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Fabrication of highly sensitive and selective electrochemical sensor by using optimized molecularly imprinted polymers on multi-walled carbon nanotubes for metronidazole measurement

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ABSTRACT

A novel electrochemical sensor for determining metronidazole (MNZ) is developed based on a composite structure of molecularly imprinted polymer (MIP) and multi-walled carbon nanotubes (MWCNTs). The morphology characterization by SEM displayed the successful deposition of polymeric layer on MWCNTs surface. A series of parameters including loading quantity of MWCNTs, pH value of polymerization system, and ratio of template and monomer are investigated and optimized during sensor preparation. It is clearly found that the MIP-decorated MWCNTs significantly enhance the electric signal response in MNZ measurement, giving rise to a remarkably low detection limit of 4.92×10^{-5} mg L^{-1} ($S/N = 3$), while the electro-synthesized MIP layer affords simultaneous identification and quantification of the target molecules by using $Fe(CN)_6^{3-/4-}$ as probe to indicate the current intensity. In addition, the established sensor is completely reusable and maintains excellent stability. These predominant properties enlist this hybrid electrode to exhibit high reliability for analyzing real samples and detection of MNZ directly in pharmaceutical dosage form and in fish tissue is successfully carried out without assistance of any separation techniques.

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1. Introduction

Metronidazole (MNZ) is a commonly used nitroimidazole antibiotic to treat parasitic infections in human being, including Giardia infections, amebic liver abscess, bacterial vaginosis [1,2], etc. It is also employed as veterinary medicine to prevent and treat infections and as growth-promoting feed additive in aquaculture industry. When the accumulated dose of MNZ exceeds a certain value in human being, some toxic reactions will be caused, for instance, seizures, peripheral neuropathy and ataxia [3]. Therefore, accurate and reliable determination of trace MNZ in biological samples is of great importance for the assurance of consumers' health.

A variety of quantitative analytical strategies have been reported to detect MNZ in different matrices, including high performance liquid chromatography (HPLC) [4], gas chromatography [5], thin layer chromatography [6], supercritical fluid chromatography [7], ultraviolet spectrophotometry [8], fluorescence spectrophotometry [9,10] and electrochemical sensor [11–22]. However, most of these protocols are deficient either in cost-effectiveness, easy access or in sensitivity. Among the methods mentioned above, electrochemical analysis is more attractive due to its simplicity, high sensitivity, fast response and relatively low cost [23,24]. Therefore, different chemically modified electrodes have been developed for sensing MNZ quantitatively [11–22].

High sensitivity and selectivity, among others, are common requirements in sensor industry, for which large efforts have been spent on design and integration of recognition elements with transducers. One approach for preparing this kind of recognition agent is molecularly imprinting technique (MIT) [25] which is able to generate the so-called artificial antibody-molecularly imprinted polymers (MIPs). Utilization of MIPs in modifying sensor enables its sensing ability comparable to that of biosensor [26–28]. In addition, different varieties of nanomaterials [29–31], such as multi-walled carbon nanotubes (MWCNTs) were reported to decorate electrodes [32–34], which provide sensor with unique merits like enlarged surface area and enhanced electronic property, thereby increasing the detecting sensitivity.

Herein, we constructed a novel electrochemical sensor for measuring MNZ by coupling MIPs and MWCNTs as sensitive materials for the purpose of recognition and signal-enhancement. The hybrid

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sensor yields ultra-sensitivity and selectivity in MNZ analysis, and remains satisfactory repeatability and stability. Meanwhile, the sensor was applied for accurate determination of MNZ in the pharmaceutical dosage form and biological matrices.

2. Experimental

2.1. Instruments and reagents

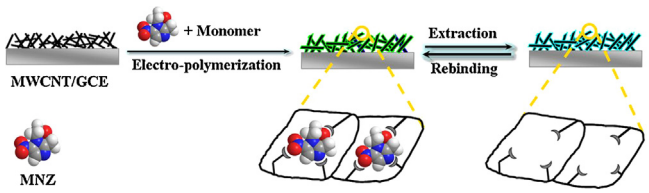
All electrochemical experiments were carried out with a CHI 760E electrochemical workstation (CHI Instruments Co., Shanghai, China). A three-electrode system was used, consisting of a bare or modified glassy carbon electrode (GCE, 3 mm in diameter) as working electrode, a saturated calomel electrode (SCE) as reference electrode and a Pt wire as counter electrode. The surface morphology of MWCNTs and polymer were characterized with a Zeiss Supra 55VP scanning electron microscope (SEM) operating at 20 kV and a JEM-1200EX transmission electron microscope (TEM) operating at 120 kV. The high performance liquid chromatography (HPLC) was performed using an Essentia LC-15C system equipped with two LC-15C Solvent Delivery Units, an LC Solution 15C workstation and an SPD-15C UV-Vis Detector (Shimadzu, Japan). LC condition was as follows: chromatographic separation was performed on a Shimadzu WondaSil C18 column (150 mm × 4.6 mm i.d., 5 μm). The mobile phase was methanol–water (2:8, v/v) with a flow rate of 1.0 mL/min, and the detection wavelength was set at 315 nm.

