

The Fabrication of in Situ Triton X-100 on Multi-Walled Carbon Nanotubes Modified Gold Electrode for Sensitive Determination of Caffeine

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A new type of modified electrode based on a multi-walled carbon nanotubes (MWCNTs) was fabricated onto gold electrode (Au) and used to determine the electrochemical behavior of caffeine (CAF) in the presence of triton X-100 (TX-100). The MWCNTs/Au and TX-100...MWCNTs/Au were prepared by simple and rapid method. The fabricated TX-100...MWCNTs/Au showed excellent electrochemical catalytic activities towards CAF with bare AuE by differential pulse voltammetry (DPV) and offer anodic peak at 1.45 V. The oxidation potential of CAF at the TX-100...MWCNTs/Au shifted negatively and the anodic peak currents were greater than MWCNTs/Au and bare Au. In the optimum conditions, the voltammogram peak current of CAF for TX-100...MWCNTs/Au increased linearly and the linear range was from 0.58 to 11.50 μM . The limits of detection (S/N=3) for CAF was 0.08 μM . The recoveries of the CAF from spiked tea samples were 83.9–100.3%. The proposed method has high potential for use as a sensitive sensor for detection of CAF in beverage samples.

Keywords: Caffeine; Multi-walled carbon nanotube; Differential Pulse Voltammetry; Triton X-100

1. INTRODUCTION

Caffeine ($\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$, 1,3,7-trimethyl purine-2,6-dione) is an N-methyl of xanthine [1] which is widely contaminated in natural products and beverages such as coffee, cola, tea cocoa beans and chocolate [2, 3]. Caffeine (CAF) is one of the most widely applied drugs in the world and has many significant pharmacological effects including the stimulation of central nervous system, diuresis, and a positive effect on the cardiovascular system [4, 5]. CAF can be also used to treat bronchopulmonary dysplasia of prematurity and to prevent apnea of prematurity [6, 7]. Therefore, the detections of CAF not only have clinical research, but also can give advantageous guidance to people's health and life.

The determination of CAF is usually conducted by spectrophotometry [8–10] and chromatography [11, 12]. These techniques are the use of solvents and time consuming. Modern electrochemical methods provide powerful analytical techniques including speed, high sensitivity and simple techniques applicable to biomedical fields, and in the most areas of analytical chemistry [13]. However, electrochemical analysis of the analytes on unmodified electrode are difficult to detect because of similar oxidation potentials and poor reproducibility from the electrode fouling [14]. Therefore, the modification of electrodes is a major goal to solve these problems.

Various modified electrodes have been fabricated for the analysis of CAF by voltammetric techniques for example, single-walled carbon nanotubes modified on carbon-ceramic electrode (SWCNT/CCE) [15, 16], multi-walled carbon nanotubes modified on glassy carbon electrode (MWCNTs/GCE) [17] and using boron-doped diamond electrode [6]. Carbon nanotubes have appeared as one kinds of nanomaterial receiving considerable interest to modify surface of electrode [18–20] including single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). The multi-walled carbon nanotubes (MWCNTs) have unique properties that are especially important modifiers to promote electron transfer in electrochemical reactions, improve sensitivity and chemical inertness when used as electrode materials in electrochemical devices [21].

Surfactant could improve the property of the electrode and solution interface and could increase the detection efficiency in electrochemistry [22–26]. In situ surfactant-modified multi-walled carbon nanotube paste electrode (ISSM-CNT-PE) was fabricated as a new sensor for the individual and simultaneous determination of acetaminophen (ACOP), aspirin (ASA) and caffeine (CF) [27]. D'Souza presented incorporating platinum decorated multi-walled carbon nanotubes (PtMWCNTs) into the carbon paste electrode and TritonX-100 as a working electrode (MCPE-PtMWCNTs-TX100) for the detection of paracetamol (PA) [28]. The electrocatalytic oxidation of dopamine (DA) using the murexide and TX-100 modified carbon paste electrode (TX-100/Mu-MCPE) was developed [29]. Triton X-100 (TX-100) is nonionic surfactant which has a hydrophilic head on one side and a hydrophobic tail on another side [29]. TX-100 forms a monolayer with the hydrophobic group end directed outside the electrode [30]. There is electrostatic interaction between the analytes and the nonionic TX-100 which increases the diffusion of the analytes through surface of electrode [27].

