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Multi-walled Carbon Nanotube Modified Electrode for Sensitive Determination of an Anesthetic Drug: Tetracaine Hydrochloride

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Carboxylated multi-walled carbon nanotubes (MWNTs) were directly cast on a glassy carbon electrode (GCE) to fabricate a MWNT-modified GCE. The modified electrode exhibited good electrocatalytic activity to the electrochemical oxidation of tetracaine hydrochloride (TCH) with greatly enhanced peak currents and negative shift of oxidation peak potential. The results showed that the electrochemical reaction of TCH was an irreversible, diffusion-controlled and two-electron coupled with two-proton process. Effects of scan rate, pH of electrolyte solution, accumulation condition and the cast volume of MWNTs suspension had been discussed and optimized. Under optimized conditions, the amperometric current-time response on the MWNT-modified electrode was proportional to the TCH concentration in the range of 1.0×10^{-7}-2.0×10^{-5} mol L^{-1} with a detection limit (defined as 3Sb/m) of 3.6×10^{-8} mol L^{-1}. The proposed method was successfully applied to the determination of tetracaine hydrochloride in commercial tablets. This simple, convenient, sensitive and inexpensive method could possibly be employed in quality control and routine determination of drugs in pharmaceutical formulations.

Keywords: Tetracaine hydrochloride, Multi-walled carbon nanotubes, Modified electrode, Electrochemical determination

1. INTRODUCTION

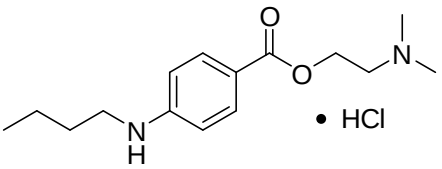
Drug analysis is undertaken during various phases of pharmaceutical development, such as formulation and stability studies, quality control and toxicology and pharmacological testing in

animals and man [1]. Therefore, the development of simple, sensitive, rapid and reliable analytical methods for the determination of drug is of great importance.

By now, the techniques based on chromatography, especially high performance liquid chromatography (HPLC), are the most common methods for the determination of drug in commercial pharmaceutical dosage form and body fluids. Although, these methods have high selectivity and sensitivity, the drawbacks that they present could not be neglected, such as expensive instruments and maintenance, intensive solvent usage, time-consuming sample pretreatment and optimization of chromatogram conditions.

Compared with chromatography, electroanalytical methods based on chemically modified electrode (CME) have distinct advantages of low cost, simplicity in operative procedure, high sensitivity, rapid response and low detection limit, so CMEs have been widely studied and extensively used for the determination of numerous electroactive components in pharmaceutical analysis [2-7]. Among many electrode modified materials, carbon nanotubes have been one of the most actively studied materials and continued to receive remarkable attention in electrochemistry [8, 9] due to their exclusive structure and extraordinary physical properties, such as high surface area, excellent electronic conductivity and good electrocatalytic activity. The carbon nanotubes modified electrode has been proved as an excellent working electrode owing to the enhancement of response signal, increased sensitivity and better reproducibility.

Tetracaine hydrochloride (TCH) is an estertype local anesthetic. This drug is very potent, long-acting agent with a low therapeutic dose, being commonly used to induce spinal anesthesia [10]. The proper chemical name for TCH is 4-(butylamino) benzoic acid 2-(dimethylamino) ethyl ester hydrochloride and the chemical structure is:



Structure of tetracaine hydrochloride

Excessive dose and abuse of local anesthetics occasionally results in sudden death of the patient. Therefore, it is very necessary to develop an accurate and quick examination technique for TCH. According to The Pharmacopoeia of People's Republic of China, TCH can be determined by neutral titration [11], however the sensitivity of method is low and the method is time consuming, for the samples have to be heated [12]. In recent years, high performance liquid chromatography (HPLC) [13-15], gas chromatograph-mass spectrometer (GC-MS) [16], chemiluminesence (CL) [17], fluorescence [12], sequential injection analysis (SIA) [18], resonance rayleigh scattering (RRS) [19], etc have been mainly used for the determination of TCH. However, as we discussed above, some of these methods have high sensitivity, but the apparatus used are always complex, the manipulations are time-consuming and their costs are higher.

