



Electrochemical determination of cefotaxime based on a three-dimensional molecularly imprinted film sensor



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ABSTRACT

A novel electrochemical sensor is presented for the determination of cefotaxime (CEF), which is constructed by molecularly imprinted polymer (MIP), gold networks@IL (IL, 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄]) (GNWs@IL), porous platinum nanoparticles (PPNPs) and carboxyl graphene (COOH-r-GO). The GNWs@IL is prepared by directly reducing HAuCl₄ with sodium citrate in [BMIM][BF₄] aqueous solution. The PPNPs are well embedded in GNWs@IL due to the adhesion of IL to form GNWs@IL-PPNPs suspension, which is coated on a COOH-r-GO modified glassy carbon electrode to construct a porous three-dimensional networks modified electrode. Then, MIP is prepared by cyclic voltammetry at the modified electrode, using CEF as template and o-phenylenediamine as monomer. The factors concerning this assay strategy are carefully investigated. Under the optimal conditions, the electrochemical sensor offers an excellent response for CEF, the linear response range is $3.9 \times 10^{-9} \sim 8.9 \times 10^{-6} \text{ mol L}^{-1}$ and the detection limit is $1.0 \times 10^{-10} \text{ mol L}^{-1}$. The electrochemical sensor has been applied to the determination of CEF in real samples with satisfactory results.

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1. Introduction

Cefotaxime (CEF) belongs to semisynthetic cephalosporin antibiotics and is widely used to treat bacterial infections, mostly respiratory and urinary infections, because it is active against many bacteria (Gehanno et al., 1991). It is also illegally used in food preservation and processing, etc (Shvedene and Borovskaya, 2003). Therefore, it is necessary to develop sensitive and selective methods for the determination of this compound in biological fluids, food and fermentation industry.

From now on, different analytical methods have been reported for the determination of CEF, including high-performance liquid chromatography (Wang et al., 2010), spectroscopic methods (Wang et al., 2009) and electrochemical methods (Afkhami et al., 2013; Golcu et al., 2005; Jain et al., 2010; Nigam et al., 2009; Shahrokhian and Rastgar, 2012; Zhang et al., 2013). Among these methods, chromatographic methods are commonly used. At the same time, electrochemical methods become popular because of their higher sensitivity, lower cost and faster operation than other methods. Some electrodes have been prepared for the determination of CEF. For instance, Au–Pt nanoparticles (NPs)–multi-walled carbon nanotubes modified glassy carbon electrode

(GCE) (Shahrokhian and Rastgar, 2012), gold nanoparticles (GNPs) (Afkhami et al., 2013), GNPs/poly(L-arginine) (Zhang et al., 2013) and Zn(II) complex (Nigam et al., 2009) modified carbon paste electrodes were utilized to detect CEF. Generally, the direct electrochemical methods present high sensitivity, but their selectivity is poor. Hence, it is important to exploit an alternative electrode with high selectivity and sensitivity for the determination of CEF.

Molecularly imprinted polymer (MIP) is a powerful medium to enhance selectivity and/or sensitivity in electrochemical sensors field (Malitesta et al., 2012; Sharma et al., 2012a; Suryanarayanan et al., 2010). Recently, MIP electrochemical sensors have attracted considerable attention and have been widely utilized to detect different molecules ranging from small hazardous molecules (pharmaceuticals, pesticide residue and food additives etc.) (Sharma et al., 2012a; Xue et al., 2013; Zang et al., 2013) to biomacromolecules (peptides and proteins, etc.) (Cai et al., 2010; Lv et al., 2013; Wang et al., 2013c) using chronoamperometry (Lian et al., 2013, 2012), differential pulse voltammetry (DPV) (Yang et al., 2013; Zang et al., 2013) and impedimetric methods (Uygun and Dilgin, 2013; Wu et al., 2012), etc. At the same time, these reports pointed out that the fabrication of MIP on electrode surface was critical factor. Hitherto, several methods have been developed for fabricating MIP on electrode surface, including in situ polymerization by electrochemical, optical and thermal technologies, and to coat electrode surface with MIP suspension

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containing glutinous agents (Malitesta et al., 2012; Sharma et al., 2012b; Suryanarayanan et al., 2010). Among these methods, electrochemical polymerization has advantages of easy adherence of the polymeric film, controllable film thickness and easy to handle (Lian et al., 2013, 2012; Sharma et al., 2012b). To achieve high sensitivity, nanomaterials were used with MIP, such as metal nanomaterials (Lian et al., 2013, 2012; Wang et al., 2013a, 2013c; Xue et al., 2013), graphene (r-GO) (Kong et al., 2013; Lian et al., 2013; Wang et al., 2013c), carbon nanotube (Yang et al., 2013), TiO₂ nanotube array (Wang et al., 2013a) and sol-gel film (Yang et al., 2013) etc. Nanomaterials have large specific surface which provide more area for polymerization on electrode surface so that the imprinting sites increase (Malitesta et al., 2012; Suryanarayanan et al., 2010). Furthermore, they have excellent electrocatalytic activity and electron transfer ability such as metal NPs (Lian et al., 2013, 2012; Wang et al., 2013c; Xue et al., 2013), r-GO (Kong et al., 2013; Wang et al., 2013c) and functionalized r-GO (Zang et al., 2013). Therefore, nanomaterials can enhance sensitivity. However, the materials were usually assembled to two-dimensional structure (Kong et al., 2013; Wang et al., 2013c; Zang et al., 2013), and large part of them were buried in modified films (Lian et al., 2013, 2012; Wang et al., 2013c; Xue et al., 2013). To improve the situation, a three-dimensional structure was constructed on electrode surface (Wang et al., 2013a). Comparing with two-dimensional structure, three-dimensional architecture exhibits large surface area, high electrical conductivity and the electron transfer ability (El-Said et al., 2010; Garcia-Mendiola et al., 2013; Yamauchi et al., 2012).

