GCE (Nafion/GCE) was prepared using the same way. Before use, a new fabricated Nafion/GO/GCE was equilibrated for about 3 h in  $0.01 \text{ mol L}^{-1}$  phosphate solution (pH 7.0) and stored in this solution at 4 °C for conserving when it was not used. All measurements were carried out at room temperature.

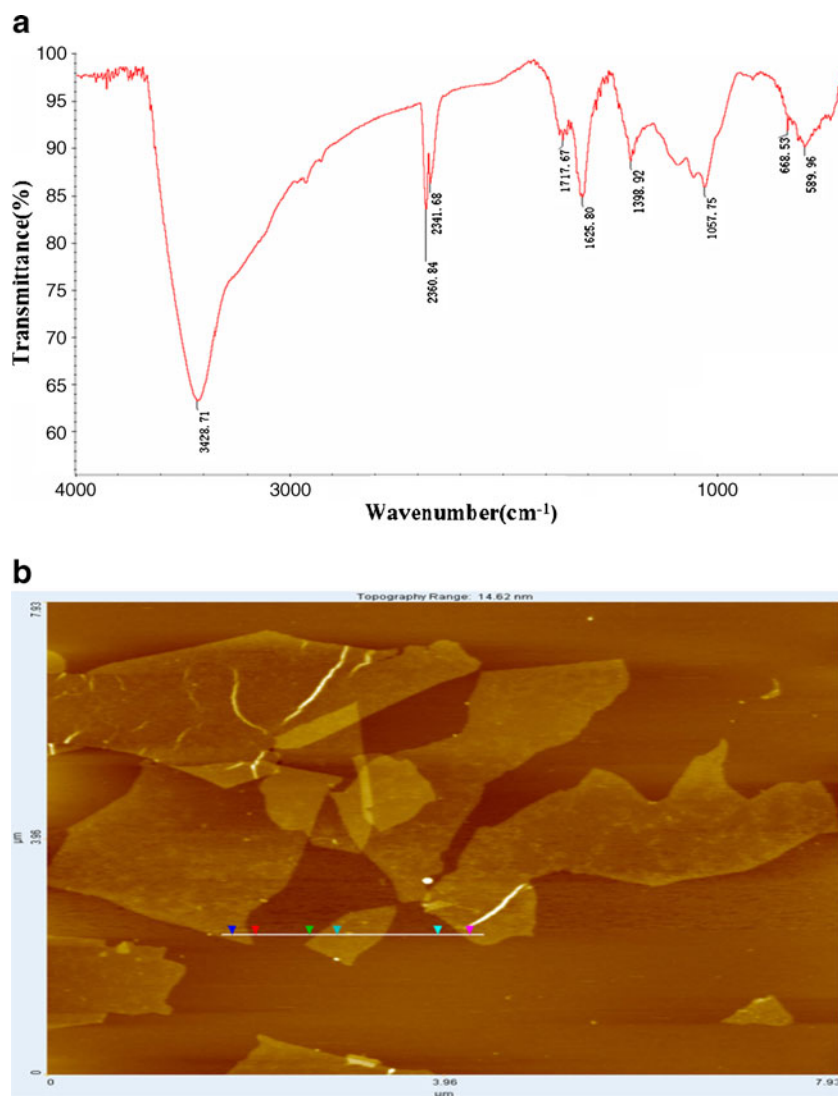
## Results and discussion

### Characterization of the GO

The GO used was synthesized in our laboratory. As shown in Fig. 1a, the spectrum of FT-IR of GO showed that the peak at  $3428.71 \text{ cm}^{-1}$  attributes to O–H stretching vibration, the peak at  $1717.67 \text{ cm}^{-1}$  attributes to C=O stretching vibration, the peak at  $1398.92 \text{ cm}^{-1}$  attributes to deformation of O–H, and the peak at  $1057.75 \text{ cm}^{-1}$  attributes to vibration of C–O (alkoxy), indicating that GO was successfully prepared. The morphology characterization of GO was performed by atomic force microscopy

