Analytical Methods

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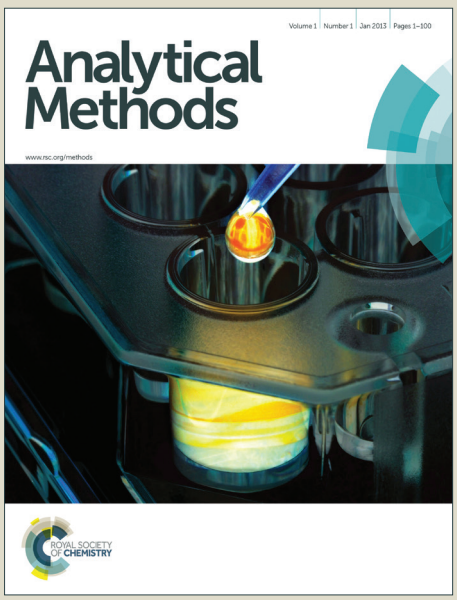

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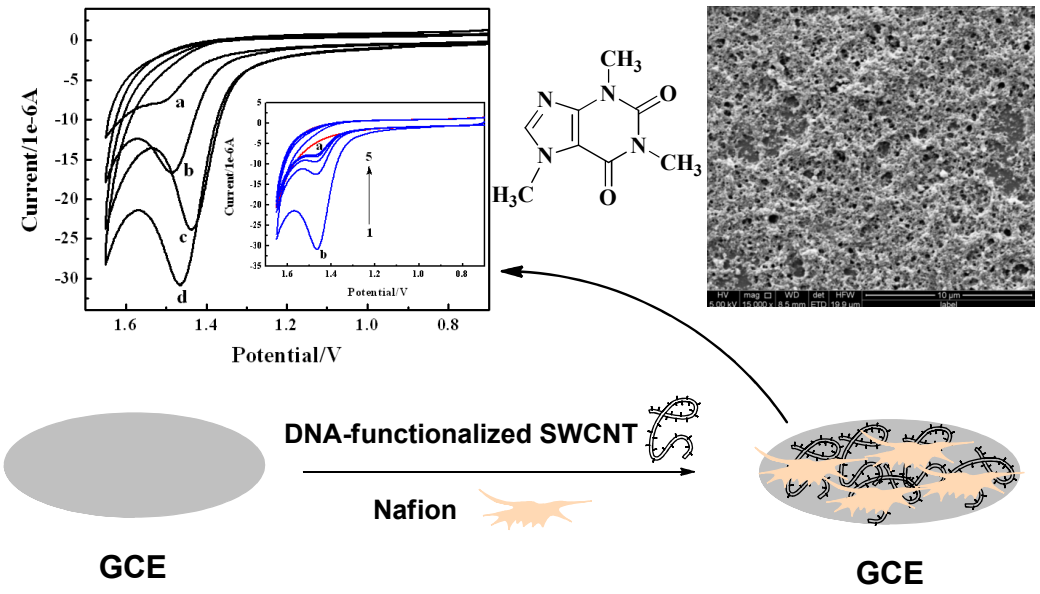

An electrochemical sensor, based on DNA-functionalized single-walled carbon nanotube (DNA-SWCNT) and Nafion composite film modified GCE, was developed and used for detection of caffeine.

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ARTICLE TYPE

Sensitive voltammetric detection of caffeine in tea and beverage based on DNA-functionalized single-walled carbon nanotube modified glassy carbon electrode

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A simple and sensitive electrochemical method, based on the DNA-functionalized single walled carbon nanotube (DNA-SWCNT) and Nafion composite film modified glassy carbon electrode, was proposed to determine caffeine. The electrochemical behavior of caffeine at the modified electrode was investigated by cyclic voltammetry (CV), chronocoulometry (CC) and chronoamperometry (CA), and the results reveal that DNA-SWCNT and Nafion composite film can remarkably enhance the electro-oxidation signal of caffeine. More, the dependence of the current on pH, the nature of buffer, instrumental parameters, accumulation time and potential were investigated to optimize the experimental conditions for the determination of caffeine. Under the selected conditions, the oxidation peak current of caffeine was proportional to its concentration in the range of $2.0 \times 10^{-8} \sim 1.5 \times 10^{-6}$ mol L^{-1}, with a detection limit of 8.0×10^{-9} mol L^{-1}. The developed method showed excellent selectivity, good stability and repeatability. The fabricated electrode was also used to determine caffeine in tea and beverage with acceptable recovery.

