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Sensitive Differential Pulse Stripping Voltammetry of Caffeine in Medicines and Cola Using a Sensor Based on Multi-Walled Carbon Nanotubes and Nafion

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A sensitive electrochemical sensor for the determination of caffeine (3,7 – dihydro - 1, 3, 7 – trimethyl - 1H – purine - 2, 6 – dione) based on a multi-walled carbon nanotube and a Nafion-modified glassy carbon electrode (MWCNT-Nafion/GCE) using differential pulse adsorptive stripping voltammetry is presented. The surface micromorphology of the MWCNT-Nafion/GCE as well as the effects of pH, scan rate, accumulation potential and time were investigated by scanning electron microscopy, atomic force microscopy and other electrochemical techniques. At optimal test conditions, the calibration curves for the determination of caffeine showed two linear responses. The first linear range was from 2.945 to 377.0 μM, with a detection limit of 0.513 μM (based on 3σ), and the second linear range was from 377.0 to 2356 μM. The sensor was then successfully utilised for the determination of caffeine in real samples of "Sanlietong" tablets and Cola.

Keywords: Differential pulse stripping voltammetry, sensor, carbon nanotube, nafion, caffeine

1. INTRODUCTION

Caffeine (3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione) is an N-methyl derivative of xanthine that is widely distributed in natural products and beverages. The use of caffeine as an analgesic and antipyretic is well established in pharmaceutical formulations. However, intense use of

caffeine over time can lead to nervousness, irritability, anxiety, and tremors, among other side effects [1].

Many methods, including ultraviolet spectrophotometry [2-4], high-performance liquid chromatography [5,6] and quasi-flow injection analysis [7] have been reported for the detection of caffeine. Usually, these methods are more expensive, time-consuming and complicated than comparable electroanalytical methods. Despite these facts, a few electroanalytical methods have been used for the analysis of caffeine. This is likely the case both because there is significant interference from caffeine analogues and because the oxidation of caffeine occurs at a very positive potential that overlaps with the discharge of the background electrolytic solution. Several solutions have been proposed, including the choice of anodic potential [8], supporting electrolyte [9], a new electrode material [10-14] or modified electrodes [15]. The use of Nafion-modified glassy carbon electrodes (Nafion/GCE) [16] as an electrode substrate is now well established, mainly due to their good cation-exchange ability and stability as well as the strong adsorptive ability of Nafion, widely applied in electroanalysis [17-18]. Zen and Ting [19] used a Nafion/ruthenium oxide pyrochlore chemically-modified electrode for the determination of caffeine in drug formulations by square wave voltammetry, obtaining a detection limit of 2.2 μM. Brunetti et al. [20] developed a voltammetric method based on a Nafion-covered electrode for the quantitative determination of caffeine with a detection limit of 0.8 μM.

Multi-wall carbon nanotubes (MWCNT) as an immobilisation matrix for the construction of a modified electrode on the surface of a glassy carbon electrode (GCE) not only exhibited several distinct advantages, including extraordinary stability, good reproducibility and wide linear concentration ranges in comparison with GCE alone, but it also showed excellent electrocatalytic activity for many materials, such as phenolics [21], malachite green [22], malathion [23], paracetamol [24], tetracycline [25], caffeine [26-28], ascorbic acid [29], glucose [30], adrenaline and uric acid [31].

In this work, the use of an MWCNT-Nafion/GCE with differential pulse adsorptive stripping voltammetry (DPASV) as a selective and sensitive electrochemical sensor for the determination of caffeine is reported. The surface micromorphology of the MWCNT-Nafion/GCE and the effects of pH, scan rate, accumulation potential and time were all investigated. Furthermore, the sensor proved to have a good response towards caffeine in real samples under user-friendly conditions.

2. EXPERIMENTAL

All chemicals were of analytical grade and were used as received without any further purification. Nafion (5% ethanol solution，SE-5112) was purchased from the Du Pont Co. (USA). Caffeine standard aqueous solutions were prepared in 0.04 M H_3PO_4, HOAc, H_3BO_3 and 0.2 M NaOH BRBS at pH 4.1. All solutions were prepared with double-distilled water. Bamboo-like carboxylic MWCNTs (purity > 99.9%) were purchased from Chengdu Organic Chemicals Co., Chinese Academy of Sciences.