**Fig. 1** Characterization of GO:

**a** FT-IR spectrum of GO; **b** AFM image of GO from its dilute aqueous dispersion on freshly cleaned mica



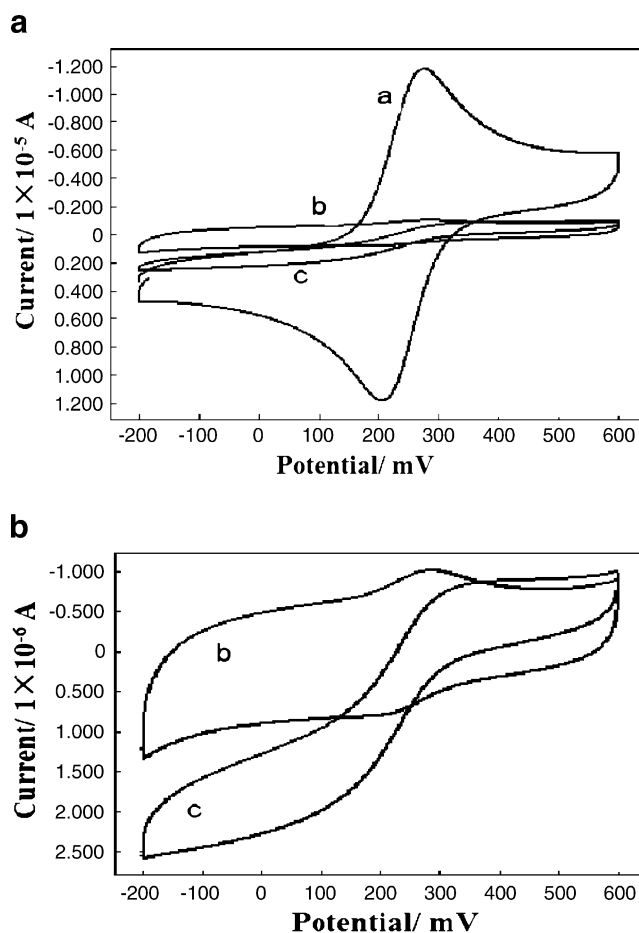
(AFM) using a mica as matrix on which GO was deposited. It can be seen in Fig. 1b that the GO sheets were almost single-layer. And the average thickness of single-layer GO sheets was approximately 1 nm.

#### The electrode characterizations

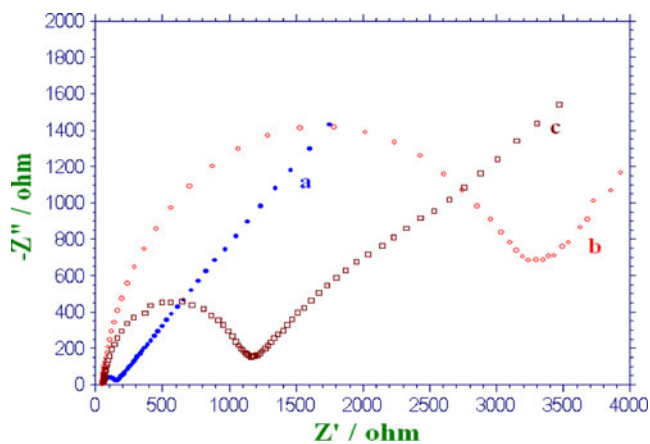
The characterizations of fabricated modified electrode were investigated using cyclic voltammetry in  $2.0 \times 10^{-3}$  mol L<sup>-1</sup> K<sub>3</sub>Fe(CN)<sub>6</sub> containing 0.1 mol L<sup>-1</sup> KCl solution first. Figure 2a showed the voltammograms compared using a bare GCE (curve a), a Nafion/GCE (curve b) and a Nafion/GO/GCE (curve c) respectively. Figure 2b was the magnified voltammograms of curve b and c. A pair of well-defined redox peaks were observed at the bare GCE. The anodic and cathodic peaks were almost disappeared at Nafion/GCE, showing that Nafion acted as a blocking layer for electron and mass transfer that hindered the diffusion of

ferricyanide toward the electrode surface. This was from the electrostatic (negative charge) repulsive effect between Nafion and K<sub>3</sub>Fe(CN)<sub>6</sub>. However, the peak current increased and the charging current decreased compared with curve b at Nafion/GO/GCE, showing GO can accelerate the electron transfer of ferricyanide due to its electric conductivity. This investigation also demonstrated that the electrodes were prepared just as design.