TCH contains a secondary amine group which is the electrochemically active reducible center, so TCH can also be studied by electrochemical methods [20, 21], and literature survey indicated that the determination of tetracaine hydrochloride by carbon nanotubes modified electrode has not been reported.

In this work, the electrochemical behavior of TCH was investigated using a MWNT-modified glassy carbon electrode (GCE) by cyclic voltammetry (CV) and amperometry. Compared with that of a bare GCE, at the MWNT-modified GCE, a great increase in the magnitude of the oxidation peak currents occurred to TCH. The electrochemical behavior of TCH revealed that the MWNT-modified GCE exhibited strong electrocatalytic activity toward the oxidation of TCH. The effects of some experimental variables, such as the pH of electrolyte solution, influence of scan rate, accumulation condition and the cast volume of MWNTs suspension were investigated and optimized. Consequently, a simple, convenient, sensitive and inexpensive amperometric method for the determination of TCH with MWNT-modified GCE was developed. According to the best of our knowledge, this was the first application of amperometric method for the determination of TCH. Finally, the applicability of the proposed method had been investigated for the determination of TCH drug in pharmaceutical tablets. The present method could possibly be employed in quality control and routine determination of drugs in pharmaceutical formulations.

2. EXPERIMENTAL SECTION

2.1 Chemicals

Tetracaine hydrochloride and nafion were purchased from Sigma. A 1×10^{-3} mol L^{-1} standard solution of tetracaine hydrochloride was prepared by dissolving tetracaine hydrochloride in redistilled water. Tetracaine hydrochloride tablets (each tablet containing 10mg TCH) which were made by Shandong Jinan Qilu Pharmaceutical Factory (Jinan, China) was a gift from The First Affiliated Hospital of Xinxiang Medical University. The multi-wall carbon nanotubes (MWNTs) were obtained from Chengdu Organic Chemicals Co., Chinese Academy Sciences. All other chemicals were of analytical grade.

2.2 Instruments

A CHI 830 electrochemical workstation (CH Instruments) was used for cyclic voltammetry (CV) and amperometry. A regular three-electrode cell was used with a MWNT-modified GCE or a bare GCE as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, a platinum wire as the counter electrode. Buffers were purged with highly purified nitrogen for at least 10 min prior to electrochemical experiments.

FTIR spectra was taken with a Spectrum 400 spectrometer (PerkinElmer).

Scanning electron microscopy (SEM) was run with an environmental scanning electron microscope (SEM) (Quanta 200, Frequency Electronic, Inc.).

2.3 Preparation of electrode

MWNTs were pretreated with concentrated HNO_3 for 10 h to cause segmentation and carboxylation. After being washed thoroughly with water until the washing solution became neutral, the MWNTs were dispersed in nafion solution at a concentration of 1 mg mL^{-1}. 5 mg MWNTs was added into 5 mL nafion solution, then sonicated for about 30 min with an ultrasonicator (55 kHz) to get a stable and homogeneous MWNTs suspension.

Prior to modification, glassy carbon electrodes (diameter: 3 mm) were polished with 0.05 mm alumina slurry to a mirror finish and ultrasonicated successively in 1:1 HNO_3-H_2O (v/v), absolute ethanol and doubly distilled water. Typically, 10 μL of the prepared MWNTs dispersions were cast onto the surface of glass carbon electrodes. A small bottle was fit tightly over the electrode so that slovent was evaporated slowly and more uniform films were formed. The MWNT films were then dried at room temperature in air overnight. The nafion-modified GCE was prepared by the same procedure as explained above, but without MWNTs.

2.4 Analytical procedure

The MWNT-modified GCE was first activated in pH 7.4 phosphate buffer by cyclic voltammetric sweeps between 0.2 and 1.0 V until stable cyclic voltammograms were obtained, then transferred into another 10 mL of pH 7.4 phosphate buffer containing proper amount of TCH. After 3 min of open-circuit (0.0 V vs. SCE) accumulation, the cyclic voltammetry from 0.2 to 1.0 V at 100 mV s^{-1} were recorded for TCH. The oxidation peak current at 0.76 V was measured. After every measurement, the MWNT-modified GCE was retransferred into the pure phosphate buffer (pH 7.4) to remove the adsorptive substances and give a reproducible electrode surface by successive cyclic voltammetric sweeps until the voltammograms were kept unchanged.