Metronidazole (MNZ), ronidazole, 4-nitroimidazole, 1,2-dimethylimidazole and dimetridazole were purchased from Shanghai Aladdin Co. (Shanghai, China). COOH-r-multi-walled carbon nanotubes (MWCNTs) were supplied by Chengdu Organic Chemicals Co. (Sichuan, China). Dopamine (DA) was obtained from Shanghai Jianglai Reagent Co. (Shanghai, China). MNZ tablet was purchased at local drugstore. Fish was obtained at local market. Reagents and materials, such as starch, sucrose, dextrin glucose, sodium dodecyl sulfate (SDS), $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$, $CaCl_2$, NH_4Cl, NaCl, KNO_3, H_2SO_4, methanol and phosphate buffer solution (PBS, KH_2PO_4 and NaOH), were of analytical grade. All solutions were prepared with double distilled water.

2.2. Preparation of sensor

Prior to modification, the surface of the bare GCE was carefully hand-polished with 0.3 and 0.05 μm alumina-water slurry in sequence. After being sonicated successively in nitric acid–water (1:1, v/v), acetone and ethanol, the electrode was rinsed with deionized water and dried at room temperature. A certain amount of COOH-r-MWCNTs was dispersed in distilled water containing 0.5 mg SDS by ultrasonication for 1 h. MWCNTs-modified GCE (MWCNT/GCE) was prepared by drop coating of 5 μL of the suspension on electrode surface and evaporation of the solvent under infrared lamp. Electropolymerization of DA in the presence of MNZ on the electrode surface was realized by cyclic voltammetry (CV), which was performed in the potential range from −0.8 to 0.8 V (vs. SCE) for 50 cycles at a scan rate of 50 mV s^{-1}. After that, the MWCNT/GCE bearing the electropolymerized poly-DA film was immersed in diluted H_2SO_4 to extract embedded MNZ by scanning from −1.0 to 1.0 V for several cycles until no obvious redox peak could be observed in probe solution (containing 1.01 g L^{-1} KNO_3, 16.46 g L^{-1} $K_3Fe(CN)_6$ and 21.12 g L^{-1} $K_4Fe(CN)_6$). The sensor modified with composites of MWCNTs and MNZ-imprinted MIP (MNZ-MIP/MWCNT/GCE) was then prepared and stored at room temperature for further experiments (Scheme 1).

As a control, non-imprinted polymer (NIP)-modified electrode, which is named as NIP/MWCNT/GCE, was fabricated in the same way except for the addition of template molecules during electropolymerization.



Scheme 1. Schematic representation of MNZ-MIP/MWCNT/GCE synthesis.

2.3. Electrochemical measurement

The three-electrode system was assembled in a cell with 25 mL probe solution, and the changes of peak current intensity of $Fe(CN)_6^{3-/4-}$ was recorded through CV to analyze the binding action of differently modified electrodes towards MNZ or other substances. The electrodes were firstly incubated in a solution containing analyte for 5 min, and then washed with deionized water. Afterwards, the electrodes were placed in the above-mentioned probe solution for CV measurement.

A washing step was followed after detection of one kind of analyte to extract adsorbed compounds, by the use of diluted H_2SO_4. Then the modified electrode was incubated in the next analyte for following survey.

2.4. Measurement of MNZ tablet and MNZ in biological sample

In order to verify the performance and feasibility of the modified sensor in monitoring pharmaceutical product and complex matrix of real sample, the MNZ-MIP/MWCNT/GCE was employed to determine MNZ in tablet form and in fish meat.

Ten pieces of MNZ tablets (each containing 200 mg MNZ) were accurately weighed and ground to fine powder. A portion of the powder equivalent to 250 mg MNZ was dissolved with methanol, ultrasonicated for 5 min and filtered. The filtrate solution was diluted to a certain concentration with methanol for MNZ analysis. For the spiked recovery experiment, a certain amount of MNZ was added into the tablet powder.

As for MNZ detection in fish meat, the experiment was carried out as follows. A healthy crucian carp fish fasted for 24 h, and was given a certain amount of MNZ mixed in feed. After feeding for 48 h, 2.0 g fish meat with fishskin and bones removed was homogenized with 7 mL methanol. Subsequently, methanol was added into the homogenate at a volumetric ratio of 1:1 to get rid of protein, followed by centrifugation. The supernatants were used for MNZ analysis. For the spiked recovery experiment, a certain amount of MNZ was added in the samples during homogenization.

3. Results and discussion

3.1. Preparation and characterization of MNZ-MIP/MWCNT/GCE

Electropolymerization could be an attractive way of modifying electrodes with thin molecularly imprinted layer in a simple and rapid manner. The film grows on the electrode surface, so good adherence to the transducer is guaranteed. Film thickness can be easily controlled by varying the amount of monomer deposited. Besides, polymerization is carried out in aqueous electrolyte solutions, and it is therefore expected that measurement could also be taken in aqueous media, which is difficult to realize through traditional MIPs as water could damage the non-covalent interaction between polymer and template [35,36].

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