To our knowledge, there is no report on the multi-walled carbon nanotubes modified on gold electrode (MWCNTs/Au) in the presence of TX-100 for the determination of CAF. The electrochemical properties of modified electrodes were studied by using differential pulse voltammetry (DPV). It was found that the TX-100···MWCNTs/Au showed high potential for the determination of CAF. Moreover, it showed a high level of sensitivity and excellent performance in stability and reproducibility. The proposed method was applied for the determination of CAF in tea samples without any extraction or separation steps prior to measurement, and the results were satisfactory.

2. EXPERIMENTAL

2.1 Chemicals and Reagent

All the chemicals used were of analytical grades. Caffeine ($C_8H_{10}N_4O_2$) was obtained from Sigma. Ascorbic acid ($C_6H_8O_6$), Sodium hydroxide (NaOH), sodium phosphate monobasic dehydrate

($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$), sodium phosphate dibasic (Na_2HPO_4) and sodium acetate ($\text{C}_2\text{H}_3\text{NaO}_2$) were obtained from Sigma-Aldrich (Germany). Glucose and fructose were obtained from Aldrich (Germany). Sodium chloride (NaCl) and potassium chloride (KCl) were obtained from Sigma (Germany). Xanthine was obtained from Sigma (USA). Acetic acid glacial was purchased from QRĕc (New Zealand). Potassium hexacyanoferrate (III) ($\text{K}_3\text{Fe}(\text{CN})_6$) was purchased from Sigma-Aldrich (Japan). N,N-dimethylformamide (DMF) was purchased from Sigma-Aldrich (United Kingdom). Sodium dodecyl sulfate (SDS), Triton X-100 (TX-100), cetyl trimethylammonium bromide (CTAB) were purchased from Fluka (Denmark).

Stock solution of CAF (50 mM) was prepared daily by dissolving a suitable amount of the reagent in water. A 0.1 M acetate buffer solution in the pH range of 2.5–5.0 and the mixing solutions of 0.1 M $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and 0.1 M Na_2HPO_4 at different ratios in the pH range of 6.0–7.0 were employed as the supporting electrolyte. All aqueous solutions were prepared using deionized water.

2.2 Apparatus

A potentiostat (CHI 1040A electrochemical workstation) was used for carrying out the electrochemical experiments by using a three electrode system including a Ag/AgCl (3 M NaCl) as reference electrode, a platinum wire as counter electrode and gold electrode modified with MWCNTs (MWCNTs/Au) as working electrode.

Electrochemical impedance spectroscopy (EIS) was performed with the same three-electrode configuration in an electrolyte solution of 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ containing 0.1 M KCl, in a frequency range from 1 Hz to 100 kHz with an AC probe amplitude of 50 mV.

DPV experiments for determination of CAF were carried out with the following parameters: amplitude, 0.05 V; pulse width, 0.2 s; sample width, 0.0167 s; pulse period, 0.5 s; quiet time, 2 s.

2.3 Preparation of the MWCNTs/Au

MWCNTs powder (5 mg) was dispersed in 5 mL N, N-dimethylformamide (DMF), then ultrasonicated for 30 min until a homogenous suspension was obtained. MWCNTs dispersion was studied in the range of 1 to 7 μL and carefully dropped on the top of Au. The solvent was evaporated at room temperature and MWCNTs/Au was then obtained. Finally, the MWCNTs/Au (4 μL) as modified electrode was rinsed with 0.1 M acetate buffer (pH 3.0) to remove any physically adsorbed substances by applying a potential of -1.0 V to 1.0 V with a scan rate of 50 mV/s.

Another modification provided the TX-100-MWCNTs/Au electrode was carried out by the 2×10^{-5} M TX-100 with 10 μL in buffer (pH 3.0). After that, stirring was carried out for 1 min and was then hold for 1 min before running the experiment.

2.4 Sample analysis

The tea samples were purchased from department store in Thailand. The one of tea bag was soaked in hot water (20 mL) for 30 min before analysis. After that, the tea sample was diluted using

0.1 M acetate buffer (pH 3.0) with the ratio of sample to buffer approximately 2:2. An appropriate amount of sample was added into 5 mL 0.1 M acetate buffer (pH 3.0) before analysis. For spiked sample, the three different concentrations of standard solutions (1.92, 3.70 and 5.36 μM) were spiked into tea samples before the determination using the proposed TX-100...MWCNTs/Au.

3. RESULTS AND DISCUSSION

3.1 Morphological characterization

The SEM is a powerful tool to study the surface morphology of modified electrodes. Figure 1 shows the SEM image of a MWCNTs/Au. The MWCNTs were distributed uniformly without aggregation on the surface of Au electrode. The nanotubes entangle like spaghetti and have a network-like structure proposed high surface area. Therefore, it can be confirmed that the MWCNTs dispersed on Au electrode surface.