Infrared (RAIR) spectra of primary MWNTs and concentrated acid-treated MWNTs were performed by mixing the MWNTs with KBr, respectively.

3. RESULTS AND DISCUSSION

3.1 Structure and morphology characterization

To successfully perform the deposition, the carbon nanotubes had to be uniformly dispersed in nafion solution to make sure that less aggregation happened during deposition. To address this need, MWNTs were pretreated with concentrated acid following the described procedure.

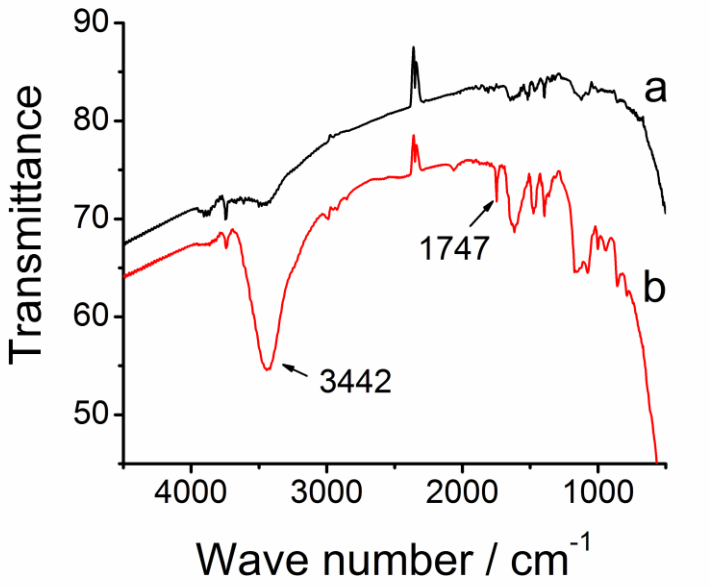


Figure 1. Mid-IR spectra of primary MWNTs (a) and concentrated acid-treated MWNTs (b)

After the oxidation process, the MWNTs were slightly shortened, which made it easier for the abundantly negative charged MWNTs to stay uniformly dispersed in the suspension for longer period of time. The mid-IR spectrum of primary MWNTs and concentrated acid-treated MWNTs were displayed in Figure 1. For the concentrated acid-treated MWNTs, two drastically enhanced absorption peaks at 3442 and 1747cm^{-1} were clearly displayed, which were typically attributed to the O-H stretching vibration and C=O vibrations of carboxylic group respectively, indicating a successful introduction of –COOH to the end or sidewalls of the MWNTs.The scanning electron micrographs of the surface structure of the bare GCE and MWNT-modified GCE at different magnifications were shown in Figure 2. There were some "cavities" or "holes" on the MWNT-modified films, the better porosity of MWNT films was also helpful for substrates or small inorganic ions in buffers to move into or out of the films, thus improving the electrocatalytic performances.