1 Introduction

Tea is likely to be one of the most widely consumed beverages in the world because of its excellent flavour, refreshing function and health maintenance. To show the mechanisms behind these effects, a great deal of scientific effort has been taken to separate and identify active components in tea.[1, 2] One of the major active components of tea was found to be caffeine, which played an important role in various physiological effects such as relaxation of bronchial muscle, stimulation of the central nervous system, gastric acid secretion and dieresis.[3] However, it may cause emesis and dehydration.[4] It also can mobilise calcium from cells leading to bone mass loss and is considered a risk factor for cardiovascular diseases.[5, 6] That is why there have been numerous studies of the target to develop reliable methods for determining caffeine, such as high-performance liquid chromatography (HPLC), UV spectrophotometry, capillary electrophoresis and FTIR spectrophotometry.[7-10]

Nevertheless, these techniques are time-consuming and often require sample pretreatment. Meanwhile, caffeine is an electroactive compound, and can be established by electrochemical methods.[11] However, some issues limit the electrochemical detection of caffeine. One challenge is that the oxidation of caffeine occurs at a very positive potential. Another is the presence of xanthine and theophylline, and their oxidation potential overlaps with that of caffeine at conventional solid electrodes. To resolve these problems, one of the most common routes is using a modified electrode to increase the measuring sensitivity of caffeine. Although some modified electrodes have been developed for the determination of caffeine,[12-16] there is still a need to develop a new modified electrodes with high efficiency and convenience for the detection of caffeine.

Carbon nanotubes (CNTs), discovered by Iijima,[17] has attracted much attention in the perspective of electrochemical sensor design owing to unique geometrical, mechanical, electronic and chemical properties.[18] However, the major challenge for developing such CNT-based devices is the insolubility of CNTs in all solvents. To resolve the problem and to broaden the scope of analytes to be detected, the most common route is to functionalize the surface of CNTs with specific bio/chemical molecules.[19] And many research activities have addressed the generation of DNA-functionalized CNTs hybrids,[20-22] which further expanded the scope of CNTs as the application of sensors.[23-29]

In this work, a simple and sensitive electrochemical method, based on the DNA-functionalized single walled carbon nanotube (DNA-SWCNT) and Nafion composite film modified glassy carbon electrode, was proposed to determine caffeine. Here, Nafion can increase the immobilization stability of DNA-SWCNT on GCE surface due to its excellent film forming ability. And Nafion can also attract the positive charged caffeine to electrode surface effecting as accumulation. The characteristic of the modified electrode was characterised by scanning electron microscope (SEM) and cyclic voltammetry (CV). The electrochemical behavior of caffeine at the modified electrode was investigated by cyclic voltammetry (CV), chronocoulometry (CC) and chronoamperometry (CA), and the results reveal that DNA-SWCNT and Nafion composite film can remarkably enhance the electro-oxidation signal of caffeine. Based on these, a