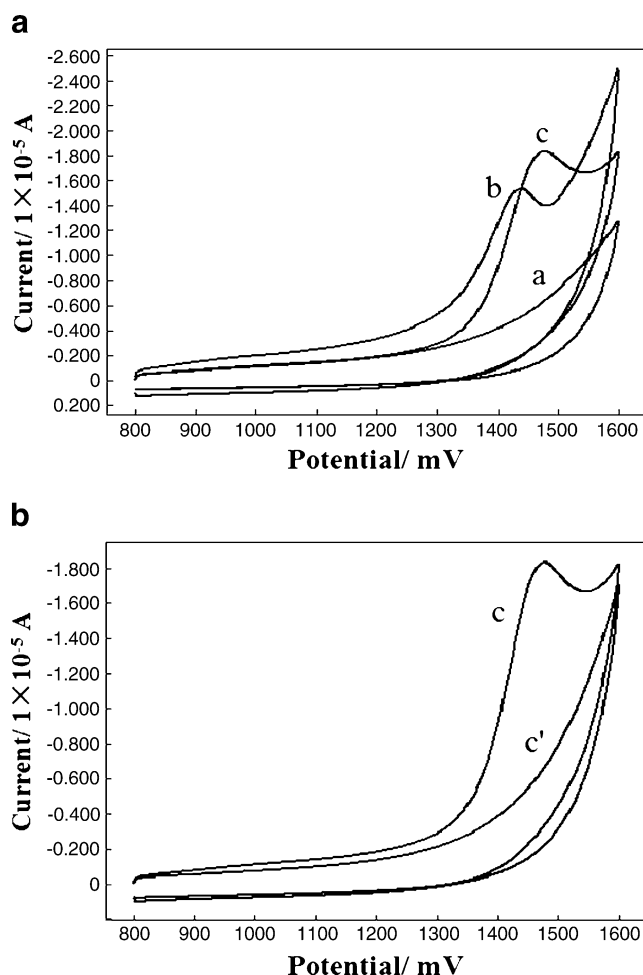
The electrode characterizations were further investigated using electrochemical impedance spectroscopy (EIS), which can give information on the impedance changes of the electrode surface. The Nyquist plots of impedance spectroscopy at bare GCE (curve a), Nafion/GCE (curve b) and Nafion/GO/GCE (curve c) in  $5.0 \times 10^{-3}$  mol L<sup>-1</sup> K<sub>3</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub> (1:1) containing 0.2 mol L<sup>-1</sup> KCl solution were showed in Fig. 3. For getting these data, the used open circuit potentials were 0.253 V, 0.240 V and 0.249 V for bare GCE (curve a), Nafion/GCE (curve b) and Nafion/GO/



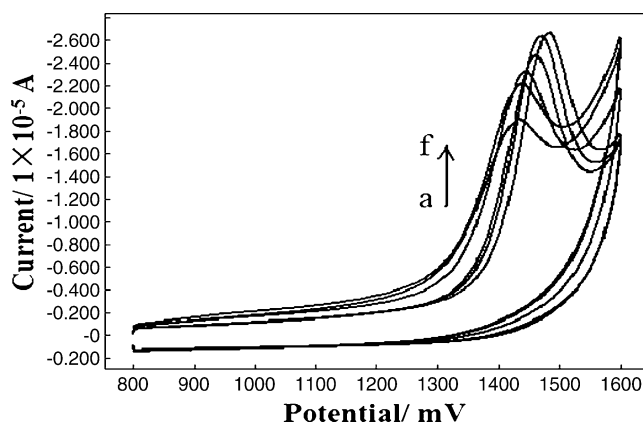
**Fig. 2** a Cyclic voltammograms of different electrodes in  $2.0 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3\text{Fe}(\text{CN})_6$  with  $0.1 \text{ mol L}^{-1} \text{ KCl}$  solution. (a): bare GCE, (b): Nafion/GCE, (c): Nafion/GO/GCE. Scan rate:  $100 \text{ mV s}^{-1}$ . b The magnified voltammograms of curve b and curve c