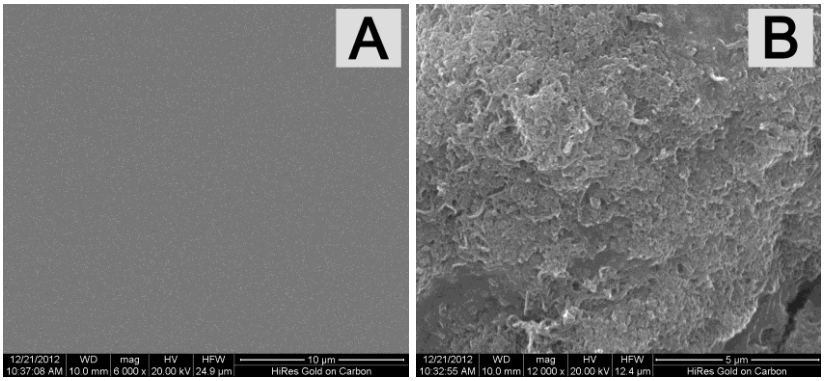


Figure 2. SEM images of (A) bare GCE and (B) MWNT-modified GCE

3.2 Improvement of the electrode quality of GCE with the modification of MWNTs

The electrochemical behavior of TCH at bare GCE, nafion-modified GCE and MWNT-modified GCE was studied by cyclic voltammetry (CV) at pH=7.4 (Figure 3). When in the absence of TCH, no obvious oxidation peak was observed at bare GCE (curve a), nafion-modified GCE (curve c) and MWNT-modified GCE (curve e) within the potential window from 0.2 to 1.0V. When in the presence of 5×10^{-6} mol L^{-1} TCH, no obvious oxidation peak could be examined at the bare GCE(curve b), only a small and broad oxidation peak occurs at about 0.80 V at the nafion-modified GCE (curve d), which was attributed to the oxidation of TCH. At the MWNT-modified GCE, a well-defined oxidation peak was observed at 0.76V and the oxidation peak current of TCH increased significantly (curve f). On the reverse scan, no corresponding reduction peak was observed indicating that the electrode process of TCH was an irreversible one. The different electrochemical behavior of TCH at three electrodes suggested that the remarkable peak current enhancement and negative shift of oxidation peak potential were undoubtedly attributed to the MWNTs, and strongly verified that MWNT-modified GCE exhibited electrocatalytic activity to the oxidation of TCH.

Based on the above study of the morphology characterization of the MWNT-modified GCE, it was highly possible that the increase of peak current and negative shift of peak potential could be attributed to the factors: (1) Since the MWNTs have good conductivity, the TCH molecules adsorbed on the surface of nanotubes would have more chance to exchange electrons with electrodes, or the rate of electron transfer from TCH to the electrode could be improved, thus demonstrating better electrocatalytic activity. (2) SEM top views of MWNT films showed there were numerous nanopores on the films, the better porosity of MWNT films was also helpful for substrates or small inorganic ions in buffers to move into or out of the films, thus improving the electrocatalytic performance. And the increased surface area could directly lead to the enhancement of the peak current. Because that the charge capacity of an electrode for a specific reaction is known to be proportional to the electroactive surface area [22].

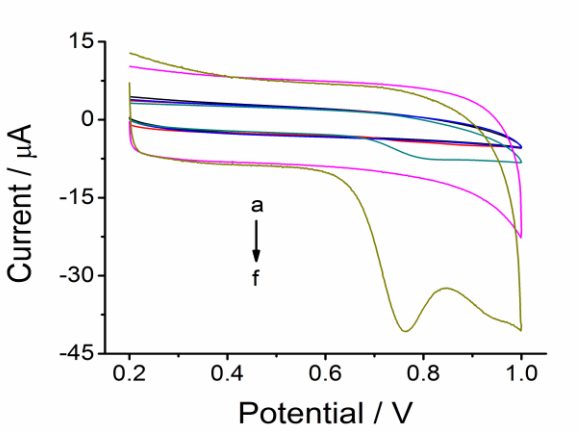


Figure 3 Cyclic voltammograms (CVs) of bare GCE, nafion-modified GCE and MWNT-modified GCE in the absence of TCH (curve a, c and e) and in the presence of 5×10^{-6} mol L^{-1} TCH (curve b, d, f) in pH 7.4 buffers. Accumulation potential: 0.0 V vs. SCE, accumulation time: 180 s, scan rate: 100 mV s^{-1}.

3.3 Optimization of the amount of modifier on the electrode

The voltammetric response of TCH was closely related to the amount of MWNTs, which was determined by the volume of MWNTs suspension casted on the GCE surface. The relationship between the volume of MWNTs suspension and the anodic peak current was examined, as shown in Figure 4. The oxidation peak current of TCH increased with the volume of MWNTs suspension dropped on the GCE surface in the range of 2 to 10 μL. However, with further increasing the volume of MWNTs suspension to 18 μL, the peak current decreased significantly. If the volume of MWNTs suspension casted on the GCE surface was too small, the amount of adsorbed TCH would also be small, and consequently the peak current was small. When the cast volume was too big, the peak current conversely showed gradual decline, probably attributed to the following reasons. Firstly, some of the MWNTs was not efficiently wired either to the electrode surface or to the solution, thus limiting the effect of MWNTs in improving the electron transport of TCH, and could not contribute to the generation of current [23]. Secondly, at higher thicknesses, the stability of the film reduced for the excessively MWNTs could be removed from the electrode surface [24]. As a result, 10μL of the 1 mg mL^{-1} MWNTs suspension was selected as the optimum volume for preparation of the modified electrode.