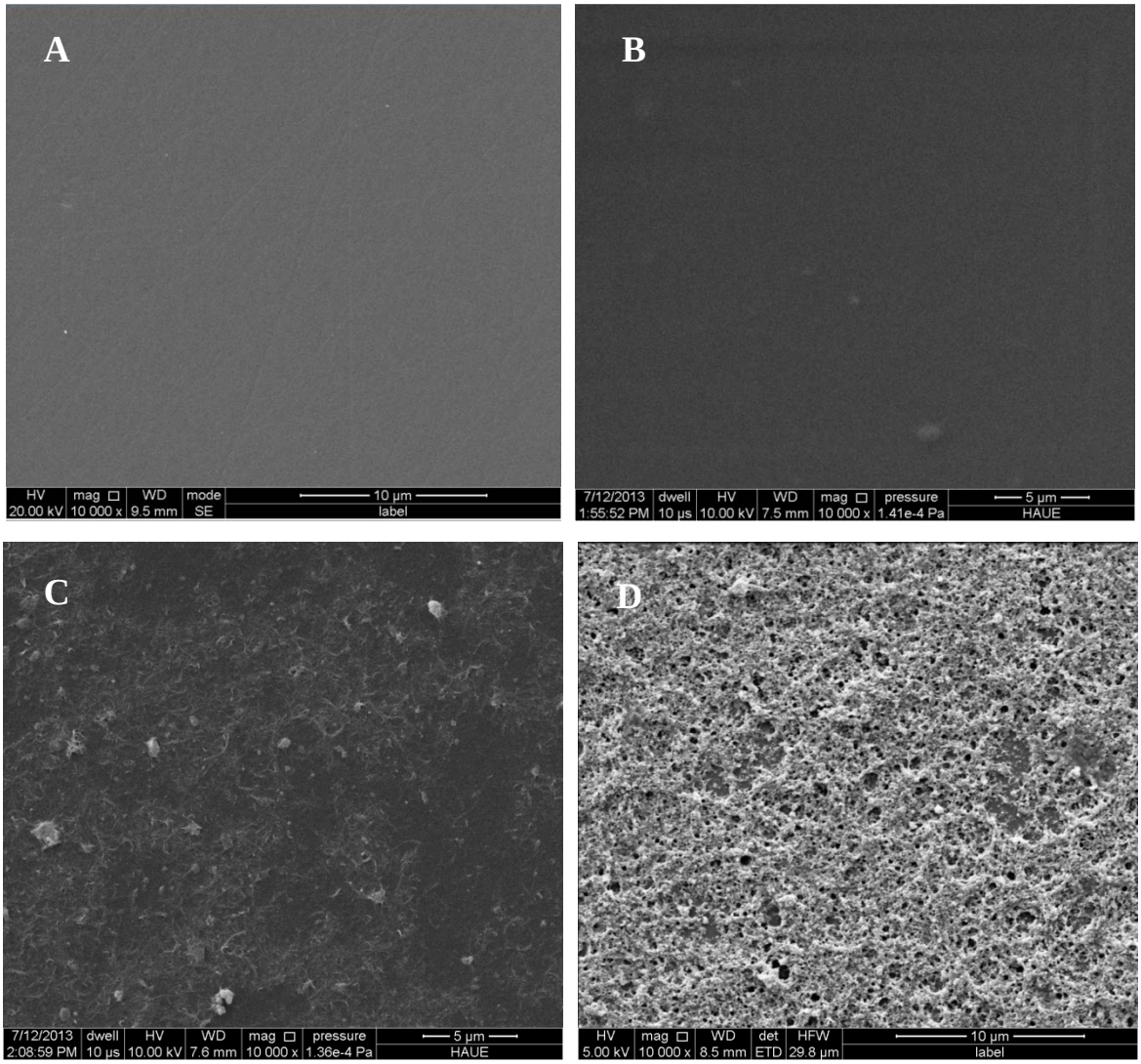

Fig. 1 SEM images obtained from the bare GCE (A), Nafion/GCE (B), Nafion/SWCNT/GCE (C) and Nafion/DNA-SWCNT/GCE (D)

simple and sensitive electrochemical method was proposed successfully for detecting the caffeine in tea and beverage.

2 Experimental

2.1 Apparatus and Reagents

Model CHI 650A electrochemical system (CHI instrumental, Shanghai, China) was employed for electrochemical techniques. SEM images were obtained with a Quonxe-2000 field emission scanning electron microscope (FEI Company, Holland). A standard three-electrode electrochemical cell was used with glassy carbon electrode (d = 3 mm) or modified GCE as working electrode, platinum (Pt) wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode (the internal solution was saturated KCl solution). All the pH measurements were made with a PHS-3C precision pH meter (Leici Devices Factory of Shanghai, China), which was calibrated with a standard buffer solution at 25 ± 0.1℃ every day.

Nafion 117 (5%, w/v in alcoholic solution) was purchased from Alfa and was diluted to 0.2% (w/v) with ethanol before use. Fish sperm ds DNA were supplied by Shanghai Sangon Company (Shanghai, China). SWCNT (95% purity) was obtained from Beijing Nachen S&T Ltd. Caffeine was bought from Shanghai Biochemical Reagent Co. Ltd, and used as received. Stock solutions (1.0×10^{-3} mol L^{-1}) of caffeine were prepared with doubly distilled water and stored at 4°C. The tea and beverage samples were obtained from Zhengzhou. All other reagents were of analytical grade and were used as received. Double distilled water was used for all preparations.

2.2 Fabrication of the DNA-SWCNT/Nafion composite film modified GCE

The wrapping of SWCNT by ds DNA was prepared according to the literature.[20] First, 2 mg SWCNT was added into 2 mL ds DNA (2 mg mL^{-1} in 0.1 mol L^{-1} NaCl) and then was sonicated in an ice-water bath for 2 h; the mixture was followed by centrifugation for 1.5 h at 10000 rpm to remove the very large aggregates that were not dispersed during the initial sonication, leaving a DNA-SWCNT hybrids solution.

Before modification, the bare GCE was polished to a mirror-like with 0.3 and 0.05 μm alumina slurry, then washed successively with redistilled deionized water, anhydrous alcohol and redistilled deionized water in an ultrasonic bath and dried in N_2 blowing. Then, 5 μL of DNA-SWCNT solution was deposited on the fresh prepared GCE surface. After the solvent evaporated, 3 μL of 0.2% Nafion was coated on the electrode, and then the solvent was evaporated in the air. The obtained electrode was noted as Nafion/DNA-SWCNT/GCE. For comparison, a Nafion and a SWCNT-Nafion modified GCEs were fabricated with the similar procedure, marked as Nafion/GCE and Nafion/SWCNT/GCE.

3. Results and Discussion

3.1 Morphological characterization of DNA-SWCNT/Nafion

To obtain information on the DNA-SWCNT and Nafion composite film and illustrate the difference of electrochemical performance, morphologies of the bare GCE, Nafion/GCE, Nafion/SWCNT/GCE and Nafion/DNA-SWCNT/GCE were characterized by using SEM, shown in Fig. 1A, B, C, D, respectively. Compared with glazed surfaces of bare GCE (Fig. 2A) and Nafion/GCE (Fig. 2B), a large number of needle-like Nafion-wrapped SWCNT particles were distributed on the electrode surface, which enables the Nafion/SWCNT/GCE to have a much higher specific area. At the same time, it is clear that a uniform three-dimensional network structure is observed on the surface of Nafion/DNA-SWCNT, indicating the formation of the DNA-functionalized SWCNT.