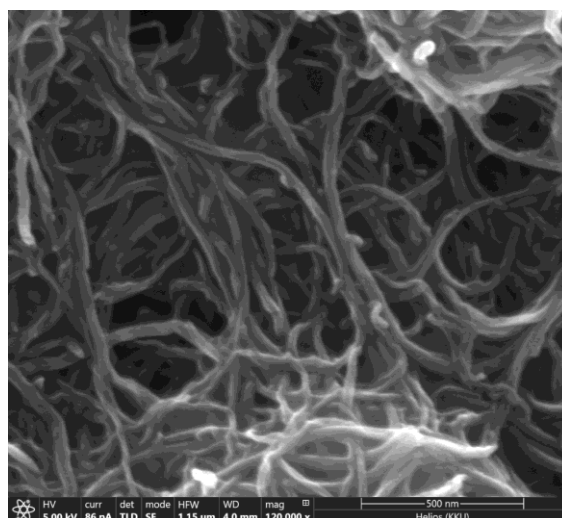


Figure 1. The SEM image of MWCNTs/Au.

3.2 Electrochemical behavior of the MWCNTs/Au

The interaction between the surface of modified electrode and the target analyte were studied using the effect of scan rate. Cyclic voltammograms of 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 M KCl solution for MWCNTs/Au were investigated with scan rate from 10 to 100 mV/s (data not shown). It can be seen that the oxidation-reduction peak currents of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ at MWCNTs/Au are increased with increasing the scan rate. Both the anodic (i_{pa}) and cathodic peak current (i_{pc}) has a linear relationship with square root of the scan rate ($v^{1/2}$) as the following Randles-Sevcik formula [31, 32]:

$$i_{pa} = 2.69 \times 10^5 n^{3/2} A C_o D_R^{1/2} v^{1/2} \quad (1)$$

where i_{pa} refers to the anodic peak current, n is the electron transfer number ($n=1$), A is the surface area of the electrode, D_R is the diffusion coefficient, C_o is the concentration of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in the 0.1 M KCl) and v is the scan rate. The linear regression equation of MWCNTs/Au is: $I_{pa}(\mu\text{A})=2.4260v^{1/2}+8.5871$ ($R^2=0.9986$) and $I_{pc}(\mu\text{A})=-2.3150v^{1/2}-9.3525$ ($R^2=0.9930$), demonstrating diffusion-controlled processes. In addition, the surface of electrodes of bare Au and MWCNTs/Au were 0.0150 cm^2 and 0.0320 cm^2 , respectively.

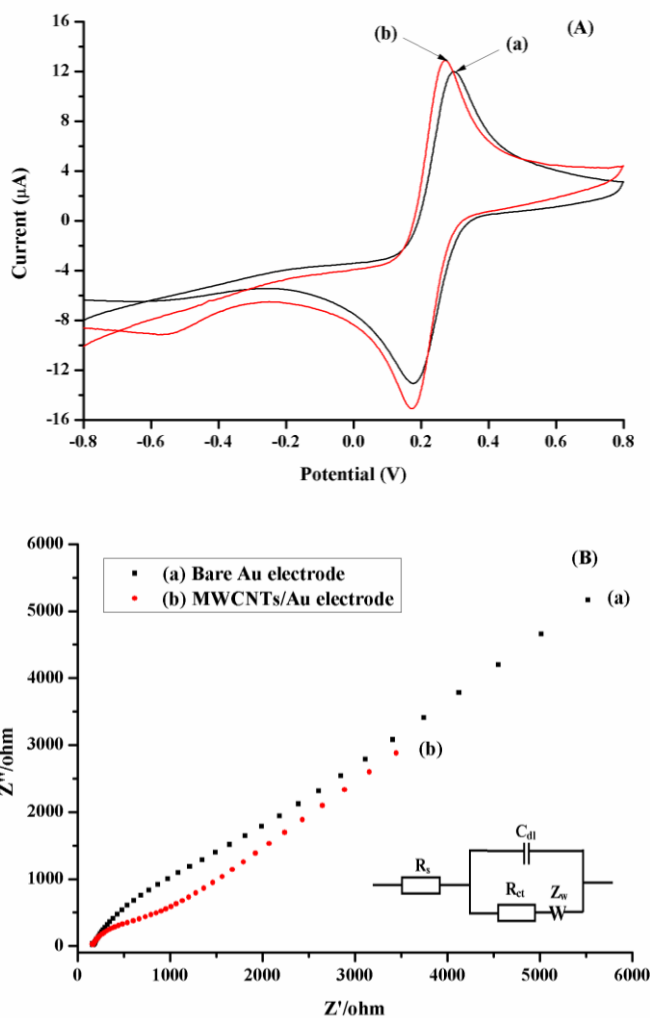


Figure 2. (A) Cyclic voltammograms of 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 M KCl solution on a bare Au (a) and a MWCNTs/Au (b). (B) Nyquist plots at the same conditions in Fig 2A. The frequency range is from 1 Hz to 100 kHz.