In this study, a novel three-dimensional gold networks@IL (1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄]) composite material loaded with porous platinum nanoparticles (GNWs@IL-PPNPs) is coated on a carboxyl graphene (COOH-r-GO) modified GCE to construct a three-dimensional MIP film for the detection of CEF. The GNWs are obtained using IL as structure-directing agent. Importantly, IL is virtually adsorbed on the surface of GNWs to form core-shell structure (i.e. GNWs@IL). The GNWs@IL provides a three-dimensional frame so that PPNPs have a chance to embed in it. Therefore, GNWs@IL-PPNPs/COOH-r-GO/GCE provides a porous three-dimensional substrate for electrochemical imprinting. To the best of our knowledge, this is the first time to construct such a unique MIP film for the electrochemical detection of CEF.

2. Experimental

2.1. Apparatus and reagents

All electrochemical experiments were performed with a CHI 617A electrochemistry workstation (Shanghai CH Instruments Co., China). A three-electrode system was used, consisting of a modified glassy carbon electrode as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum foil electrode as counter electrode. Scanning electron microscope (SEM) was performed using a Zeiss (German) with an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) was carried out by using a JEM-2100 transmission electron microscope with an accelerating voltage of 200 kV.

Carboxyl-graphene was supported by Nanjing XFANO Materials Tech Co., Ltd. (Nanjing, China). 1-Butyl-3-methylimidazolium tetrafluoroborate, chloroauric acid tetrahydrate (HAuCl₄·4H₂O), chloroplatinic acid (H₂PtCl₆·6H₂O), cefotaxime, ceftizoxime and ceftriaxone were purchased from Sigma (St. Louis, MO, USA) and used as received. Unless stated otherwise, all other reagents used were analytical grade. The human serum and urine samples were obtained from Hospital of Wuhan University and stored at 4 °C.

The supported electrolyte was a Britton-Robinson (BR) buffer solution (containing 0.04 mol L⁻¹ of glacial acetic acid, orthophosphoric acid and boric acid). The pH values of buffer solutions were adjusted by adding 0.2 mol L⁻¹ sodium hydroxide.

2.2. Preparation of GNWs@IL suspension

Under gently stirring, 400 μL 25 mmol L⁻¹ HAuCl₄, 25 μL [BMIM][BF₄] and 5 mL H₂O were mixed and then the mixture was stirred for 5 min at 100 °C. After that, 3.0 mL sodium citrate (1 wt%) was immediately added and was constantly stirred for 17 min. The obtained solution was stored at room temperature for further utilization and characterization.

2.3. Preparation of PPNPs

According to literature (Wang et al., 2013b), 1 mol L⁻¹ KOH solution (0.05 mL) and 10 mmol L⁻¹ fresh ascorbic acid (3 mL) aqueous solution were added to 2 mL H₂O, and then 4 mL 2 mmol L⁻¹ H₂PtCl₆ was added. The mixture was shaken for about 1 min and then allowed to stand at 60 °C. After 1 h, the products were separated by centrifugation and washed with water and absolute ethanol for two to three times.

2.4. Preparation of GNWs@IL-PPNPs/COOH-r-GO/GCE

Firstly, 10 mg PPNP was dispersed in 1 mL GNWs@IL (15 mg mL⁻¹) suspension under ultrasonication for 30 min. At the same time, 1 mg COOH-r-GO was dispersed in 1 mL H₂O to give 1 mg mL⁻¹ COOH-r-GO. Then, 5 μL of COOH-r-GO suspension was coated on a clean GCE surface and dried at 50 °C. When most of H₂O was evaporated, 5 μL of GNWs@IL-PPNPs suspension was coated on the COOH-r-GO modified GCE and dried at 50 °C. Thus, a GNWs@IL-PPNPs/COOH-r-GO/GCE was obtained. For comparison, COOH-r-GO/GCE, PPNPs/COOH-r-GO/GCE and GNWs@IL/COOH-r-GO/GCE were prepared under same conditions.

2.5. Preparation of MIP electrochemical sensor

A GNWs@IL-PPNPs/COOH-r-GO/GCE was immersed in an acetate buffer solution (pH=5.2) containing 0.4 mmol L⁻¹ *o*-phenylenediamine (*o*-PD) and 0.1 mmol L⁻¹ CEF, and polymerization was performed by using cyclic voltammetry (CV). The potential range was 0–800 mV, the scan rate was 100 mV s⁻¹, and the polymerization time was 140 s. After polymerization, the electrode was dried at room temperature and then immersed in 0.2 mol L⁻¹ HCl for 10 min in order to remove template molecule (Scheme 1). For comparison, MIP/COOH-r-GO/GCE, MIP/PPNPs/COOH-r-GO/GCE, MIP/GNWs@IL/COOH-r-GO/GCE were prepared under the same conditions. Furthermore, non-imprinted polymer (NIP)/GNWs@IL-PPNPs/COOH-r-GO/GCE was fabricated following the same procedure, but in the absence of template molecules.

2.6. Electrochemical measurements

The sensor was immersed in a BR buffer solution (pH 2.0) containing a certain concentration of CEF for 500 s, under mildly magnetic stirring. Then, it was rinsed with H₂O. After that, the three-electrode system was assembled on a cell with 10 mL BR buffer solution (pH 2.0), and the DPV was performed in the potential range from 400 mV to 1100 mV (versus SCE).

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