3.2 Electrochemical characterization of the electrode

For further information on the electrochemical properties of the modified electrode, the electrochemical impedance spectroscopy (EIS) was performed. Fig. 2 presents the Nyquist diagrams of GCE (curve a), Nafion/GCE (curve b), Nafion/SWCNT/GCE (curve c) and Nafion/DNA-SWCNT/GCE (curve d) in 5.0×10^{-3} mol L^{-1} $[Fe(CN)_6]^{3-/4-}$ (1:1) containing 0.1 mol L^{-1} KCl. It can be seen that a small well-defined semi-circle at higher frequencies was obtained at the bare GCE (curve a), indicating small interface electronic resistance (R_{ct}). When Nafion was deposited on the surface of GCE, the R_{ct} increased obviously (curve b). This phenomenon could be attributed to the negatively charged Nafion, blocking the diffusion of $[Fe(CN)_6]^{3-/4-}$ from solution to the electrode surface. However, the R_{ct} decreased remarkably after SWCNT was immobilized on the Nafion/GCE (curve c), indicating that SWCNT can effectively increase the electron transfer rate of $[Fe(CN)_6]^{3-/4-}$ due to its large surface area and good conductivity. Compared with Nafion/SWCNT/GCE, the R_{ct} of Nafion/DNA-SWCNT/GCE increased slightly, demonstrating that DNA had been immobilized on the surface of the SWCNT. The reason may be that DNA was non-conductivity, and the negatively charged phosphate skeletons of DNA immobilized on the SWCNT had a repulsive force to $[Fe(CN)_6]^{3-/4-}$ anion, which make it more difficult for the electron transfer to take place. The results also demonstrated that DNA-SWCNT and Nafion composite film was successfully immobilized on the GCE surface just as designed. In further research, an equivalent circuit (EC) as showed in the insert of Fig. 2 was designed, and the fit obtained

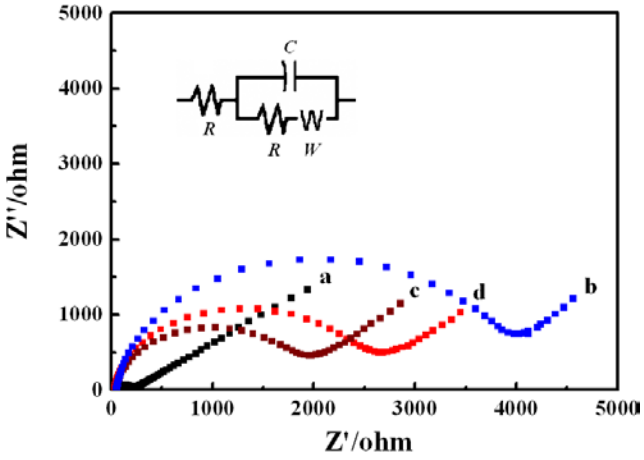

Fig. 2 Electrochemical impedance spectroscopy (EIS) of a bare GCE (curve a), Nafion/GCE (curve b), Nafion/SWCNT/GCE (curve c) and Nafion/DNA-SWCNT/GCE (curve d) in 5.0×10^{-3} mol L^{-1} $[Fe(CN)_6]^{3-/4-}$ (1:1) solution containing 0.10 mol L^{-1} KCl; open circuit potential and amplitude of 5 mV; frequency range: 100000 Hz to 0.01 Hz; the inset is equivalent circuit

from the EC was also plotted and showed in the Fig.1S. The R_{ct} obtained is about 165.9 Ω, 3379 Ω, 1608 Ω and 2198 Ω for GCE, Nafion/GCE, Nafion/SWCNT/GCE and Nafion/DNA-SWCNT/GCE, respectively.

3.3 Electrochemical oxidation behavior of caffeine at the Nafion/DNA-SWCNT/GCE

The inset of Fig.3 shows the cyclic voltammograms (CVs) of the background (curve a) and 1.0×10^{-5} mol L^{-1} caffeine (curve b) in 0.1 mol L^{-1} H_2SO_4 solutions (pH = 0.95) at the Nafion/DNA-SWCNT/GCE. It is obvious that the anodic peak current (i_{pa}) decreased obviously in the second scan compared with that of the first one, and gradually reduced with successive cyclic sweep. The reason may be that the oxidation product of caffeine, which is non-electroactive, adhered to the electrode surface and hindered the access of caffeine. At the same time, we found that if the electrodes were kept in 0.1 mol L^{-1} H_2SO_4 solutions in the absence of caffeine for 3 min under constant stirring, and then CV was carried out in the solution, until the peaks of caffeine disappeared. Finally, the Nafion/DNA-SWCNT/GCE surface will be restored to the initial state so that new CVs then exhibit the same characteristics as those of the first cycle in the inset of Fig. 3. Therefore, in the following discussion, the peak current is taken from the first cycle.