Cyclic voltammetry was used to characterize the MWCNTs/Au. Cyclic voltammograms of 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 M KCl on a bare Au (a) and a MWCNTs/Au (b) are shown in Figure 2 (A). The quasi-reversible one-electron redox behavior of ferricyanide ions was observed on the bare Au with a peak separation (ΔE_p) of 0.118 V at the scan rate of 50 mV/s. After being modified with MWCNTs, the peak current of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ was increased; however, the ΔE_p decreased compared

with that observed at the bare Au, indicating that the MWCNTs played a role in the increase of the electroactive surface area and provide the conducting bridges for the electron-transfer of $[\text{Fe}(\text{CN})_6]^{3-/4-}$.

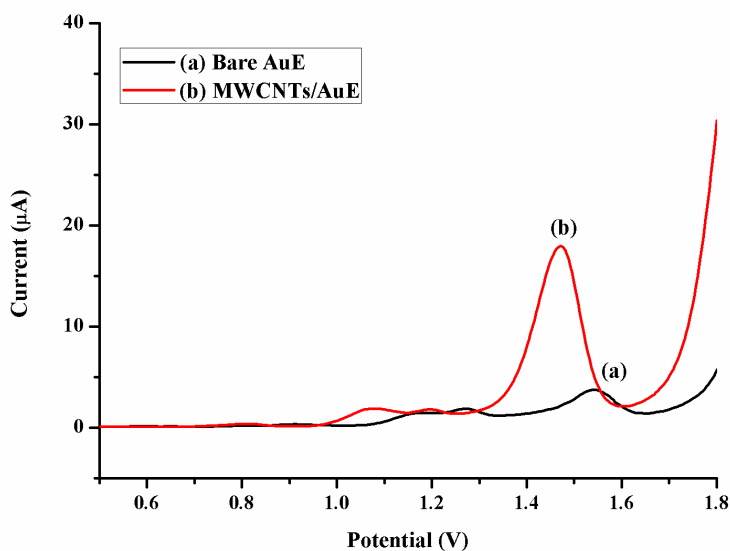


Figure 3. DPV of 3.70 μM CAF in 0.1M acetate buffer (pH 3.0) with a bare Au (a) and a MWCNTs/Au (b) with a scan rate of 50 mV/s.

Electrochemical impedance spectroscopy (EIS) is an efficient tool and used to explain the interface properties of the electrode. The semicircle part at higher frequencies in impedance spectra corresponds to the charge-transfer limited process and the diameter of the semicircle is equal to the electron transfer resistance (R_{ct}) at the electrode surface [33]. Figure 2 (B) shows the results for impedance spectrum on (a) a bare Au and (b) a MWCNTs/Au. The measurements in this work were carried out in a background solution of $\text{Fe}(\text{CN})_6^{3-/4-}$. The R_{ct} at the bare Au was estimated to be 320 Ω that has dropped to 80 Ω at the MWCNTs/Au. The decrease of R_{ct} showing that there is a much lower electron-transfer resistance on the MWCNTs/Au.

In addition, DPV was utilized to investigate the electrochemical behavior of 3.70 μM CAF in 0.1 M acetate buffer (pH 3.0) with a bare Au (a) and a MWCNTs/Au (b) as shown in Figure 3. The DPV of CAF showed a broad oxidation peak at 1.55 V on the bare Au. On the MWCNTs/Au, CAF oxidation occurred at 1.45 V with a negative shift of 0.10 V and 4 fold increased in the peak current compared with the bare Au, showing the electrocatalytic effect and high surface area of the MWCNTs.

3.3 Electrochemical behavior of CAF

3.3.1 Effect of the amount of MWCNTs

The MWCNTs dispersion was studied and related to the peak current of CAF using the DPV. The oxidation peak current of 3.70 μM CAF on the MWCNTs/Au increased markedly when the volume of MWCNTs increased from 1 to 4 μL . However, when the volume of MWCNTs exceeded 4

μL , the peak current dropped slightly in Figure 4. From the results, it can be explained that the electrical conductivity was blocked from the thicker film of MWCNTs. Therefore, the MWCNTs suspension of $4 \mu\text{L}$ was used to modify the Au.