All of the electrochemical experiments were conducted using a three-electrode configuration in a self-made glass cell. The working electrode (3 mm in diameter) was prepared from a MWCNT-doped Nafion film dropped on a GCE. An Ag/AgCl (3.0 M KCl) electrode was used as reference, and the counter electrode was a Pt wire. Prior to the experiments, the multi-walled carbon nanotube and a Nafion-modified glassy carbon electrode (MWCNT-Nafion/GCE) was submerged in 0.04 M H_3PO_4, HOAc, H_3BO_3 and 0.2 M NaOH Britton-Robinson buffer solution (BRBS) at pH 4.1 for 10 min. Cyclic voltammetry (CV) and DPASV were carried out using a CHI660C electrochemical workstation (CH Instruments, USA). The surface morphology of the prepared MWCNT-Nafion/GCE was investigated by scanning electron microscopy (SEM, S-3400N, Hitachi, Japan) and atomic force microscopy (AFM, HL-II, Beijing Zhongke Mechanical & Electrical Equipment Co., China).

The MWCNT-Nafion/GCE was fabricated using the following method. 2 mg of MWCNTs was dispersed in 10 mL of a 0.5% Nafion ethanol solution under ultrasonication for 30 min. 10 μL of a viscous, black MWCNT-Nafion mixture was dropped onto the cleaned GCE surface with a syringe. The modified electrode was allowed to sit at room temperature for 24 h to evaporate the ethanol. The Nafion film was fabricated by the same procedure described above, but without MWCNTs. Before use, the modified electrode was scanned through six laps using CV in supporting electrolyte for activation.

The high-purity nitrogen was passed through the system for 10 min to remove oxygen. Unless otherwise stated, 0.04 M H_3PO_4, HOAc, H_3BO_3 and 0.2 M NaOH BRBS at pH 4.1 was used as the supporting electrolyte for caffeine determination. The analysis of caffeine by DPASV included two main steps: the accumulation step and the stripping step. The first step was a reduction process where caffeine was preconcentrated onto the MWCNT-Nafion/GCE at the accumulation potential of –1.0 V for 9 min. In the following step, reduced caffeine was oxidised between 1.20 and 1.45 V during the course of the potential sweep from 0.8 to 1.7 V, with an increment potential of 2 mV, a pulse amplitude potential of 50 mV, a pulse width of 10 ms and a pulse period of 20 ms. The stripping peak current (I_p) for caffeine was measured between 1.20 and 1.45 V.

3. RESULTS AND DISCUSSION

The structure and morphology of the MWCNT-Nafion film on the GCE were characterised using SEM (Fig. 1a) and AFM (Fig. 1b-d). As can be seen in Fig. 1a, large numbers of needle-like Nafion-wrapped MWCNT particles were distributed on the electrode surface. From the magnified AFM diagram (Fig. 1b), it is very clear that the penetrating or exterior MWCNTs were either packaged by the Nafion film or exposed to the film surface.

We also further studied the modality of the Nafion film. There was a stratiform scaly texture, as shown in Fig. 1c, indicating that the film-forming process was inerratic, not random. This may be related to the surface structure of GCE and the special nature of Nafion. The inerratic convex-concave-shaped surface, like the grating shape shown in the three-dimensional surface profile image (Fig. 1d), not only increased the electrode's surface area but also supported the embedding of analytical small molecules into the 100-200 nm wide gaps. The caffeine cations in acidic solution are organic

nanomolecules, and they are in the ideal particle size range for ions passing through Nafion. In addition, adding MWCNTs could increase the electrical conductivity of MWCNT-Nafion/GCEs.

Fig. 2 illustrates the potential application of MWCNTs and Nafion film for the determination of trace levels of caffeine by DPASV. A weak oxidation peak (I_p = 0.03578 μA) between 1.20 and 1.60 V (E_p = 1.456 V) was observed for the low concentration of 17.67 μM caffeine on the bare GCE after being preconcentrated at the accumulation potential of –1.0 V for 9 min. Under comparable conditions, an obvious stripping peak (I_p = 0.2085 μA) was observed between 1.20 and 1.45 V (E_p = 1.374 V) for the Nafion/GCE. From these results, one can see that the oxidation peak current greatly increased for the Nafion/GCE compared to the bare GCE.