Fig. 3 compares the electrochemical responses of caffeine (1.0×10^{-5} mol L^{-1}) at bare GCE (curve a), Nafion/GCE (curve b), Nafion/SWCNT/GCE (curve c) and Nafion/DNA-SWCNT/GCE activation on all these four electrodes. At bare GCE, a weak anodic peak could be discerned. When Nafion/GCE was applied, the anodic peaks became noticeable, probably due to that Nafion has an enriched ability for caffeine by an electrostatic interaction. After SWCNT was added, the oxidation peak current (i_{pa}) increased and the oxidative potential (E_{pa}) shifted negatively. This result indicated that the interfusion of SWCNT into Nafion would improve the electrochemical response of caffeine; due to the large surface area and good conductivity were provided. Importantly, a distinct well-defined anodic peak appeared at the

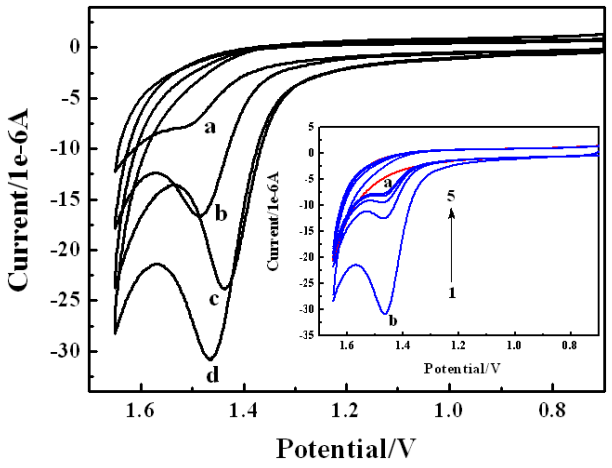

Fig. 3 CVs of caffeine (1.0×10^{-5} mol L^{-1}) at bare GCE (curve a), Nafion/GCE (curve b), Nafion/SWCNT/GCE (curve c) and Nafion/DNA-SWCNT/GCE (curve d) in 0.1 mol L^{-1} H_2SO_4 solutions with scan rate v= 0.05 V s^{-1}; the inset show CVs of the background (curve a) and caffeine (1.0×10^{-5} mol L^{-1}, curve b) at the Nafion/DNA-SWCNT/GCE.

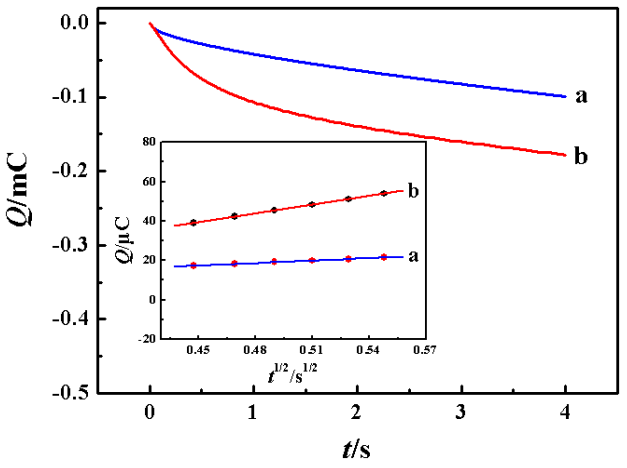

Fig. 4 Chronocoulometric curves of the background (curve a) and caffeine (1.0×10^{-4} mol L^{-1}) (curve b) in 0.1 mol L^{-1} H_2SO_4 solutions at the Nafion/DNA-SWCNT/GCE; the inset is the corresponding $Q \sim t^{1/2}$ plots.

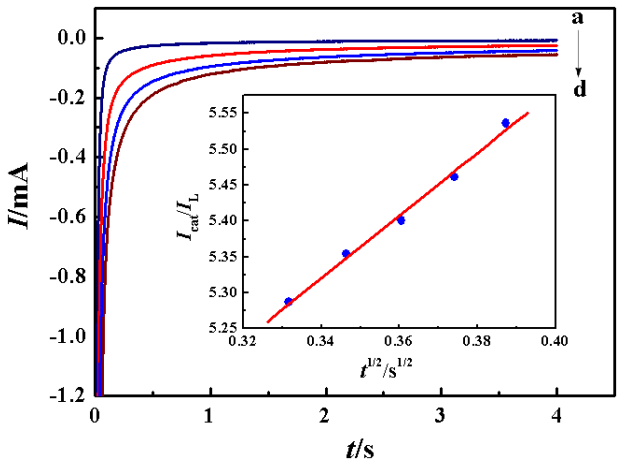

Fig. 5 Chronoamperograms of Nafion/DNA-SWCNT/GCE in 0.1 mol L^{-1} H_2SO_4 containing (a) 0, (b) 20, (c) 50 and (d) 100 μmol L^{-1} caffeine; inset shows the relationship of i_{cat}/i_L versus $t^{1/2}$ for 50 μmol L^{-1} caffeine.

Nafion/DNA-SWCNT/GCE under the same experimental condition, of which the i_{pa} is about 7.8-fold, 2.0-fold and 1.6-fold higher than that of bare GCE, Nafion/GCE and SWCNT/Nafion/GCE, respectively. As for the E_{pa}, no significant changes were observed. This results suggested that DNA-SWCNT cannot improve the electrocatalytic activity for the oxidation of caffeine relative to SWCNT alone, but can increase in the adsorbed amount of caffeine on the electrode. According to the literature, [29, 30] different from SWCNT alone, DNA-functionalized SWCNT hybrids exist in water as a solution rather than a dispersion, which is helpful in forming stable and uniform film. Besides, it can provide plenty of π-electrons, hydrogen bond binding sites and the large surface area, which are highly beneficial in enriching the caffeine. So the Nafion/DNA-SWCNT/GCE can obtain higher current response.