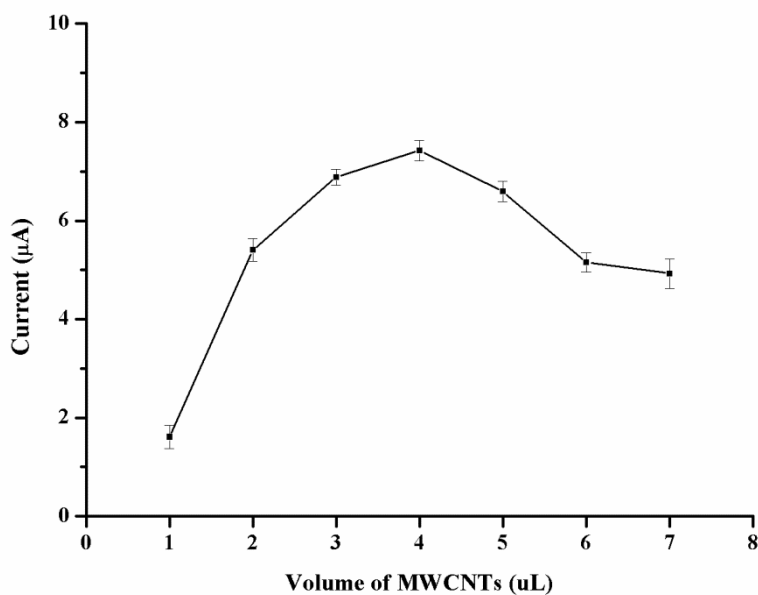


Figure 4. The relationship between the volume of MWCNTs and the oxidation peak current of $3.70 \mu\text{M}$ CAF in 0.1 M acetate buffer (pH 3.0).

3.3.2 Electrochemical behavior of CAF at modified electrodes in the presence of TX-100

The effect on the peak current of CAF was investigated using the following: cationic surfactants such as CTAB; anionic surfactants such as SDS; and non-ionic surfactants such as TX-100. In the presence of cationic and anionic surfactants, its oxidation peak disappeared and its determination was not observed. TX-100 gave the best response in terms of peak current for CAF and was employed for further studies (data not shown). The effect of concentration of TX-100 was studied in the range of 5 to $20 \mu\text{L}$ on the surface of MWCNTs/Au electrode. The results showed that the $2 \times 10^{-5} \text{ M}$ TX-100 with $10 \mu\text{L}$ concentration gave a good oxidation current toward the detection of CAF.

Figure 5 shows the electrochemical behavior of CAF at different modified electrodes (MWCNTs/Au and TX-100...MWCNTs/Au). The electrochemical oxidation of CAF at MWCNTs/Au in the presence of TX-100 shows a noticeable increase in the oxidation current (Figure 5b) compared to that without TX-100 (Figure 5a). The results clearly show that the addition of $10 \mu\text{L}$ of 10 mM TX-100 leads to the increasing of oxidation current and decreasing of the oxidation potential. The TX-100 system, the peak current of CAF increased as 1.5 fold. The schematic model illustrating the possible interaction between CAF and TX-100...MWCNTs/Au electrode is shown in Figure 6. The observed increase in peak current could be attributed to the TX-100, which has hydrophobic C-H chains and hydrophilic head groups that adsorb strongly at the surface of the electrode. The CAF could interact with C-H chains of surfactant as preconcentration step via

hydrophobic interactions and could easily reach the electrode surface. Therefore, the oxidation current of CAF increased significantly in the presence of TX-100.

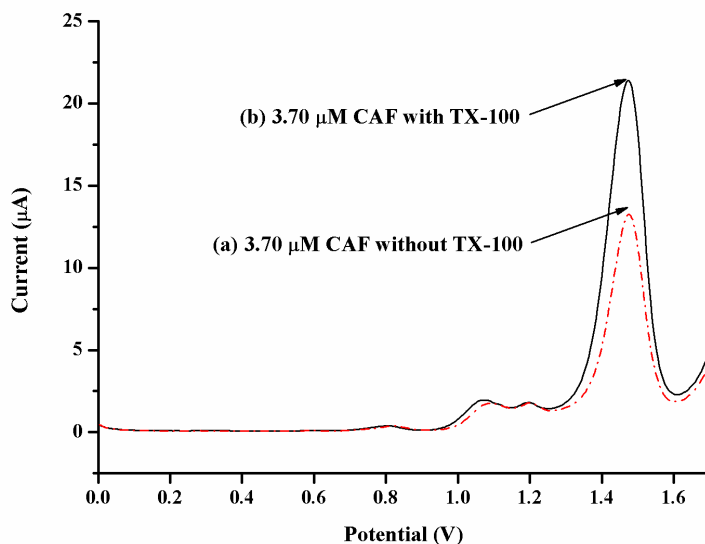


Figure 5. DPV of 3.70 μM CAF in 0.1M acetate buffer (pH 3.0) at a scan rate of 50 mV/s (a) without TX-100 and (b) with 10 μL of 10 mM TX-100. Pulse amplitude: 50 mV, step potential: 4 mV, pulse width: 0.2 s, pulse period: 0.5 s.

