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Electrochemical oxidation behavior of nitrite on a chitosan-carboxylated multiwall carbon nanotube modified electrode

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Abstract

A novel chitosan-carboxylated multiwall carbon nanotube modified glassy carbon electrode (MC/GCE) was developed to investigate the oxidation behavior of nitrite using cyclic voltammetry and differential pulse voltammetry modes. The electrochemical mechanism of the MC/GCE towards nitrite was discussed. The MC/GCE exhibited fast response towards nitrite with a detection limit of 1×10^{-7} mol l^{-1} and a linear range of 5×10^{-7}–1×10^{-4} mol l^{-1}. The possible interference from several common ions was tested. The proposed method was successfully applied in the detection of nitrite in real samples.

Keywords: Chitosan; Nitrite; Multiwall carbon nanotube; Electrochemistry; Cyclic voltammetry

1. Introduction

Nitrite is ubiquitous within environment, food and physiological systems as it is commonly used as an additive in some foods [1] and as a corrosion inhibitor [2]. The nitrite ions can interact with amines to form carcinogenic nitrosamines [3], so as its potential toxicity, its determination is then important for environmental reason and for public health. As a result, many methods for nitrite determination have been developed in recent years, such as spectroscopic analysis [4–7], chromatography [8,9], etc., and a review on these techniques that have been focused on environmental nitrite analysis has been made by Davis and co-worker [10]. However, the operation of the spectrophotometric methods requires close control of pH and temperature during the diazotization step and a relatively long coupling time. In contrast, owing to the rapid response and simple use, electrochemical detection techniques are favorable for nitrite determination [11–13]. For example, chitin modified electrode have been used to determine NO_2^- [11], but chitin was inhomogeneous in carbon paste, which affected the repeatability of determination. Some methods that use mercury electrodes may have higher sensitivity, but the environmental pollution they cause cannot be neglected [14–16].

Although nitrite is electroactive at carbon electrodes, its oxidation requires undesirably high overvoltages [17]. The voltammetric determination of nitrite is, therefore, prone to suffer interference from other readily oxidizable compounds. In order to improve the selectivity of the determination of nitrite, the operating potentials should be efficiently lowered. The purpose can be achieved by modifying suitable electrocatalyst on the surface of carbon electrodes. While, those methods that used chemically modified electrodes also have some limitation [18,19], such as lower sensitivity and modified film is

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not stable, beside some have not been applied in samples [20,21].

Chitosan, which is derived from chitin (a naturally occurring polysaccharide found in insects, arthropods and crustaceans) by de-acetylation, has excellent biological compatibility, and has been extensively used as modifier due to its amino groups and hydroxy groups [22–24]. Besides, chitosan is a natural polymer, using it as a dispersant is the requirement of environment of protection. Carbon nanotubes (CNT) are molecular scale wires with high electrical conductivity, high chemical stability, and extremely high mechanical strength and modulus. The active site being the end of the tubes make CNT hold excellent properties [25,26], so CNT modified solid electrode has attracted much attention. But the insolubility of it in most solvents restrained its application in electroanalysis [27,28].

In this paper, a novel chitosan-carboxylated multiwall carbon nanotube (MWCNT) modifier was obtained by putting carboxylated MWCNT into chitosan solution (0.5%), achieving a chitosan-carboxylated MWCNT modified glassy carbon electrode (MC/GCE). The MC/GCE was used for the detection of nitrite, excellent properties of this MC/GCE towards the electrochemical oxidation of nitrite were observed.

2. Experimental

2.1. Apparatus

All the electrochemical measurements were carried out with a bioanalytical system CV-50W electrochemical analyzer. The three-electrode system consisted of a modified GCE, a saturated calomel reference electrode, and a platinum auxiliary electrode. All potentials were referred to the SCE.

2.2. Reagents

A 10^{-2} mol l^{-1} stock solution of nitrite was prepared by direct dissolution of sodium nitrite in water and store in the dark. The chitosan solution (0.5%) was prepared by dissolving 0.05 g chitosan (Sigma Corp.) in 10 ml acetic acid (2 mol l^{-1}) [29]. The MWCNT used in this work (obtained from the Institute of Nanometer, China Central Normal University) were synthesized by the catalytic pyrolysis. And purification begins with a 7 h reflux under the condition of magnetic heat stirring in 2 mol l^{-1} nitric acid (typically 1 l of acid per 2 g of raw material), then ultrasonic dispersing for 1 h in thick muriatic acid, washing with deionized water until a neutral solution is gained [30]. After these processes, the black solution is filtrated leaving a black sediment at the bottom of the filler. Dry and rubbing the sediment, thus carboxylated MWCNT is achieved. IR spectra showed that there is carboxyl in the structure of puried MWCNT.

2.3. Preparation for MWCNT–chitosan modified electrode

Putting 0.5 mg carboxylated MWCNT into 5 ml chitosan solution (0.5%), ultrasonic agitation for a few minutes to give 0.1 mg ml^{-1} black suspension. Before being modified, the GCE was polished with 0.3 and 0.05 μm aluminum slurry, rinsed thoroughly with redistilled water, then ultrasonically rinsed with alcohol, redistilled water for 1 min each, and dried under an infrared lamp. After the GCE was cooled, it was smeared evenly with 6 μL of a MWCNT–chitosan (0.5%) solution by a micro-syringe, and then dried under an infrared lamp for 10 min. After cooling, the MC/GCE could be used.

2.4. Experimental procedures

A Britton-Robinson (B-R) buffer solution (pH 3.5) was used as the supporting electrolyte for the determination of nitrite. Before and after every measurement, the MC/GCE was activated by the successive cyclic voltammetric sweeps between 0.45 and 1.00 V at 100 mV s^{-1} in the blank B-R buffer solution (pH 3.5).

3. Results and discussion

3.1. Electroxidation behavior of nitrite on the MC/GCE

In B-R buffer solution (pH 3.5) containing 1×10^{-5} mol l^{-1} nitrite, the cyclic voltammograms of nitrite at the chitosan–MWCNT modified GCE and bare GCE were shown in Fig. 1. At the bare GCE, the CV of nitrite demonstrated an irreversible wave with anodic peak potential (Ep_a) at 0.884 V. While at the MC/GCE, the anodic peak potential shifted negatively to 0.808 V

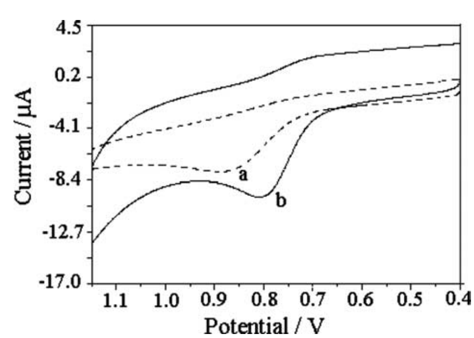

Fig. 1. Cyclic voltammograms of 1×10^{-5} mol l^{-1} NO_2^- at bare electrode (a) and MC/GCE (b), in a B-R buffer solution (pH 3.5). Scan rate, 100 mV s^{-1}.