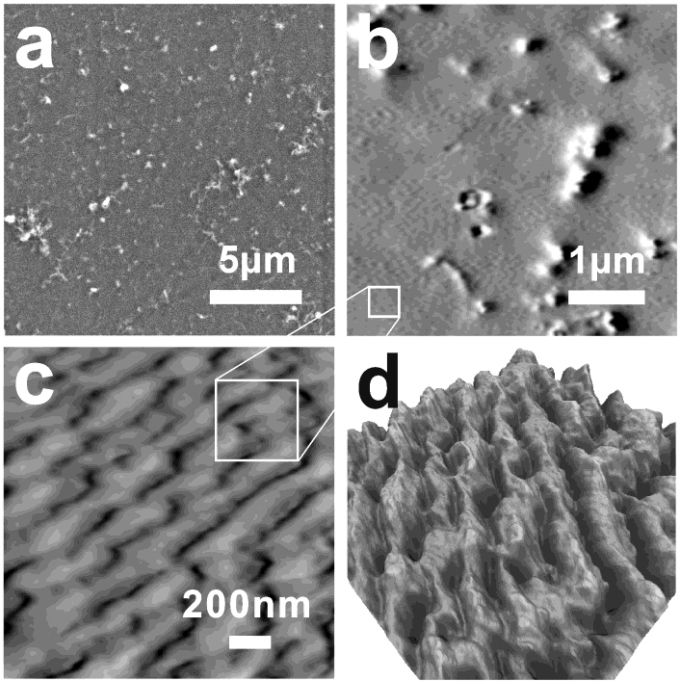

Figure 1. (a) SEM image of MWCNT-Nafion film on the GCE, acceleration voltage = 5 KV. (b) Contact-mode AFM image of MWCNT-Nafion film on the GCE. (c) AFM image and (d) AFM three-dimensional surface profile image of the magnified Nafion film on the GCE.

This finding may be due to the fact that Nafion is a cation-exchanger and attracts caffeine from the bulk solution to the electrode surface. The stripping peak (I_p = 0.3783 μA) also was observed to increase strongly on the MWCNT-Nafion/GCE between 1.20 and 1.45 V (E_p = 1.310 V). As can be seen from the Fig. 2, there was a large difference between the magnitude of the caffeine signal on the MWCNT-Nafion/GCE as compared to a bare GCE or even a Nafion/GCE, probably reflecting the larger surface area (Fig. 1) and better electrical conductivity of the MWCNT-Nafion/GCE. The lower oxidation peak potential of the MWCNT-Nafion/GCE and the Nafion/GCE indicated that they were more electrochemically active relative to the other tested electrodes. Furthermore, as depicted in Fig. 2, the faradic peak current for oxidation of caffeine by the MWCNT-Nafion/GCE was approximately two times greater than the Nafion/GCE and ten times greater than the bare GCE. The peak current

enhancement further indicated that the catalytic activity of MWCNTs contributed to the oxidation of caffeine, which could be attributed to the unique structure and extraordinary properties of the MWCNTs. This comparison undoubtedly demonstrated that the MWCNT-Nafion film exhibited bifunctionality: the cation-exchange ability and strong adsorptive ability of Nafion and the excellent catalytic activity of the MWCNTs. Thus, MWCNT-Nafion film could clearly improve the sensitivity in determinations of caffeine.

