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Electrochemical behaviors and determination of isoniazid at ordered mesoporous carbon modified electrode

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ABSTRACT

In this work, an electrochemical sensor based on ordered mesoporous carbon (OMC) for the amperometric detection of isoniazid was developed. OMC was dispersed in a solution of Nafion, and the suspension was modified onto the surface of glassy carbon (GC) electrode. Cyclic voltammetry and amperometry were used to investigate the electrochemical behaviors of isoniazid on Nafion-OMC modified electrode (Nafion-OMC/GC). The results indicate that OMC can facilitate the electrochemical oxidation of isoniazid with a great decrease of overpotential in pH 7.0 phosphate buffer solution. The proposed biosensor provides excellent performance towards the determination of isoniazid with a high sensitivity of 0.031 μA/μM, a low detection limit of 8.4×10^{-8} M and wide linear range from 1.0×10^{-7} M to 3.7×10^{-4} M at +0.20 V vs. Ag/AgCl. The method was successfully applied to the determination of isoniazid tablets with satisfying results. All the results suggest that Nafion-OMC/GC electrode is a potential candidate for a stable and efficient electrochemical sensor to detect isoniazid.

1. Introduction

Isoniazid (INZ) is one of the most effective tuberculostatic agents against mycobacterium strains, which is useful to prevent the development of clinical tuberculosis. Several mechanisms of drug action have been proposed that isoniazid may have bacteriostatic or bacteriocidal action to interfere the metabolism of bacterial proteins, nucleic acids, carbohydrates and lipids [1], which depends on the concentration of the drug. But the poisoning accidents, even death, have happened occasionally owing to overdosage in isoniazid. Therefore, the control of the isoniazid dose for sufferers is very important in clinical chemistry, which makes it necessary to develop a rapid and effective method for the detection of isoniazid in pharmaceutical formulations.

Many analytical methods have been developed for the determination of isoniazid, including titrimetry [2,3], spectrophotometry [4,5], high performance liquid chromatography (HPLC) [6,7], chemiluminescence [8], fluorimetry [9], capillary electrophoresis [10] and electroanalytical methods [11–13]. Among these approaches, electroanalytical techniques are of particular advantage because of their practicality, simplicity, low-cost, good sensitivity, precision and rapidity for real-time detection. In electroanalytical area, the concept of chemically modified electrodes has been developed gradually instead of conventional electrodes to improve the reactivity, sensitivity and selectivity of the electrode reactions in many applications. Various types of modified electrodes have also been used to detect isoniazid. Gao et al. reported the electrocatalytic oxidation of isoniazid at (ferrocenylmethyl) trimethylammonium [(FcM)TMA] modified platinum electrode by cyclic voltammetry [14]. A multi-walled carbon nanotube paste electrode (MWCPE) has been developed as an electrochemical sensor to monitor the oxidation of isoniazid by cyclic and differential pulse voltammetry [15]. Amidosulfonic acid has been electropolymerized onto the surface of GC electrode by Yang et al, the chemically modified electrode showed distinct electrocatalytic effect on the oxidation of isoniazid, and was successfully applied to the direct determination of isoniazid in pharmaceutical formulations [16]. A screen-printed carbon electrode (SPCE) modified with poly-L-histidine was employed to determinate isoniazid in human urine samples successfully [17]. Jena and Raj developed a silicate network decorated with Au nanoparticles for the amperometric sensing of isoniazid, the nanoparticles efficiently catalyzed the oxidation of isoniazid in PBS (pH 9.2) with high sensitivity [18]. But in most cases, the oxidation of isoniazid at aforementioned modified electrodes always required a high overpotential, and acidic or alkaline supporting electrolyte, which brought great inconvenience to the analytical procedure and was unsuitable for the detection on site. Hence, it is required imminently to find a sensitive modified electrode which could decrease the overpotential of isoniazid oxidation and electrochemically detect isoniazid in neutral media simultaneously.

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Carbon materials possess many suitable properties for the design of modified electrodes used in electroanalytical chemistry. There are several available microstructures of carbon materials, such as graphite, carbon fibers (CNF) [19], carbon nanotubes (CNTs) [20], graphene, etc. Ordered mesoporous carbon (OMC) is a kind of novel advanced carbon material. Since the discovery of OMC in 1999 [21], increasing attention has been focused on the fundamental research and applications of OMC owing to their extremely uniform pore structure, large pore volume, high specific surface area, tunable pore size distribution and chemical inertness. Largely due to the ability of fast electron transfer, avoiding surface fouling and excellent electrocatalytic activity, OMC has been widely used in sensing [22–24], bioreactor construction [25], energy storage [26], electrocatalytic application [27–30], etc.. The improved electrochemical reactivity of OMC suggests that it will be a promising alternative candidate for electrode materials.In our work, an OMC-modified GC electrode was successfully fabricated by coating Nafion-OMC onto GC electrode, and the Nafion-ONC/GC electrode was employed to investigate the electrochemical behaviors and detect isoniazid by amperometry. The modified electrode can promote the electrochemical oxidation of isoniazid with an obvious decrease in the overvoltage in neutral media (pH 7.0). Then the modified electrode was successfully applied to the amperometric determination of isoniazid in standard solution and tablets.