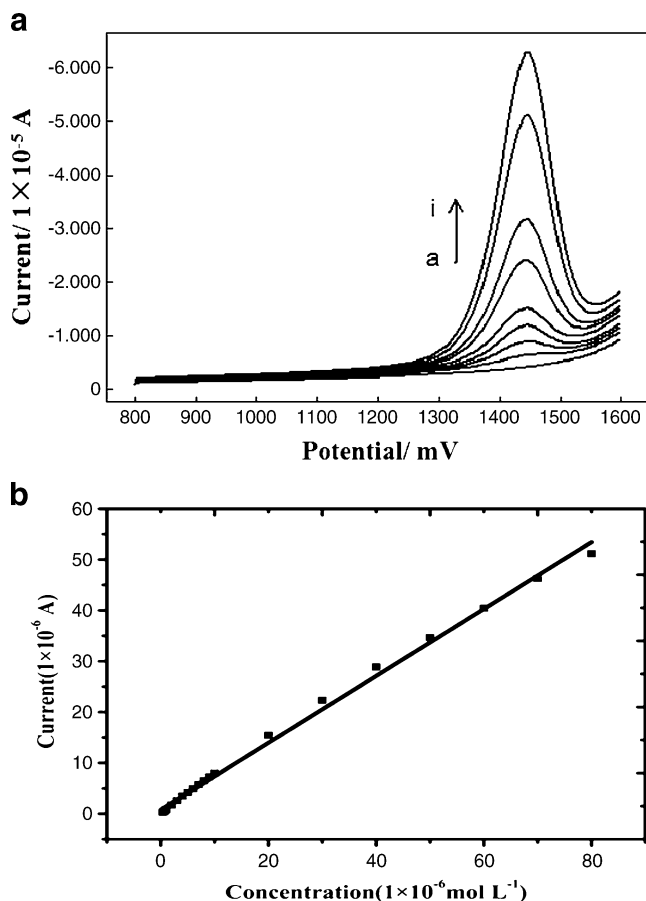
**Fig. 3** Nyquist plots of bare GCE (a), Nafion/GCE (b) and Nafion/GO/GCE (c) in  $5.0 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3/\text{K}_4\text{Fe}(\text{CN})_6$  (1:1) with  $0.2 \text{ mol L}^{-1} \text{ KCl}$  solution respectively. Frequency range: 100000 Hz to 0.01 Hz; Perturbation signal: 5 mV



**Fig. 4** a Cyclic voltammograms recorded at the bare GCE (a), Nafion/GCE (b) and Nafion/GO/GCE (c) in the presence of  $1.0 \times 10^{-5} \text{ mol L}^{-1}$  caffeine in  $0.10 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  at a scan rate of  $100 \text{ mV s}^{-1}$ . b Cyclic voltammograms of Nafion/GO/GCE with absence (c') and presence (c) of  $1.0 \times 10^{-5} \text{ mol L}^{-1}$  caffeine



**Fig. 5** The cyclic voltammograms of Nafion/GO/GCE in  $\text{H}_2\text{SO}_4$  with  $2.0 \times 10^{-5} \text{ mol L}^{-1}$  caffeine at different pH (a→f): 2.19, 1.97, 1.79, 1.38, 1.21, 0.95; scan rate  $100 \text{ mV s}^{-1}$



**Fig. 6** **a** Differential pulse voltammeters at Nafion/GO/GCE in  $0.10 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  with some different caffeine concentrations (a→i):  $0 \text{ mol L}^{-1}$ ,  $9 \times 10^{-7} \text{ mol L}^{-1}$ ,  $3 \times 10^{-6} \text{ mol L}^{-1}$ ,  $6 \times 10^{-6} \text{ mol L}^{-1}$ ,  $9 \times 10^{-6} \text{ mol L}^{-1}$ ,  $2 \times 10^{-5} \text{ mol L}^{-1}$ ,  $3 \times 10^{-5} \text{ mol L}^{-1}$ ,  $6 \times 10^{-5} \text{ mol L}^{-1}$ ,  $8 \times 10^{-5} \text{ mol L}^{-1}$ . **b** linear relationship of caffeine concentrations versus peak currents

GCE (curve c) respectively. After fitting suitable equivalent circuit and calculation, the electron transfer resistance ( $R_{ct}$ ) obtained was about  $86 \Omega$ ,  $2713 \Omega$  and  $1031 \Omega$  for the bare GCE, Nafion/GCE and Nafion/GO/GCE, respectively. When Nafion was deposited on the surface of GCE, the  $R_{ct}$  increased obviously. However, the  $R_{ct}$  decreased

remarkably after GO was immobilized in the Nafion film modified electrode. This resistance controlled the electron transfer kinetics of the redox probe at the electrode, indicating the GO added can reduce the  $R_{ct}$  due to its electroconductibility, while Nafion can help GO to attach on the GC electrode surface. And we can obviously know that Nafion/GO composite film was successfully existed on the GC electrode surface just as design.