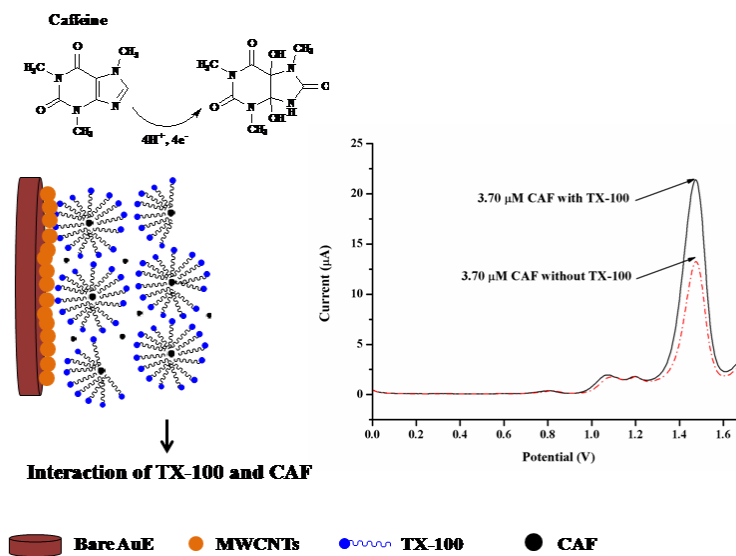


Figure 6. Schematic model illustrating interaction of CAF and TX-100...MWCNTs/Au electrode.

3.3.3 Effect of pH

The effect of pH on the electrochemical behavior of 3.70 μM CAF at the MWCNTs/Au was studied in the absence and presence of TX-100 by DPVs in the range of pH 2.5 to 5.0 in 0.1 M acetate buffer and pH 5.0-6.0 in 0.1 M PBS. Similar tendencies of pH dependence were observed for the oxidation of CAF in the absence (a) and the presence (b) of TX-100 as shown in Figure 7. In Figure

7A, the peak current of CAF initially increased and reached a maximum value at pH 3.0, and then slightly decreased with pH increasing.