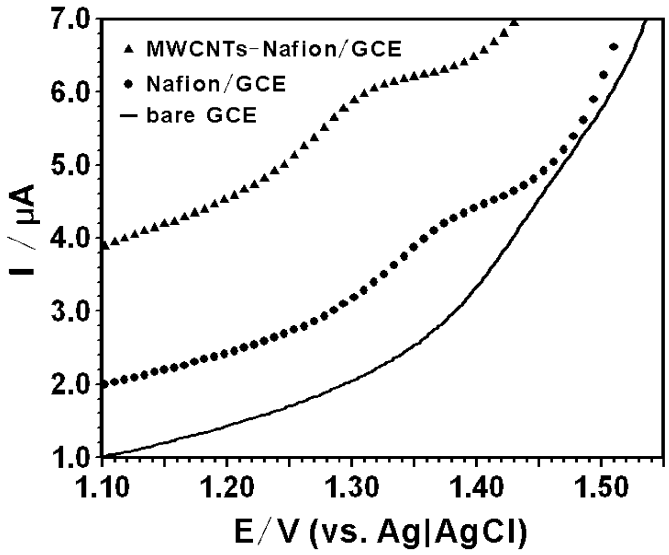

Figure 2. DPASVs of the bare GCE, Nafion/GCE and MWCNT-Nafion/GCE in the presence of 17.67 μM caffeine. The supporting electrolyte was 0.04 M BRBS at pH 4.1, accumulation potential = −1.0 V, accumulation time = 9 min, initial E = 0.9 V, final E = 1.6 V, increment E = 2 mV, pulse amplitude E = 50 mV, pulse width = 10 ms, pulse period = 20 ms.

The effect of pH on the electrochemical response of caffeine was studied over the pH range of 1.0−12.0 in BRBS. These solutions were prepared from an acidic solution that contained 0.04 M each of H_3PO_4, HOAc, and H_3BO_3; it was then adjusted to the appropriate pH using 0.2 M NaOH. The MWCNT-Nafion/GCE was placed in 47.12 μM of caffeine in BRBS, adjusted to the appropriate pH and caffeine accumulated for 10 min at –1.0 V. Next, the reduced caffeine was oxidised between 1.20 and 1.45 V during the potential sweep from 0.9 to 1.7 V. The DPASV and stripping peak current from 1.20 to 1.45 V for caffeine was measured and recorded. This procedure was repeated for each studied pH using the same MWCNT-Nafion/GCE and conditions.

Fig. 3 shows the DPASVs at different pH values for 47.12 μM caffeine. As can be seen, the peak shape was better defined for DPASV of caffeine in acid solution. When the pH values were raised to neutral (pH 7.0), the oxidative peak of caffeine faded away and the oxidative peak current was gradually decreased. However, with an increase in pH values, the problem of interference appeared and became more and more serious as the pH increased from 9.2 to 11.9. This observation was probably due to the fact that dominant hydroxyl anions (OH^-) and several oxidation products of

caffeine develop in the basic solution systems. Considering its user-friendly condition, pH 4.1 was used throughout the analytical caffeine.

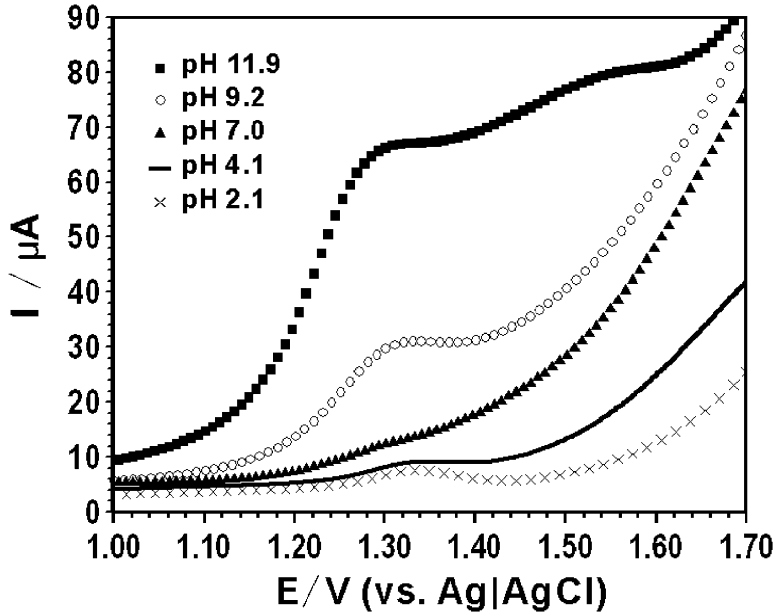

Figure 3. DPASVs of the MWCNT-Nafion/GCE for 47.12 μM caffeine in 0.04 M BRBS with pH values of 2.1, 4.1, 7.0, 9.2, and 11.9. Accumulation potential = −1. 0 V, accumulation time = 10 min, initial *E* = 0.9 V, final *E* = 1.7 V, increment *E* = 2 mV, pulse amplitude *E* = 50 mV, pulse width = 10 ms, pulse period = 20 ms.

