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Electrochemistry and voltammetry of procaine using a carbon nanotube film coated electrode

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Abstract

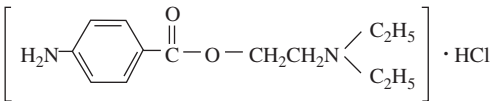
A new rapid, convenient and sensitive electrochemical method is described for the determination of procaine in pharmaceutical preparations, based on the unique properties of a multi-wall carbon nanotube (MWNT) thin film. The electrochemical behavior of procaine at the MWNT film-coated glassy carbon electrode (GCE) was investigated in detail, showing that the MWNT-coated GCE exhibits electrocatalytic activity to the oxidation of procaine because of the significant peak current enhancement and the lowering of oxidation overpotential. Furthermore, the mechanism for the oxidation of procaine at the MWNT-coated GCE was also studied. Finally, various experimental parameters such as solution pH value, the amount of MWNT, accumulation conditions and scan rate were optimized for the determination of procaine, and a new method with detection limit of 2×10^{-7} mol/L was developed for procaine determination. This newly proposed method was successfully demonstrated with procaine hydrochloride injection.

Keywords: Procaine; Electrochemical determination; Carbon nanotube-modified electrode

1. Introduction

The drug analysis, an important branch of analytical chemistry, has extensive impact on public health. Therefore, the establishment of simple, rapid, sensitive and reliable method for the determination of active ingredient is welcomed and necessary.

Procaine was first synthesized in 1905, and was the first injectable man-made local anesthetic. It was introduced into medical use by surgeon Heinrich Braun. The proper chemical name for procaine hydrochloride is 2-diethylaminoethyl 4-aminobenzoate hydrochloride and the chemical structure is:



To date, numerous methods have been reported for the determination of procaine and its salts in pharmaceutical preparations or biological samples. The present United States Pharmacopoeia method is an extration-spectrophotometric method based on the absorbance of procaine hydrochloride at 280 nm [1]. The Chinese Pharmacopoeia method is dead-stop titration [2]. Additionally, many other methods including spectrophotometry [3–5], high-performance liquid chromatography [6,7], gas chromatography [8], fluorimetry [9], ion-pairing flow injection analysis with piezoelectric detection [10], and chemiluminescence [11], were also reported.

Recently, much effort has been made to the electrochemical determination of procaine, since electroanalytical method possesses many advantages such as high sensitivity, rapid response and extreme simplicity. For instance, a pumice-modified glassy carbon electrode [12] and a modified polymetric electrode [13] were employed to detect procaine, respectively. Wang and coworkers [14] reported a method of amperometric detection using liquid chromatography with a metal-oxide dispersed glassy carbon electrode. Ion-selective-

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electrode (ISE) was also exploited to detect procaine [15], and unfortunately, its detection limit is very poor (just 10^{-5} mol/L). Otherwise, polarography [16,17], coulometric titration [18] and potentiometric titration [19] were also reported. However, voltammetric determination of procaine using a carbon nanotube-modified electrode has not been reported.

The objective of the current work is to develop a convenient and sensitive method for the determination of procaine, based on the unusual properties of carbon nanotubes such as strong adsorptive ability, huge specific area, subtle electronic properties as well as excellent electrocatalytic activity. The electrochemical behavior of procaine on the multi-wall carbon nanotube (MWNT)-coated glassy carbon electrode (GCE) strongly revealed that the electrochemical oxidation of procaine was facilitated and the determination sensitivity of procaine was significantly improved. At the MWNT-coated GCE, the remarkable peak current enhancement and negative shift of oxidation peak potential occurred to procaine, compared with that of a bare GCE. Consequently, a voltammetric method based on the carbon nanotube-modified electrode was first developed for the determination of procaine. This newly proposed method possesses following advantages such as high sensitivity, rapid response, low cost and simplicity.

2. Experimental

2.1. Reagents

A 1×10^{-3} mol/L stock solution of procaine hydrochloride (Sigma) was prepared in redistilled water and then stored in the dark at 0 °C. Standard solutions of procaine were prepared by dilution of the stock solution with redistilled water. All reagents were of analytical grade and used directly without purification. Redistilled water was used throughout.

The multi wall carbon nanotube (MWNT) with an average diameter of 30 nm was obtained from Chengdu Organic Chemicals Co., Chinese Academy Sciences, and then refluxed in concentrated HNO_3 for 10 h to cause segmentation, purification and carboxylation [20].

2.2. Apparatus

All the electrochemical measurements were carried out with a CHI 660A Electrochemical Workstation (CH Instruments, Austin, USA). A conventional three-electrode system, including a MWNT-coated GC working electrode, a saturated calomel reference electrode (SCE) and a Pt wire counter electrode, was employed.

2.3. Fabrication of MWNT-coated GCE

In our previous work [21], it was found that insoluble carbon nanotubes can be dispersed into water in the presence of a kind of surfactant — dihexadecyl hydrogen phosphate (DHP), to form a stable and well-distributed suspension. In the present work, an amount of 5 mg MWNT and 5 mg DHP were added into 5 mL of redistilled water, and then sonicated for about 30 min with an ultrasonicator (55 kHz) to get a stable and homogeneous MWNT–DHP suspension. Prior to modification, the GCE was polished successively with alumina pastes of 0.5 and 0.1 μm to a mirror finish, rinsed and sonicated (3 min) in redistilled water. Finally, the GCE was coated with 7.5 μL of the resulting MWNT–DHP suspension and allowed to evaporate water at room temperature in air. The DHP-modified GCE was prepared by the same procedure as explained above, but without MWNT.

2.4. Analytical procedure

The MWNT-coated GCE was first activated in pH 7.0 phosphate buffer by cyclic voltammetric sweeps between 0.2 and 1.0 V until stable cyclic voltammograms were obtained, and then transferred into another 10 mL of pH 7.0 phosphate buffer containing a certain concentration of procaine. After 4 min of open-circuit accumulation, the linear sweep voltammograms from 0.3 to 0.9 V at 100 mV/s were recorded for procaine. The oxidation peak current at 0.75 V was measured. After every measurement, the MWNT-modified GCE was retransferred into the pure phosphate buffer (pH 7.0) to remove the adsorptive substances and give a reproducible electrode surface by successive cyclic voltammetric sweeps until the voltammograms were kept unchanged.

3. Results and discussion

3.1. Electrochemical behavior of procaine

The electrochemical behavior of procaine on the MWNT-coated GCE was examined by cyclic voltammetry (CV). Fig. 1 shows the cyclic voltammograms of a MWNT-modified GCE in phosphate buffer at pH 7.0 in the absence and presence of procaine. Within the potential window from 0.2 to 1.0 V, no redox peak was observed (dotted line). However, in the case of 2×10^{-5} mol/L procaine, a well-defined oxidation peak with very high current is observed at 0.75 V (solid line). Nevertheless, the oxidation peak current of procaine shows a remarkable decrease during the successive cyclic voltammetric sweeps. After the second sweep, the peak current decreases slightly and finally remains unchanged. This phenomenon may be caused by the fact that the adsorption of procaine or its oxidative product occurs at the MWNT-modified GCE surface. Thus, the oxidation peak current in the first anodic sweep was recorded for procaine analysis in the following studies. Fig. 1 also shows that there is no corresponding reduction peak during the reverse potential scan from 1.0 to 0.2 V.