3.4 Chronocoulometry investigations

The chronocoulometry (CC) was employed to determine the saturating absorption capacity of caffeine at the Nafion/DNA-SWCNT/GCE surface. The Nafion/DNA-SWCNT/GCE was immersed in a caffeine solution (1.0×10^{-4} mol L^{-1}) for several minutes to achieve saturated absorption. And then, a step potential from 0.70 to 1.65 V was applied. $Q \sim t$ curve was recorded (Fig. 4, curve b) to calculate the saturated absorption capacity. For control, $Q \sim t$ curve was recorded in the blank solution too (Fig. 4, curve a). The corresponding $Q \sim t^{1/2}$ plots were also performed and shown as the inset in Fig 4. According to the formula given by Anson:[31]

$$Q = \frac{2nFAc(Dt)^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads} \quad (1)$$

Where Q_{dl} is the double-layer charge and Q_{ads} is the Faradaic charge due to the oxidation of adsorbed caffeine. Using Laviron's theory of $Q = nFA\Gamma^*$ and intercept difference between curves a and b, a Γ^* value of 7.82×10^{-9} mol cm^{-2} was obtained, which is higher than that at bare GCE (4.60×10^{-9} mol cm^{-2}), Nafion/GCE (5.45×10^{-9} mol cm^{-2}) and Nafion/SWCNT/GCE (6.78×10^{-9} mol cm^{-2}). This results also confirmed that DNA-SWCNT can increase in the adsorbed amount of caffeine on the electrode.

3.5 Chronoamperometry investigations

The evaluation of the catalytic rate constant (k_{cat}) was investigated by chronoamperometry. Fig. 5 shows chronoamperograms of Nafion/DNA-SWCNT/GCE in 0.1 mol L^{-1} H_2SO_4 solutions in the absence (curve a) and presence (curves b-d) of caffeine. The k_{cat} for the chemical reaction between caffeine and Nafion/DNA-SWCNT/GCE is determined according to the method described in the literature:[32]

$$\frac{i_{cat}}{i_L} = \pi^{1/2}(k_{cat}c_o t)^{1/2} \quad (2)$$

Where i_{cat} and i_L were the currents in the presence and the absence of caffeine, respectively; k_{cat} was the catalytic rate constant (mol L^{-1} s^{-1}), c_o was the bulk concentration (mol L^{-1}) of

Table 1 Comparison of determination of caffeine by different sensing methods reported.

Electrode	Modifier	Methods	Linear range	Detection limit (mol L^{-1})	Reference
GCE	Nafion	DPV	9.95×10^{-7} ~ 1.06×10^{-5}	7.79×10^{-7}	12
GCE	MWCNTs/Nafion	DPV	6.0×10^{-7} ~ 4.0×10^{-4}	2.3×10^{-7}	13
GCE	Graphene oxide/Nafion	DPASV	4.0×10^{-7} ~ 8.0×10^{-5}	2.0×10^{-7}	14
GCE	Graphene/Nafion	DPV	4.0×10^{-7} ~ 4.0×10^{-5}	1.2×10^{-7}	15
Boron-doped diamond electrode	—	DPV	4.0×10^{-7} ~ 2.5×10^{-5}	1.5×10^{-7}	16
GCE	DNA-SWCNTS/Nafion	SWASV	5.0×10^{-7} ~ 1.0×10^{-4}	1.0×10^{-7}	This work

DPV: differential pulse voltammetry;
DPASV: differential pulse anodic stripping voltammetry;
SWASV: square wave anodic stripping voltammetry;

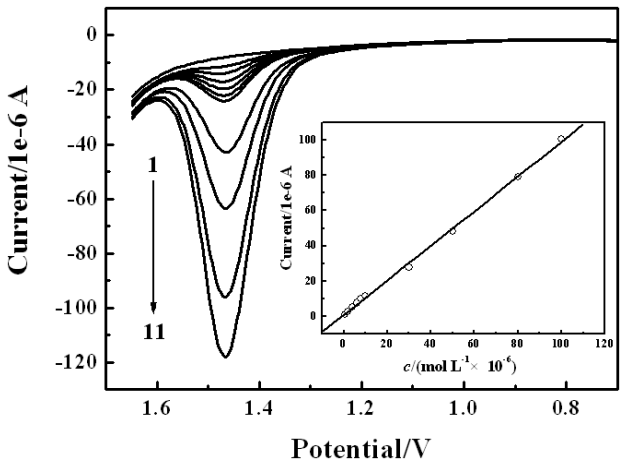

Fig. 6 SWASVs and their associated calibration plot (insert) for increasing concentrations of caffeine at Nafion/DNA-SWCNT/GCE under optimum conditions; caffeine concentration: 1) 0.0 mol L^{-1}, 2) 5.0×10^{-7} mol L^{-1}, 3) 2.0×10^{-6} mol L^{-1}, 4) 4.0×10^{-6} mol L^{-1}, 5) 6.0×10^{-6} mol L^{-1}, 6) 8.0×10^{-6} mol L^{-1}, 7) 1.0×10^{-5} mol L^{-1}, 8) 3.0×10^{-5} mol L^{-1}, 9) 5.0×10^{-5} mol L^{-1}, 10) 8.0×10^{-5} mol L^{-1}, 11) 1.0×10^{-4} mol L^{-1}.