The effect of scan rate (increment potential / pulse period) on the oxidative peak currents of the MWCNT-Nafion/GCE for 47.12 μM caffeine in pH 4.1 BRBS was also studied. Fig. 4 shows the DPASVs of caffeine obtained in the range of 10 to 130 mV s^{-1} (corresponding increment potential 2−26 mV) in order to investigate whether or not the oxidative behaviour of caffeine was due to caffeine adsorbing on the MWCNT-Nafion/GCE. In this graph, the oxidative peak currents of caffeine gradually increased as the scan rates were increased from 10 to 100 mV s^{-1}. Furthermore, upon improving the scan rate to 110 mV s^{-1}, the peak currents remained almost stable. When the scan rate exceeded 110 mV s^{-1}, however, the peak currents conversely decreased. The oxidation peak potentials shifted positively as the scan rates increased from 10 to 130 mV s^{-1}. This observation indicated that the caffeine was adsorbed onto the MWCNT-Nafion/GCE surface and the catalytic activity of the MWCNTs contributed to the oxidation of caffeine. The optimum scan rate for caffeine determination was found to be 100 mV s^{-1}.

The effect of accumulation potential on the stripping peak current is depicted in Fig. 5a. In the graph we can see where the accumulation potential shifted from –0.4 to –1.0 V, the point at which the stripping peak current greatly increased. This could be because, as the accumulation potential became more negative, caffeine was reduced more completely, and, consequently, the stripping peak current increased. When the accumulation potential was more negative than –1.0 V, the stripping peak current changed only very slightly while the background current increased greatly. Clearly, high sensitivity

and better responses could be achieved with an accumulation potential of –1.0 V. Therefore, –1.0 V was selected as the accumulation potential for caffeine analysis.

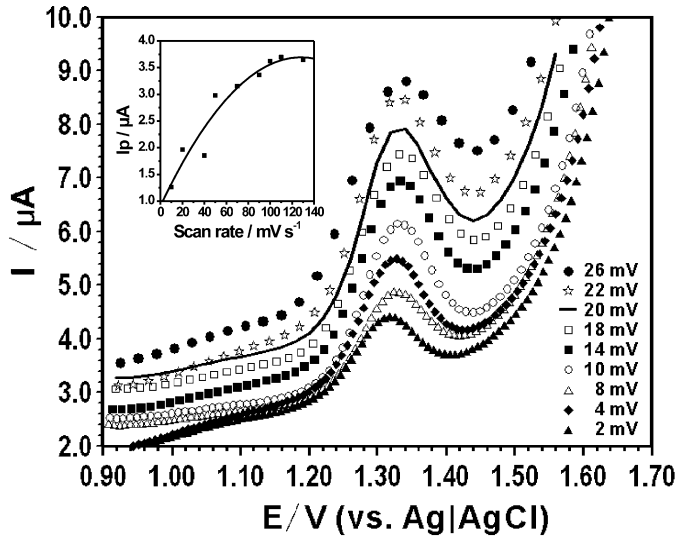

Figure 4. DPASVs of the MWCNT-Nafion/GCE for 47.12 μM caffeine in 0.04 M pH 4.1 BRBS at different increment potentials from 2 to 26 mV. Accumulation potential = −1. 0 V, accumulation time = 10 min, initial *E* = 0.9 V, final *E* = 1.7 V, pulse amplitude *E* = 50 mV, pulse width = 10 ms, pulse period = 200 ms. Inset: variation of the electrocatalytic peak current with the scan rate as calculated from increment potentials and the pulse period.