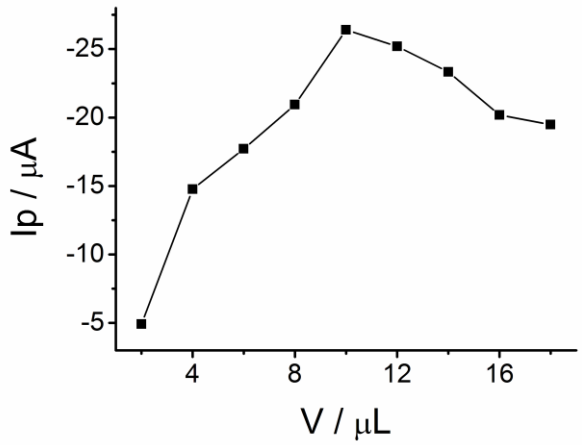


Figure 4. Influence of the amount of MWNTs suspension on the oxidation peak current of 5×10^{-6} mol L^{-1} TCH in pH 7.4 buffers. Other conditions were as in Figure 3.

3.4 Influence of accumulation conditions

It is important to fix the accumulation potential and time when adsorption studies are undertaken. Both conditions could affect the amount of analyte adsorption at the electrode, and then influence the subsequent CV responses of TCH. To improve the determining sensitivity, the effects of the accumulation potential and time on peak current response were studied by cyclic voltammetry.

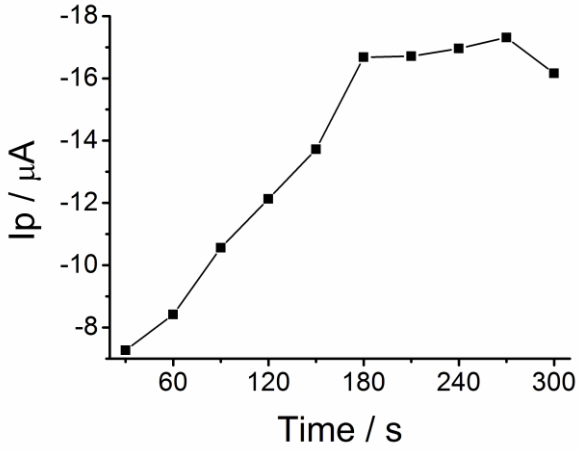


Figure 5. Variation of the oxidation peak current of 3×10^{-6} mol L^{-1} TCH in pH 7.4 buffers with accumulation time. Scan rate: 100 mV s^{-1}, accumulation potential: 0.0 V vs. SCE

The effect of accumulation time on the oxidation peak current of TCH was shown in Figure 5. The oxidation peak current increased rapidly with increasing accumulation time for the first 180s, revealing rapid and effective adsorption of TCH on the surface of the modified electrode. The plot nearly leveled off after 180s, this indicated the saturation of active sites of electrode surface by adsorption of TCH molecules. As too long an accumulation time might reduce the stability of the film, 180 s was chosen as the accumulation time.

The influence of accumulation potential on the CV behavior of TCH after 180s accumulation was investigated at different potentials from -0.4 to 0.4V, and the peak current was almost kept unchanged, implying that the accumulation potential had no influence on the oxidation peak current of TCH. Thus, an open-circuit (0.0V vs.SCE) accumulation was employed.