caffeine and t was the elapsed time (s). From the slope of the i_{cat}/i_L versus $t^{1/2}$ plot (see the inset of Fig. 5), the mean value of k_{cat} for the electrooxidation of caffeine was calculated to be 2.67×10^4 mol L^{-1} s^{-1} when the concentration of caffeine was 5.0×10^{-5} mol L^{-1}.

3.6 Analytical applications and methods validation

3.6.1 Influence of supporting electrolytes and pH

To optimize the determination conditions of caffeine, the current responses of 1.0×10^{-5} mol L^{-1} caffeine was estimated by square wave voltammetry (SWV) in different supporting electrolytes such as H_2SO_4 (pH=0.9~3), NaOH (pH=9~11), phosphate buffer (pH=6.0~8.0), acetate buffer (pH=4.0~7.0), Britton-Robinson (pH=2.0~10.0) and borate buffer (pH=7.5~9.0) solutions. The results showed that the best compromise between sensitivity and reproducibility of the signal could be obtained in H_2SO_4 solution. Therefore, H_2SO_4 solution was adopted.

For the variation of solution pH from 0.90 to 3.0, it was found that the i_{pa} decreased and peak potentials (E_{pa}) shifted negatively by increasing the solution pH in the range from 0.90 to 2.47 (achieved by diluting 0.20 mol L^{-1} H_2SO_4). So pH 0.95 (0.10 mol L^{-1} H_2SO_4) was chosen as the most suitable value due to the excellent peak response.

3.6.2 Instrumental parameters

In order to obtain a much more sensitive peak current, the SWV was employed in the determination of caffeine. The optimum instrumental conditions (pulse-amplitude E_{sw}, frequency f) were studied for a 1.0×10^{-5} mol L^{-1} caffeine solution following accumulation time (t_{acc}) of 300 s under open circuit. The results indicated that the i_{pa} increased with the increasing of square wave amplitude from 10 to 50 mV or square wave frequency in the range of 10 - 40 Hz, but the peak potential shifted to more positive values, and the peak changed unshapely. Therefore, the optimum amplitude and frequency were choosen as 30 mV and 35 Hz, respectively.

3.6.3 Accumulation conditions

For consideration of the adsorption of caffeine at the Nafion/DNA-SWCNT/GCE surface, SWV technique coupled with accumulation procedure was used for study. With an increase in accumulation time (t_{acc}), the peak current increased. When the t_{acc} was 180 s, peak current achieved a maximum value in a caffeine solution of 1.0×10^{-5} mol L^{-1}. A plateau was appearance for prolonging the t_{acc} afterwards. And the accumulation potential (0.1 - 0.7 V) had little effect on the peak current. So the t_{acc} of 180 s was used for further studies. And the accumulation of caffeine was carried out under open circuit.

3.6.4 Calibration curve, detection limit, repeatability and stability

Fig. 6 displays the response of different concentration of caffeine in the optimized working conditions by square wave adsorptive stripping voltammetry (SWASV) using DNA-SWCNT/Nafion/GCE. A linear relationship could be established between i_{pa} and the concentration of caffeine in the range of 5.0×10^{-7} ~ 1.0×10^{-4} mol L^{-1} (the inset of Fig.6). The linear regression equation and correlation coefficient are:

Table 2 Determination results of caffeine in some tea and beverage samples by SWASV (n=5)

Sample	Amount found	R.S.D. (%)	Standard added	Total found	Recovery (%)
Green tea	19.45 mg g^{-1}	2.5	20.00 mg g^{-1}	39.56 mg g^{-1}	100.6
Black tea	29.45 mg g^{-1}	2.9	20.00 mg g^{-1}	50.09 mg g^{-1}	102.2
Oolong tea	23.45 mg g^{-1}	3.3	20.00 mg g^{-1}	43.19 mg g^{-1}	98.9
Cola	5.81×10^{-4} mol L^{-1}	3.5	6.00×10^{-4} mol L^{-1}	11.53×10^{-4} mol L^{-1}	95.2
Energy drink	1.10×10^{-3} mol L^{-1}	2,9	1.00×10^{-3} mol L^{-1}	2.12×10^{-3} mol L^{-1}	101.8