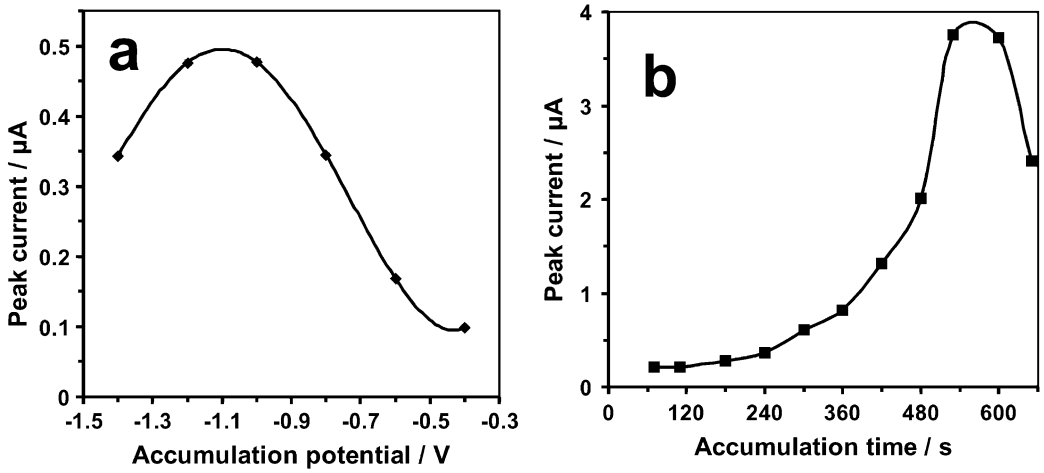

Figure 5. (a) Effect of accumulation potential on the stripping peak current of the MWCNT-Nafion/GCE for 11.78 μM caffeine in 0.04 M BRBS at pH 4.1 with accumulation potentials of –0.4, –0.6, –0.8, –1.0, –1.2 and –1.4 V. Accumulation time = 30 s, initial *E* = 0.9 V, final *E* = 1.7 V, increment *E* = 2 mV, pulse amplitude *E* = 50 mV, pulse width = 10 ms, pulse period = 20 ms. (b) Effect of accumulation time on the stripping peak current of the MWCNT-Nafion/GCE for 11.78 μM caffeine in 0.04 M BRBS at pH 4.1 with accumulation times of 70, 110, 180, 240, 300, 360, 420, 480, 530, 600 and 650 s. Accumulation potential = −1. 0 V, initial *E* = 0.9 V, final *E* = 1.7 V, increment *E* = 2 mV, pulse amplitude *E* = 50 mV, pulse width = 10 ms, pulse period = 20 ms.

The dependence of stripping peak current on accumulation time was also studied. As the accumulation time was increased, more caffeine could be exchanged and adsorbed onto the MWCNT-Nafion/GCE surface, so the stripping peak current should undoubtedly increase. As shown in Fig. 5b, the stripping peak current for 11.78 μM caffeine gradually increased as the accumulation time was increased to 9 min, indicating that the sensitivity of the determination of caffeine would improve as the accumulation time was extended. With the increase in accumulation time, however, the stripping peak decreased when the accumulation time was beyond 10 min. This observation probably reflects that there was a limit on the quantity of accumulation for reduced caffeine in relation to the thickness of the MWCNT-Nafion film. In this work, 9 min was chosen both to achieve the highest possible sensitivity and to save analysis time.

To evaluate the applicability of MWCNT-Nafion/GCEs for analysing caffeine, DPASV was used for the determination of caffeine in standard and real samples. The MWCNT-Nafion/GCE was first immersed in pH 4.1 BRBS of caffeine to accumulate caffeine for 9 min at the potential of –1.0 V, and then caffeine was oxidised during a potential sweep from 0.9 to 1.7 V. Fig. 6 depicts the response of the addition of caffeine in pH 4.1 BRBS using a MWCNT-Nafion/GCE after 9 min accumulation at –1.0 V. In the plots of oxidation peak current versus concentration of caffeine, two linear ranges were obtained, as shown in Fig. 6a and b. The first linear range was from 2.945 to 377.0 μM, and the corresponding calibration equation was (I_p /μA = 0.02252 c /μM ― 0.01948, n = 8). The correlation coefficient for this equation was 0.9999 (Fig. 6a), and the calculated detection limit based on 3σ was 0.513 μM. The second linear range was between 377.0 and 2356 μM (I_p /μA = 0.0064 c /μM + 6.407, n = 4), and the correlation coefficient was 0.9941 (Fig. 6b).