3.5 Influence of pH

Due to the presence of NH group on the structure of TCH, its electrochemical behaviors strongly depend on the pH of the solution. The effect of pH of the supporting electrolyte on the electrooxidation of TCH was studied over the pH range of 5.0-9.0 by cyclic voltammetry. It was found that the electrochemical behaviors of TCH at a MWNT-modified GCE electrode, including the oxidation peak current and the peak potential, showed strong dependence on pH of external buffers. The oxidation peak current gradually increased as pH increased from 5.0 to 6.5, and then showed an obvious decline as pH value continuously increased to 9.0. The pH value also strongly affected Epa of TCH, it showed that the Epa shifted toward more negative potentials as pH increased from 5.0 to 9.0, and a good linear relationship was observed between pH value and Epa. The linear regression equation for this line was expressed as Epa = 1.08 - 0.044 pH (correlation coefficient R=0.9921). As shown in the inset plot of Figure 6, the slope of 0.044 V/pH unit indicated that the number of protons and electrons involved in the oxidation of TCH was equal [24,25]. Although the oxidation peak current achieved the maximum value at pH 6.5, the oxidation peak of pH 7.0 was best-shaped. Considering the

effects of solution pH on both current and potential, as well as the actual pH of human body, a pH 7.4 PBS was used as the supporting electrolyte in all experiments.

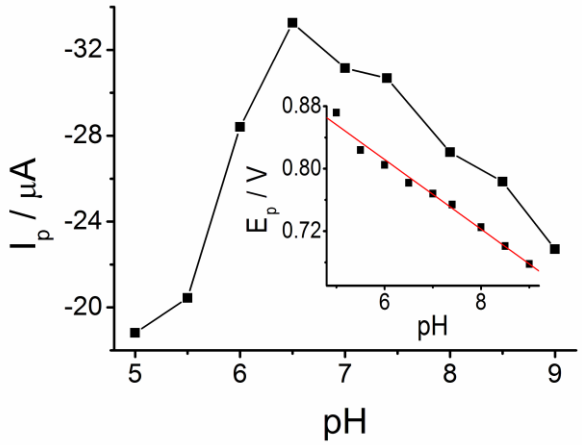


Figure 6. Influence of pH value on the oxidation peak current of TCH. Other conditions were as in Figure 3. Inset is influence of pH on the oxidation peak potential.

3.6 Influence of scan rate

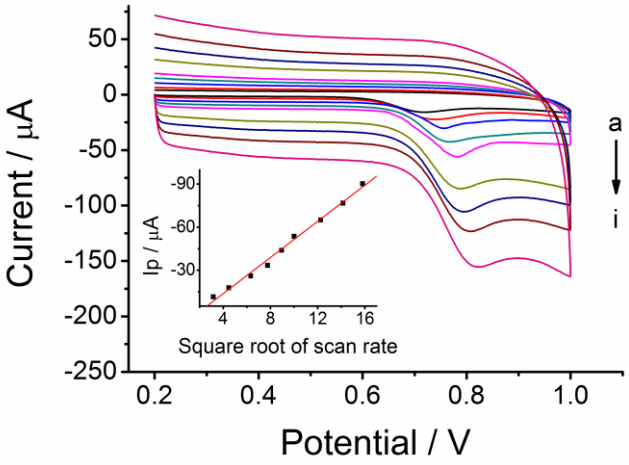


Figure 7A. Cyclic voltammograms of 1×10^{-5} mol L^{-1} TCH in pH 7.4 buffers at different scan rate (from a to i: 10, 20, 40, 60, 80, 100, 150, 200, 250 mV s^{-1}). Inset was the relationship between the oxidation peak current and the square root of scan rate. Accumulation potential: 0.0 V vs. SCE, accumulation time: 180 s.

Useful information involving electrochemical mechanism generally can be acquired from the relationship between peak current, peak potential and scan rate. Therefore, the effect of scan rate on the electrochemical response of TCH was investigated by CVs at different scan rate from 10 to 250 mV s^{-1} (Figure 7). There is a good linear relationship between peak current and the square root of scan rate (inset plot of Figure 7A). This indicated the electrochemical reaction of TCH at the MWNT-

modified GCE was a diffusion-controlled process. The peak potential shifted to less positive values on increasing scan rate, which confirmed the irreversible nature of the oxidation process. The plot of Epa versus lnv was linear having a correlation coefficient of 0.9935 and the relationship between the potential of the oxidation peak (Epa) and scan rate (v) could be expressed by the equation: Epa = 0.64 + 0.032 lnv (Figure 7B).