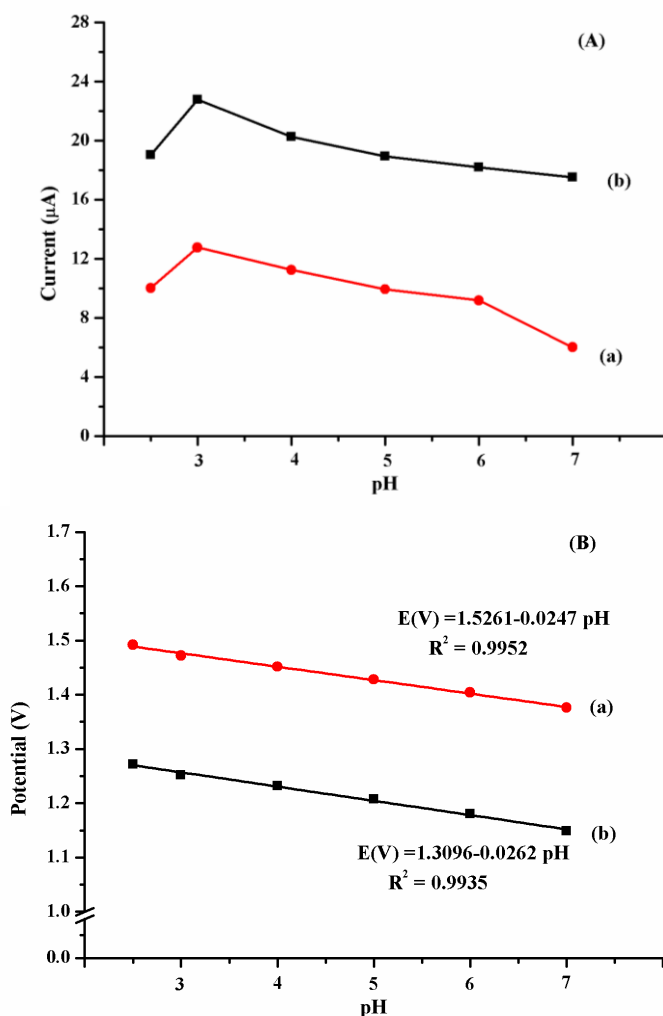


Figure 7. (A) Dependence of the anodic peak current of 3.70 μM CAF containing 3.70 μM CAF at MWCNTs/Au in the absence (a) and the presence (b) of TX-100. (B) Anodic peak potential of CAF vs. pH at MWCNTs/Au in the absence (a) and the presence (b) of TX-100.

The linear regression equations for CAF in Figure 7B were $E_{CAF}(V)=1.5261-0.0248pH$ ($R^2=0.9952$) in the absence of TX-100 (a) and $E_{CAF}(V)=1.3096-0.0262pH$ ($R^2=0.9935$) in the presence of TX-100 (b). The peak potentials of CAF shifted to more negative direction with the increasing of pH. The calculated slopes are 24.8 and 26.2 mV/pH for the system in the absence (a) and presence (b) of TX-100, respectively. According to the Nernst equation [34,35], our calculated number of protons for oxidation of caffeine is close to the theoretical value (4.00) suggesting that the electrochemical oxidation of CAF at the modified electrode are four-electron process [36]. The first step is a $2e^-$, $2H^+$ oxidation to give the substituted uric acid. The second step is followed by an immediate $2e^-$, $2H^+$ oxidation to the 4,5-diol analog of uric acid [15], which rapidly fragments; however it is not possible to

detect CAF by voltammetry. Therefore, pH 3.0 was selected as the optimized pH for determination of CAF.

3.4 The determination of CAF

The determination of CAF at TX-100...MWCNTs/Au was carried out in the potential range of 0 V to 1.6 V in 0.1 M acetate buffer (pH 3.0) by DPV. Figure 8 shows the peak current of CAF increased linearly with the increase of CAF concentration in the linear range of 0.58 μM to 11.50 μM with the regression equation of $I(\mu\text{A})=0.0019C_{\text{CAF}}+0.3336$ and the correlation coefficient was 0.9956.

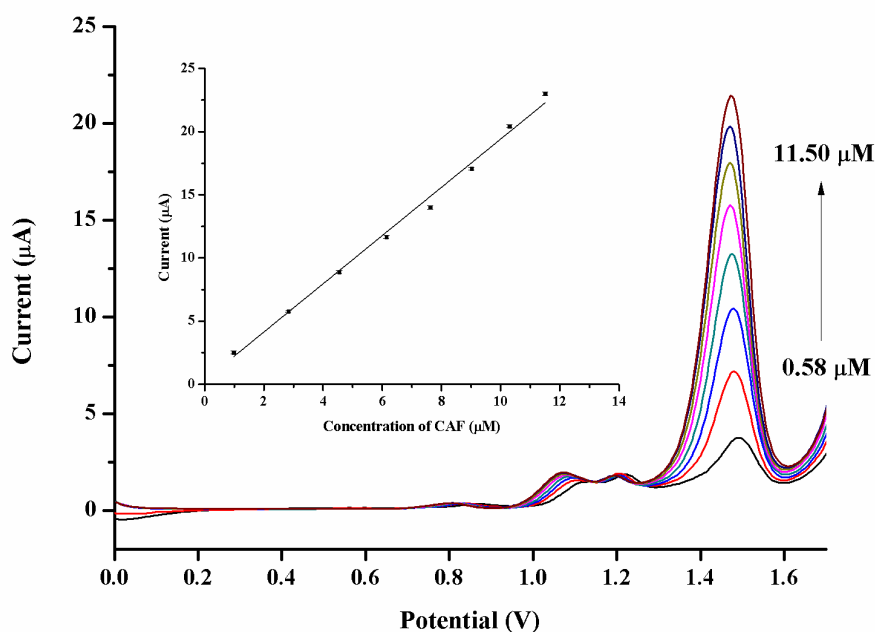


Figure 8. The DPV of CAF concentrations at TX-100...MWCNTs/Au in 0.1 M acetate buffer (pH 3.0). Inset: calibration plot obtained from DPV recording of CAF concentrations.

Table 1. Analytical performances of the proposed method for the determination of CAF with the literature methods.