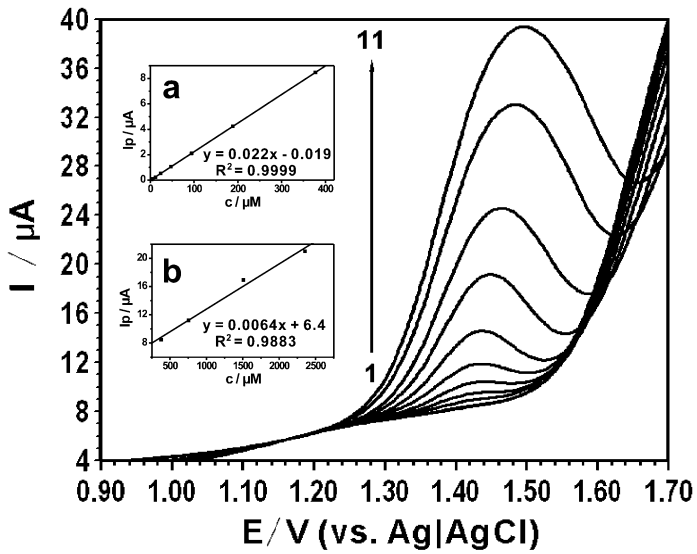

Figure 6. DPASVs of the MWCNT-Nafion/GCE in BRBS (pH 4.1) containing different concentrations of caffeine. Numbers 1–11 correspond to 2.945, 5.891, 11.78, 23.56, 47.12, 94.25, 188.5, 377.0, 754.0, 1508 and 2356 μM of caffeine. Accumulation potential = −1. 0 V, accumulation time = 9 min, initial E = 0.9 V, final E = 1.7 V, increment E = 2 mV, pulse amplitude E = 50 mV, pulse width = 10 ms, pulse period = 20 ms. Insets: The plots of the electrocatalytic peak current as a function of caffeine concentration within the range of (a) 2.945–377.0 μM and (b) 377.0–2356 μM caffeine, respectively.

The two linear ranges of caffeine most likely reflected the formation of a caffeine monolayer in the first range of calibration and the formation of a caffeine multilayer in the second range during the accumulation process where caffeine was preconcentrated onto the MWCNT-Nafion/GCE.

Using the chemically modified electrode based on the MWCNT-Nafion/GCE technology, a detection limit of 0.513 μM was achieved, one of the lowest reported for the electroanalytical detection of caffeine using simple, easy handling and commonly available electrochemical techniques. This ultra-low limit of detection compared well with other spectroscopic techniques for the determination of caffeine in real samples.

To illustrate its application in practical analysis, the MWCNT-Nafion/GCE was used to detect caffeine in "Sanlietong" tablets and Cola samples. The results obtained were satisfactory when using the standard addition method. Recovery experiments carried out to evaluate the matrix effect after standard-solution additions yielded a good recovery value for caffeine, indicating that there were no important matrix interferences for the samples analysed by DPASV. These results are illustrated in Table 1, and they suggest that the MWCNT-Nafion/GCE has great potential for practical sample analysis.

Table 1. Determination of caffeine in tablets and Cola samples.

Samples	Initial /μM	Added /μM	Detected value /μM	Recovery /%	Real value
tablets	5.836	14.14	18.58	90.12	18.99 mg per tablet
		14.14	18.29	88.11	
		14.14	18.54	89.89	
Cola	10.12	23.56	32.22	93.81	85.91 mg L^{-1}
		23.56	32.74	95.98	
		23.56	32.96	96.92	

4. CONCLUSIONS

Combining the cationic-exchange capacity of Nafion with the unique catalytic activity and the great specific surface area properties of MWCNTs, a sensitive electrochemical sensor based on MWCNTs and Nafion was constructed with DPASV for the quantitative and sensitive determination of caffeine in real samples, including medicines and Cola. Compared with unmodified GCEs and Nafion-modified GCEs, the MWCNT-Nafion-modified GCE significantly enhanced the sensitivity of the determination of caffeine. The optimum pH, scan rate, accumulation potential and time were found to be 4.1, 100 mV s^{-1}, –1.0 v and 9 min, respectively. The linear calibration ranges for caffeine obtained under these conditions were 2.945 to 377.0 μM and 377.0 to 2356 μM. The detection limit was found to be 0.513 μM (based on 3σ), and the recoveries were in the range of 88.11 to 96.92% for the determination of caffeine in real samples. This technique has the added advantages of resistance against surface fouling, easy handling and low cost.

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