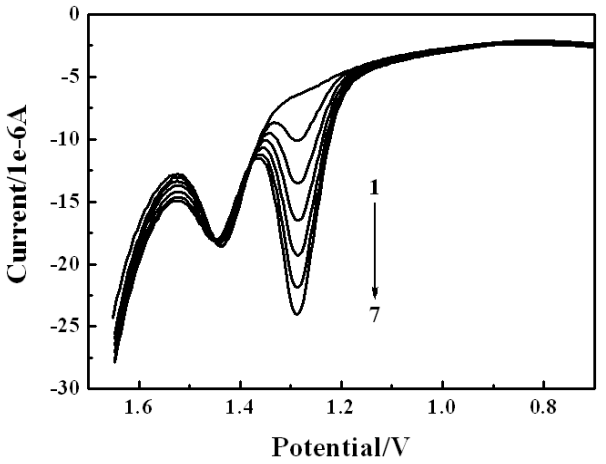

Fig. 7 SWASVs at the Nafion/DNA-SWCNT/GCE in 0.1 mol L^{-1} H_2SO_4 solutions containing 1.0×10^{-5} mol L^{-1} caffeine and different concentrations of theophylline; (1) 0 mol L^{-1}, 2) 5.0×10^{-6} mol L^{-1}, 3) 1.0×10^{-5} mol L^{-1}, 4) 1.5×10^{-5} mol L^{-1}, 5) 2.0×10^{-5} mol L^{-1}, 6) 2.5×10^{-5} mol L^{-1}, 7) 3.0×10^{-5} mol L^{-1}.

$$i_{pa} = 0.831 + 0.981 \times 10^{6}\, c,\ R = 0.995$$

where i_{pa} was the oxidation peak current in μA and c was the concentration of caffeine in mol L^{-1}. Standard deviations (SD) for the slope and intercept of the calibration curve were 0.00124 and 0.056, respectively. Based on the signal-to-noise ratio of 3 (S/N),[33] the detection limit was obtained as 1.0×10^{-7} mol L^{-1}.

Using the Nafion/DNA-SWCNT/GCE to detect caffeine (5.0×10^{-6} mol L^{-1}) by SWASVs in 0.1 mol L^{-1} H_2SO_4 solutions, no change was observed for 5 successive detections. Similarly, 10 different caffeine solutions (same concentration) were determined and the relative standard deviation observed was 3.7 %. For testing the stability of the Nafion/DNA-SWCNT/GCE, a same caffeine solution was detected on day one and a month later. The peak currents of caffeine recorded on day one and a month later were changed about 4.8 %. These experiments indicate that the Nafion/DNA-SWCNT/GCE has good stability and repeatability for the determination of caffeine.

The method developed is compared with other similar electroanalytical methods, see Table 1. Apart from the stability and simplicity in the preparation of the modified electrode, the present method gives a reasonably lower detection limit and wider linear range. The lower detection limit to the method mainly depends on the amount of substance, which is transferred to the electrode surface during accumulation. The synergetic properties of DNA-functionalized SWCNT and Nafion composite film, endowed the capability to strongly adsorb target substance, enhanced the surface concentration. This research suggests also that the modified electrode as voltammetric sensors might be a very promising direction in trace analysis of electrochemistry.

3.6.5 Interference studies

The influence of some potentially interfering species on the determination of caffeine was evaluated in detail. Fig. 7 shows SWASVs of 1×10^{-5} mol L^{-1} caffeine and different concentrations of theophylline at the Nafion/DNA-SWCNT/GCE in 0.10 mol L^{-1} H_2SO_4 solutions. As shown in Figure, two well-defined peaks appeared at the potentials of 1.29 V and 1.44 mV for theophylline and caffeine, respectively, which offered a promising possibility for the simultaneous determination of theophylline and caffeine. Moreover, other various interfering species was also evaluated under the same experimental conditions. The results showed that 50-fold of ascorbic acid, 30-fold of dopamine, 35-fold of epinephrine, 20-fold of uric acid, 2-fold of tannic acid and 2-fold of xanthine had almost no influence on the current response of caffeine (signal change below 5%). All these indicated that the Nafion/DNA-SWCNT/GCE had good selectivity for the determination of caffeine.

3.7 Determination of caffeine in tea and beverage samples

In order to evaluate the practical application of this method, the Nafion/DNA-SWCNT/GCE was used to determine caffeine in some tea and beverage samples. The samples were treated according to the literature.[14, 34] 1 mL treated sample solution was added into 9 mL 0.1 mol L^{-1} H_2SO_4 and SWASV was recorded under the optimal experimental conditions. Meanwhile, in order to calculate the recovery, caffeine standard solution was added. The results were listed in Table 2. The recovery was in the range of 95.2 – 102.2%, indicating that the sensor might be sufficient for practical applications

4 Conclusions

In the current report, we described a simple, sensitive and selective SWV method for the quantitative determination of caffeine based on the DNA-functionalized SWCNT and Nafion composite film modified GCE (Nafion/DNA-SWCNT/GCE) as voltammetric sensors. The data reported here showed that the Nafion/DNA-SWCNT/GCE was highly stable and consistent in

detecting caffeine. And the method can be used successfully to assay the caffeine in some tea and beverage samples.

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Notes and references

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