Method	Linear range (μM)	Correlation coefficient (R^2)	Detection limit (μM)	References
MWCNTs/Au in the presence of TX-100	0.58-11.50	0.9956	0.08	Present work
SWCNT/CCE	0.40-300	0.9900	0.25	[16]
LMC/Nafion/GCE	1.3-230	0.9970	0.47	[38]
Poly(AHNSA)/ GCE	10-125	0.9989	0.79	[39]
Bare BDD	0.4-25.0	0.9980	0.15	[40]

The detection limit (LOD) and quantification limit (LOQ) were calculated from the equations: $LOD=3s/m$ and $LOQ=10s/m$, respectively, where s is the standard deviation of the blank signal and m is the slope of the calibration plot. The LOD and LOQ were found to be $0.08 \mu\text{M}$ and $0.58 \mu\text{M}$, respectively. In addition, the analytical performance of the TX-100-MWCNTs/Au was compared with the literature reviews in Table 1. In term of LOD, this modified electrode provides superior performance compared to the other reported methods.

3.5 Interference and stability of modified electrode

Evaluation of possible interferences to the caffeine sensor operation of the modified electrode, TX-100-MWCNTs/Au, was performed. The species tested were ascorbic acid, NaCl, fructose, glucose and xanthine, usually found in beverages together with caffeine. The effect of potential interfering species at different concentrations on the current of a solution containing $3.70 \mu\text{M}$ CAF in 0.1M acetate buffer (pH 3.0) was tested. Tolerance limit was defined as the concentrations which gave an error of $\leq 10\%$ in the determination of CAF [37]. The effect of all examined compounds, at concentrations more than CAF, on the measured analytical signal is given in Table 2. From the results, it is concluded that the method is relatively selective for the determination of CAF.

To evaluate the stability of the MWCNTs/Au and the peak currents of $3.70 \mu\text{M}$ CAF in 0.1 M acetate buffer (pH 3.0) was studied (data not shown). The stability of the modified electrode decreased about 2% of its initial response after 2 days and still kept over 90%. The MWCNTs/Au could be used for 1 month without significant loss of electrochemical signal.

Table 2. Maximum tolerable concentration of interfering species in the presence of $3.70 \mu\text{M}$ CAF on TX-100-MWCNTs/Au ($n = 3$).

Interferents	Tolerance level	Change of current (%) ^a
	(μM) ^a	CAF
Ascorbic acid	20	-2.3%
Xanthine	20	-2.5%
Glucose	40	-2.6%
Fructose	40	+2.5%
NaCl	40	-3.6%

^a For 10% error

3.6 Sample analysis

To evaluate the applicability of proposed method, the recovery of CAF was determined in tea samples by spiking the CAF standard at three different concentrations (1.92 , 3.70 and $5.36 \mu\text{M}$) into tea samples before analysis. The standard addition method was used to analyze the prepared samples. Table 3 summarizes the results of sample analysis. High recovery was obtained in the range of 83.9–100.3%. CAF was found in tea sample I as $0.094 \mu\text{M}$. It can be concluded that the proposed method has high recovery for the detection of CAF in selected beverage samples.

Table 3. Determination of CAF in tea samples for TX-100...MWCNTs/Au electrode.

Samples	CAF (n=3)		
	Spiked (μM)	Found (μM)	Recovery (%)
Tea I	-	0.094	-
	1.92	1.71	83.9 ± 1.2
	3.70	3.69	97.1 ± 9.2
	5.36	5.14	94.1 ± 1.7
Tea II	-	nd	-
	1.92	1.90	98.7 ± 3.7
	3.70	3.66	98.8 ± 2.3
	5.36	5.06	94.4 ± 1.7
Tea III	-	nd	-
	1.92	1.93	100.3 ± 1.9
	3.70	3.62	97.7 ± 5.03
	5.36	5.35	99.9 ± 3.8

nd, not detected

4. CONCLUSIONS

This work describes the fabrication of in situ triton X-100 on multi-walled carbon nanotubes modified gold electrode for sensitive determination of caffeine (CAF) using differential pulse voltammetry (DPV). The results of the peak potential and detection limit for TX-100...MWCNTs/Au to determine the CAF were ca 1.45 V and 0.08 μM , respectively. The TX-100...MWCNTs/Au provides low detection limit, wide linear concentration range, good reproducibility and high stability. The modified electrode showed good anti-interference ability as regards ascorbic acid, NaCl, fructose, glucose and xanthine. The TX-100...MWCNTs/Au can be properly applied for the detection of CAF in tea samples with good recoveries in the range of 83.9–100.3%. Furthermore, the proposed method is rapid, simple and sensitive, and can be used for the electrochemical sensing of CAF in beverage samples.

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