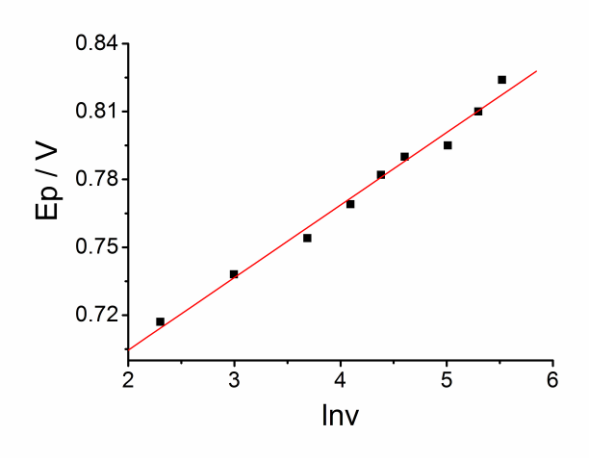


Figure 7B. The relationship between the oxidation peak potential (Ep) and the natural logarithm of scan rate (lnv).

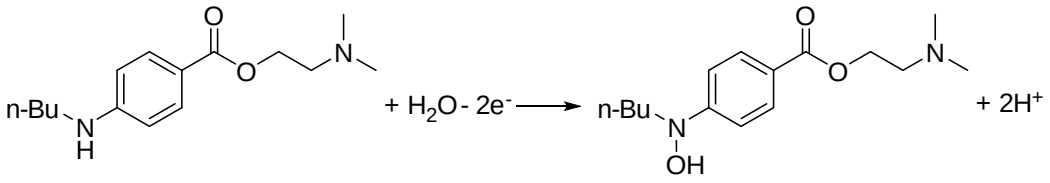
For an irreversible electrode process, according to Laviron equation [25], the oxidation peak potential (Epa) is defined by the following equation:

$$E_{pa} = E^0 + \left(\frac{RT}{\alpha n_\alpha F}\right)\ln\left(\frac{RTk^0}{\alpha n_\alpha F}\right) + \left(\frac{RT}{\alpha n_\alpha F}\right)\ln v$$

where α is the transfer coefficient, k^0 is the electrochemical rate constant, n_α is the number of the electrons transferred, v is the scan rate and E^0 is the formal potential. Other symbols have their usual meanings.

Thus, the value of αn_α can be easily calculated from the slope of Epa versus lnv. In this system, the slope was found to be 0.032, taking T=298 K and substituting the values of R and F, αn_α was calculated to be 0.80. Generally, the electron transfer coefficient (α) is about 0.5 in totally irreversible electrode process, then the n_α would be 1.6, and the number of the electron transferred should be rounded, so n_α=2. Combining the former result that the identical number of protons and electrons were transferred in the oxidation process, the oxidation reaction of TCH belonged to a two-electron and two-proton process.

Therefore, the possible oxidation reaction of TCH at MWNT-modified GCE was as the following reaction:



3.7 Calibration curve

Under the optimum conditions mentioned above, the calibration curve for TCH in 10 mL pH 7.4 phosphate buffer at MWNT-modified glass carbon electrodes was characterized by amperometry, in which the constant potential was set at 0.76V versus SCE. The amperometric current-time plot (Figure 8) showed that the successive addition of tetracaine hydrochloride standard solution (1.0×10^{-3} mol L^{-1}) caused a stepped increase in oxidation current. The MWNT-modified films responded to the addition of TCH very rapidly and reached the steady-state current within 2 s. The whole addition process was divided into three stages on the basis of the different volume of TCH standard solution added in the electrolytic cell: in the first stage 1μL was added every time, 3μL in the second stage and 30μL in the last stage. The lower-left inset plot of Figure 8 was the amperometric current-time plot of the first stage with magnification.

It was found that the oxidation peak current was linearly proportional to the concentration of TCH in the range of 1.0×10^{-7}-2.0×10^{-5} mol L^{-1} (top-right inset plot of Figure 8). The linear regression equation could be expressed as: Ip = -6.58×10^{-7} + 4.87 c (R =0.9996, c in 10^{-6}mol L^{-1}, Ip in μA). The detection limits, which defined as 3Sb/m (where Sb is the standard deviation of the blank signal (n = 8) and m is the slope of the calibration curve)[26], was found to be 3.6×10^{-8} mol L^{-1}.