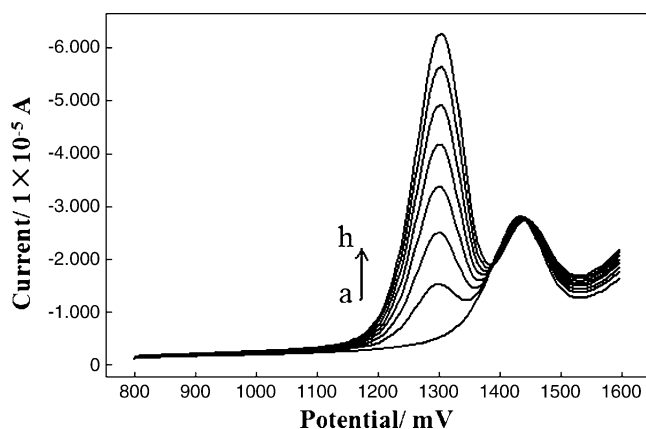
#### Electrochemical response of caffeine at electrodes

Cyclic voltammetry (CV) was employed for investigating the response of caffeine at different electrodes. Figure 4a showed the voltammograms of caffeine ( $1.0 \times 10^{-5} \text{ mol L}^{-1}$ ) at the bare GCE (a), Nafion/GCE (b) and Nafion/GO/GCE (c) in  $0.10 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  with a scan rate of  $100 \text{ mV s}^{-1}$ . As it can be seen, in the potential window between  $800 \text{ mV}$  and  $1600 \text{ mV}$ , no redox peak of caffeine was observed at the bare GCE, but an anodic peak of caffeine was observed at both Nafion/GCE and Nafion/GO/GCE under the same conditions. This was likely due to the preconcentration action of Nafion for caffeine at the film surface. Besides, the peak current using Nafion/GO/GCE showed remarkable improvements with respect to that of Nafion/GCE. It was evident that Nafion/GO/GCE had superior electrochemical performances than bare GCE and Nafion/GCE, at least in the present case. The comparison between Nafion/GO/GCE and Nafion/GCE stressed the advantages of GO, which acted an excellent electrochemical oxidation of caffeine. Figure 4b was the comparison of cyclic voltammograms at Nafion/GO/GCE with absence (c') and presence (c) of caffeine ( $1.0 \times 10^{-5} \text{ mol L}^{-1}$ ) in  $0.10 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  at a scan rate of  $100 \text{ mV s}^{-1}$ . It indicated that the peak came from the oxidation of caffeine indeed, and there was no redox peak of Nafion/GO/GCE in blank solution. The oxidation process of caffeine at Nafion/GO/GCE or Nafion/GCE is irreversible, which is consistent with the reported [9].

From the experiments, we observed that the anodic peak current increased with the time of Nafion/GO/GCE dipping in caffeine solution, and then a stable signal was reached

**Table 1** Comparison of different caffeine sensors reported with this work

Electrode	Modifier	Methods	Linear range ( $\text{mol L}^{-1}$ )	Detection limit ( $\text{mol L}^{-1}$ )	Reference
GCE	Nafion	DPV	$9.95 \times 10^{-7} - 1.06 \times 10^{-5}$	$7.98 \times 10^{-7}$	[7]
GCE	Nafion/multi-wall carbon nanotubes	DPV	$6.0 \times 10^{-7} - 1.0 \times 10^{-5}$ $1.0 \times 10^{-5} - 4.0 \times 10^{-4}$	$2.3 \times 10^{-7}$	[8]
Boron-doped diamond electrode	Nafion	DPV	$2.0 \times 10^{-7} - 1.2 \times 10^{-5}$	$1.0 \times 10^{-7}$	[10]
Graphite Pencil Electrode	Nothing	Square wave stripping voltammogram	$0 - 2.58 \times 10^{-3}$ ( $0 - 500 \text{ mg L}^{-1}$ )	$4.74 \times 10^{-5}$ ( $9.2 \text{ mg L}^{-1}$ )	[23]
GCE	Nafion/GO	DPV	$4.0 \times 10^{-7} - 8.0 \times 10^{-5}$	$2.0 \times 10^{-7}$	This work