2. Experiment

2.1. Reagents

Isoniazid (analytical purity, Guangfu Fine Chemical Research Institute, Tianjin) was used without further purification. A stock solution of isoniazid was prepared with double-distilled water and kept in a refrigerator at about 4 °C. Isoniazid tablets (100 mg/tablet) were taken from Jinhua Pharmaceutical Co., Ltd., Chengdu. Pluronic P123 (non-ionic triblock copolymer, $EO_{20}PO_{70}EO_{20}$) and Nafion (5 wt%) were purchased from Sigma–Aldrich. All the chemicals used were analytical reagent grade. Aqueous solutions were prepared with doubly distilled water and stored in the shade. The 0.1 M phosphate buffer solution (PBS), which was made up from K_2HPO_4 and KH_2PO_4 was employed as a supporting electrolyte, and adjusting the pH with H_3PO_4 or KOH.

2.2. Apparatus

All the electrochemical experiences were performed on a CHI 660C electrochemical workstation (CH Instruments, Shanghai Chenhua Instrument Corporation, China) connected to a personal computer. A three-electrode configuration was employed, consisting of a GC electrode (3 mm diameter) or Nafion-OMC/GC electrode serving as the working electrode, whereas an Ag/AgCl (in saturated KCl solution) as the reference electrode and a platinum wire served as the counter electrode, respectively. All potentials in this paper were measured and reported vs. Ag/AgCl electrode. The sample solutions were purged with high-purity nitrogen gas for at least 15 min at the beginning of the experiments to remove oxygen. XRD patterns were obtained on an X-ray D/max-2200vpc (Rigaku Corporation, Japan) instrument operated at 40 kV and 20 mA and using Cu Kα radiation (k = 0.15406 nm). TEM images were obtained using a JEM-2100F transmission electron microscope (JEOL, Japan) operating at 200 kV. All measurements were carried out at room temperature.

2.3. Preparation of ordered mesoporous carbons

The mesoporous Santa Barbara Amorphous No. 15 (SBA-15) were synthesized using Pluronic P123 as the surfactant and tetraethyl orthosilicate (TEOS) as the silica source [31]. OMC was synthesized using SBA-15 as a template, and sucrose was used as a carbon source according to the method reported by Ryoo and co-workers [32]. In a typical synthesis of mesoporous carbons, 1 g of mesoporous silica material (SBA-15) was added to a solution obtained by dissolving 1.25 g of sucrose and 0.14 g of H_2SO_4 in 5 g of water, and keeping the mixture in an oven for 6 h at 100 °C. Subsequently, the oven temperature was raised to 160 °C for another 6 h. To obtain fully polymerized and carbonized sucrose inside the pores of the silica template, the same amount of sucrose, H_2SO_4 and water were added to the pretreated sample, and the mixture was again subjected to the thermal treatment described above. After the second sucrose addition, the template–polymer composites were then pyrolyzed in a nitrogen flow at 900 °C and kept under these conditions for 6 h to carbonize the polymer. The mesoporous carbons were obtained after dissolution of the silica framework in 5 wt% hydrofluoric acid, by filtration, washed several times with ethanol, and dried.

2.4. Preparation of Nafion-OMC/GC electrode

GC electrodes were polished carefully before each experiment with 1, 0.3 and 0.05 m alumina powder, respectively, rinsed thoroughly with doubly distilled water and absolute ethanol between each polishing step. The cleaned electrode was dried with high-purity nitrogen steam. 2.0 mg of the OMC was dispersed into a mixture of 0.1 mL (5 wt%) Nafion and 0.9 mL distilled water with the aid of ultrasonic oscillation to give a 2 mg mL^{-1} black suspension. After dropping 5.0 μL of the suspension onto the electrode surface, the electrode was dried in air, a Nafion-OMC modified glassy carbon electrode was obtained (denoted as Nafion-OMC/GC).

2.5. Preparation of tablet sample

Ten tablets, each containing 100 mg of isoniazid, were finely powdered respectively. The white powder was accurately weighed to 1.0 g and dissolved into 10 mL distilled water. The mixture was shaken for 30 min and filtered into a 50 mL volumetric flask. The residue was several times washed with distilled water and solution was diluted to the mark.

3. Results and discussion

3.1. Characterization of OMC

The prepared OMC has a BET surface area of 903 $m^2 g^{-1}$ and a total pore volume of 1.07 $cm^3 g^{-1}$. The typical TEM images in Fig. 1 provide direct visualization of the morphology and internal mesostructure of OMC viewed from the [1 0 0] (A) and [0 0 1] (B) directions, which reveals that OMC has highly ordered 2D-hexagonal arrays of carbon nanorods and well-developed mesoporous between adjacent carbon nanorods. The structure of OMC was further investigated by small-angle XRD (inset Fig. 1A). The OMC sample exhibits three well-resolved peaks that can be indexed as (1 0 0), (1 1 0), (2 0 0) diffraction peaks of mesoporous hexagonal space group p6 mm, which is corresponding to the result of TEM.

3.2. Electrochemical behaviors of isoniazid on Nafion-OMC/GC electrode

Fig. 2 shows the cyclic voltammograms of isoniazid at bare GC in 0.1 M PBS (pH 7.0) with and without 1.0×10^{-4} M isoniazid and at Nafion-OMC/GC electrode in the presence of various concentrations of 0.0 M, 5.0×10^{-5} M, 1.0×10^{-4} M and 2.0×10^{-4} M isoniazid. The potential was swept from–0.2 to +0.8 V. Inset of Fig. 2