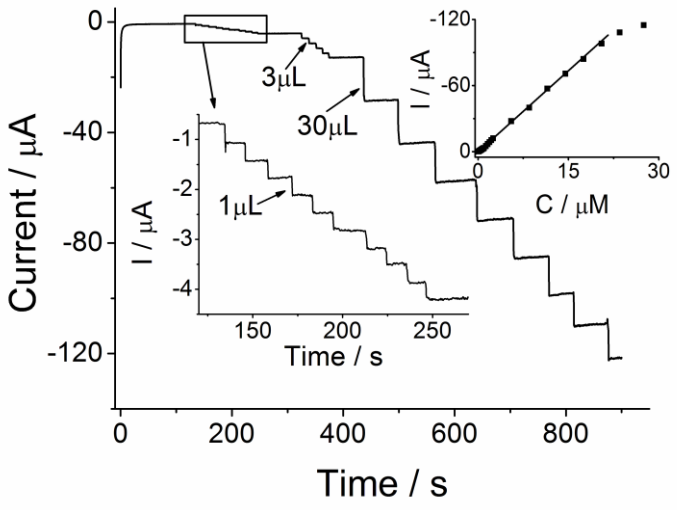


Figure 8. Amperometric responses for MWNT-modified GCE at the constant potential of 0.76 V vs. SCE in pH 7.4 buffers with injecting 1.0×10^{-3} mol L^{-1} tetracaine hydrochloride standard solutions.

3.8 Stability, repeatability

For validation of the proposed method, various parameters, such as stability of the electrode, repeatability were evaluated in the determination of TCH. The stability of MWNT-modified GCE was tested by recording the amperometry response of 5×10^{-6} mol L^{-1} TCH on the modified electrode stored in the air every several hours. The results indicated that the response of the MWNT-modified GCE to TCH showed slightly decreased after 7 days (10-15%), demonstrating the good stability of the modified electrode. To ascertain the repeatability of the method, 5×10^{-6} mol L^{-1} TCH and the same electrode (renewed every time) were used every several hours within a day. The relative standard deviation (RSD) of 5.7% for 10 times parallel detections suggested good repeatability of the modified GCE.

3.9 Real sample analysis

In order to demonstrate the measurement of TCH in pharmaceutical preparations, we examined this ability in the amperometric determination of TCH in commercial tablets (nominal each tablet contains 10 mg TCH). After grinding the tablets into powder, the tetracaine hydrochloride sample solution was made by dissolving 30.0 mg powder in 50 mL redistilled water.

Table 1. TCH analysis in commercial tablets by proposed procedures

Sample solution	Spiked /μM	Detected (Mean ± S.D.) /μM	Recovery (Mean ± S.D.), %
1	1.00	0.892 ± 0.09	97.8 ± 2.6
2	2.00	2.10 ± 0.12	103.5 ± 3.2
3	4.00	4.09 ± 0.08	101.7 ± 2.5

Then, 5 μL, 10 μL and 20 μL of the sample solution were added into an electrochemical cell containing 10 mL pH 7.4 buffer, and the amperometry response were recorded under the optimized experimental conditions. The spiked samples were prepared at different levels, and the detection results of three sample solutions obtained were listed in Table 1. The results showed good quantitative recoveries. This implied successful applicability of this method for real sample analysis.

4. CONCLUSIONS

In this work, multi-walled carbon nanotube glass carbon electrodes had been successfully used for the electrocatalytic oxidation of TCH in phosphate buffer solution (pH=7.4). MWNTs showed electrocatalytic action for the oxidation of TCH, characterized by the enhancement of the peak current, which was probably due to the high specific surface area, subtle electronic properties and strong adsorptive ability of MWNTs. As a result, a very sensitive and simple electrochemical method was

developed for TCH determination. This method had been successfully used to determine TCH in commercial tablets. The satisfactory recovery and low relative standard deviation data reflected the good accuracy and precision of the proposed method. This modified electrode could provide satisfactory results for determination of TCH without the necessity for sample pretreatment or any time-consuming extraction or separation steps prior to the analysis.

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