**Fig. 7** Differential pulse voltammograms at Nafion/GO/GCE in  $0.10 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  with  $2 \times 10^{-5} \text{ mol L}^{-1}$  caffeine and some different theophylline concentrations (a→h):  $0 \text{ mol L}^{-1}$ ,  $2 \times 10^{-5} \text{ mol L}^{-1}$ ,  $4 \times 10^{-5} \text{ mol L}^{-1}$ ,  $6 \times 10^{-5} \text{ mol L}^{-1}$ ,  $8 \times 10^{-5} \text{ mol L}^{-1}$ ,  $1 \times 10^{-4} \text{ mol L}^{-1}$ ,  $1.2 \times 10^{-4} \text{ mol L}^{-1}$ ,  $1.4 \times 10^{-4} \text{ mol L}^{-1}$

after a certain time. The reason may be that caffeine incorporated with the film firstly when the Nafion/GO/GCE was dipped into the solution. At the same time, the oxidation product of caffeine adhered to the electrode surface may hindered the access of caffeine, and the electrode surface regenerated after a certain time's stir. So equilibrium condition was achieved at a certain time. As expected, it was quicker at higher concentration to get equilibrium condition, but 400 s was enough even at the lowest analyzed concentration. Accordingly, all the reported data were collected 400 s after the immersion of the Nafion/GO/GCE in the analyzed solution.

#### Influence of supporting electrolyte and pH

Preliminary experiments were performed to choose the best supporting electrolyte for caffeine. Various types of  $0.10 \text{ mol L}^{-1}$  acids including  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{CH}_3\text{COOH}$  were tested as possible supporting electrolytes. The results allowed choosing  $0.10 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  as the optimal medium in which the best compromise between sensitivity, reproducibility of the signal was achieved.

The pH of sulfate solution can influence the peak potentials and currents of caffeine. As shown in Fig. 5, the peak currents decreased and peak potentials shifted negatively by increasing the solution pH in the range from 0.95 to 2.19 (achieved by diluting  $0.10 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ). So pH 0.95 ( $0.10 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ) was chosen as the most suitable value due to the excellent peak response.

#### Calibration curve of caffeine

For investigation of the relationship between peak currents and caffeine concentrations, the differential pulse voltammetry (DPV) was performed, which has high sensitivity and excellent separation from background current (Fig. 6a). The optimal experimental parameters were as follows: 50 mV of pulse amplitude; 6 mV of pulse increment; 20 ms of pulse width and 60 ms of pulse period. Data obtained analyzing caffeine standard solutions in  $0.10 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  allowed estimating the functional relationship (Fig. 6b), which is linear in the range of  $4.0 \times 10^{-7}$ – $8.0 \times 10^{-5} \text{ mol L}^{-1}$ . It can be described by the following linear regression equation, with a correlation coefficient  $R^2$  of 0.9965:

$$i_p (\mu\text{A}) = 0.796 + 0.658 \times 10^6 C$$

Where  $i_p$  was the oxidation peak current in  $\mu\text{A}$  and  $C$  was the concentration of caffeine in  $\text{mol L}^{-1}$ . The detection limit was obtained as  $2.0 \times 10^{-7} \text{ mol L}^{-1}$  based on the signal-to-noise ratio of 3 (S/N). Compared with some reported caffeine sensors (Table 1), Nafion/GO/GCE was more sensitive with wider linear range simultaneously. The comparison of this work with reference [7] showed the advantage of GO added. As to reference [8], it can be concluded that GO exhibited electroanalytical performance as excellent as or even better than that of carbon nanotubes. This research suggested that the modified electrode can be a very promising voltammetric sensor for the trace analysis of caffeine.

#### Stability and reproducibility of the modified electrode

The Nafion/GO/GCE showed good stability for the determination of caffeine. The relative standard deviation (RSD)

**Table 2** Determination results of caffeine in beverage samples by DPV and HPLC

DPV ( $n=3$ )						HPLC ( $n=3$ )	
Sample	Amount found ( $\text{mol L}^{-1}$ )	RSD (%)	Standard added ( $\text{mol L}^{-1}$ )	Total found ( $\text{mol L}^{-1}$ )	Recovery (%)	Amount found ( $\text{mol L}^{-1}$ )	RSD (%)
Cola 1	$5.91 \times 10^{-4}$	2.2	$8.0 \times 10^{-4}$	$1.42 \times 10^{-3}$	103.6	$6.25 \times 10^{-4}$	1.2
Cola 2	$5.75 \times 10^{-4}$	1.6	$8.0 \times 10^{-4}$	$1.43 \times 10^{-3}$	107.1	$5.89 \times 10^{-4}$	1.7
Tea drink	$7.27 \times 10^{-4}$	3.0	$1.0 \times 10^{-3}$	$1.67 \times 10^{-3}$	94.7	$8.22 \times 10^{-4}$	1.5
Energy drink	$1.06 \times 10^{-3}$	1.5	$1.2 \times 10^{-3}$	$2.32 \times 10^{-3}$	104.2	$1.17 \times 10^{-3}$	1.4

of the peak current was 3.2% ( $n=5$ ) for 5 successive measurement at the caffeine concentration of  $1.0 \times 10^{-5} \text{ mol L}^{-1}$ . The storage stability of the modified electrode was also investigated. When not in use, the Nafion/GO/GCE was stored in  $0.01 \text{ mol L}^{-1}$  phosphate solution (pH 7.0) at  $4 \text{ }^\circ\text{C}$ . The peak current of caffeine retained 98.0% of its initial response current after a week. The result showed that the modified electrode possessed a nice storage stability and long time-life.

Moreover, a GC electrode was modified for three times under the same preparing conditions and then was performed in  $1.0 \times 10^{-5} \text{ mol L}^{-1}$  caffeine. The RSD of the peak current was 3.2% ( $n=3$ ), revealing good reproducibility of the modification of the electrode.

### Interference

The influence of some potentially interfering species on the determination of caffeine was evaluated in detail. A fixed amount of  $2.0 \times 10^{-5} \text{ mol L}^{-1}$  caffeine spiked with various potentially interfering species was evaluated under the same experimental conditions. The results showed that 2000-fold of glucose, 100-fold of ascorbic acid, 50-fold of dopamine, sucrose, 35-fold of epinephrine, 20-fold of uric acid, 2-fold of tannic acid, 3-fold of xanthine and 7-fold of theophylline had almost no influence on the current response of caffeine (signal change below 5%). All these indicated that Nafion/GO/GCE had good selectivity for the determination of caffeine.

Figure 7 showed differential pulse voltammetrys at Nafion/GO/GCE in  $0.10 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  with  $2 \times 10^{-5} \text{ mol L}^{-1}$  caffeine and some different theophylline concentrations. Two well-defined peaks appeared at the potentials of 1304 mV and 1436 mV, corresponding to theophylline and caffeine respectively, which offered a promising possibility for the simultaneous determination of theophylline and caffeine.

### Real sample analysis

Some beverage samples were tested to evaluate the practical applicability of the method using a freshly prepared Nafion/GO/GCE. The standard addition method was adopted for it allowed minimizing possible matrix effects due to the presence of other components in the real samples. The beverage samples were sonicated to remove the gas content and then were diluted (1 : 201) with the supporting electrolyte to operate in the linear range of the method and to reduce the matrix effect. The values detected were listed in Table 2. The detected caffeine content in cola samples were  $5.91 \times 10^{-4} \text{ mol L}^{-1}$  and  $5.73 \times 10^{-4} \text{ mol L}^{-1}$ , which were in agreement with the regulation of the American Beverage Association [24] in the range of  $4.3 \times$

$10^{-4} \text{ mol L}^{-1}$ – $8.7 \times 10^{-4} \text{ mol L}^{-1}$  (20 mg–40 mg per 8 oz). Caffeine content of energy drink was in agreement with the declared content (50 mg/250 mL). Standard caffeine was added in the samples and the total contents of caffeine were determined to calculate the recovery (Table 2). And HPLC was employed to test the correctness of the results (Table 2). The detected results obtained from the two methods were compared using t-test under 95% confidence levels. The results showed no significant difference for Cola 2 detection, but there were some difference for the other three samples, which may be caused by the basal component difference of the samples. Whereas, the results obtained from the two methods were generally in accordance with each other, which indicated a potential technique for the quick analysis of caffeine.

### Conclusions

This study demonstrated a new caffeine voltammetric sensor, Nafion/GO/GCE, which can be applied to the detection of caffeine with excellent sensitivity and selectivity. Nafion/GO/GCE exhibited significant advantages of wide linear range and low detection limit for caffeine compared with previous works. Besides, the modified electrode presented nice reliability and stability, had a superior immunity to some interference and offered a good possibility for extending the technique in routine analysis of caffeine.

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