Biosensors and Bioelectronics 38 (2012) 163–169

Contents lists available at SciVerse ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Electrochemical sensor based on gold nanoparticles fabricated molecularly imprinted polymer film at chitosan–platinum nanoparticles/graphene–gold nanoparticles double nanocomposites modified electrode for detection of erythromycin

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ARTICLE INFO

Article history:
Received 27 February 2012
Received in revised form
8 May 2012
Accepted 15 May 2012
Available online 24 May 2012

Keywords:
Electrochemical sensor
Molecularly imprinted polymers
Graphene–gold nanoparticles composites
Chitosan–platinum nanoparticles composites
Erythromycin detection

ABSTRACT

A molecularly imprinted electrochemical sensor was fabricated based on gold electrode decorated by chitosan–platinum nanoparticles (CS–PtNPs) and graphene–gold nanoparticles (GR–AuNPs) nanocomposites for convenient and sensitive determination of erythromycin. The synergistic effects of CS–PtNPs and GR–AuNPs nanocomposites improved the electrochemical response and the sensitivity of the sensor. The molecularly imprinted polymers (MIPs) were prepared by $HAuCl_4$, 2-mercaptonicotinic acid (MNA) and erythromycin. Erythromycin and MNA were used as template molecule and functional monomer, respectively. They were first assembled on the surface of GR–AuNPs/CS–PtNPs/gold electrode by the formation of Au–S bonds and hydrogen-bonding interactions. Then the MIPs were formed by electropolymerization of $HAuCl_4$, MNA and erythromycin. The sensor was characterized by cyclic voltammetry (CV), scanning electron microscope (SEM), UV–visible (UV–vis) absorption speactra and amperometry. The linear range of the sensor was from 7.0×10^{-8} mol/L–9.0×10^{-5} mol/L, with the limit of detection (LOD) of 2.3×10^{-8} mol/L ($S/N=3$). The sensor showed high selectivity, excellent stability and good reproducibility for the determination of erythromycin, and it was successfully applied to the detection of erythromycin in real spiked samples.

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1. Introduction

During these years, antibiotics have been widely used in agricultural applications and animal aquaculture (Knapp et al., 2010). Erythromycin, a 14-membered macrolide antibiotic, exhibits high activity against nearly all Gram-positive and Gram-negative bacteria. It has been extensively used in the treatment of bacterial infection for over 50 years (Dranove et al., 2010; Wu et al., 2009; Pendela et al., 2008). And it is commonly used by many farmers to protect animals and farm crops from bacterial disease. Therefore, those animal and agricultural products may have the residues of erythromycin. These residues may lead to direct toxic effects on the consumers (Hu et al., 2010). With the problems associated with erythromycin residues in foods, many countries have set maximum residue limits for erythromycin regulation in animal products. Up to now, the usual methods for the determination of erythromycin are mainly high-performance liquid chromatography (HPLC), liquid chromatography–mass spectrometry (LC–MS), fluorimetric method and near infrared reflectance spectroscopy method. Although these analysis methods are successfully used to detect erythromycin, they also have many shortcomings such as complicated and expensive instrumentations, professional operators and complex pretreatment steps. Therefore, it is necessary for us to find a good method to detect erythromycin.

Molecular imprinting is a newly developed technology to introduce recognition properties into synthetic polymers by synthesizing molecularly imprinted polymers (MIPs) with specific molecular recognition capacity (Wu et al., 2009; Zhou et al., 2004). It has received more and more attention in recent years, and has been successfully used to recognize various molecules (Nicholls et al., 2009; Li et al., 2009). In order to prepare MIPs, cross-linkers and functional monomers are polymerized with template molecules by covalent, non-covalent and sacrificial spacer methods (Blancó-López et al., 2003; Wang et al., 2010). After removal of template from the polymers, the cavity complementary in size and

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http://dx.doi.org/10.1016/j.bios.2012.05.017

shape to the template is obtained in the polymer network, which can rebind the template with high selectivity and affinity (Dai et al., 2010). Owing to this molecular memory, MIPs are quite simple to prepare and easy to perform in a tailor-made fashion to recognize and bind target molecules (Matsui et al., 2009). In addition, MIPs have the advantages of high selectivity, low cost, high sensitivity and robustness (Hong et al., 2010). These properties make MIPs potentially very suitable for the development of electrochemical sensors to detect various materials.

As a biocompatible polymer, chitosan (CS) possess many properties such as excellent film-forming ability, remarkable biocompatibility, nontoxicity and high mechanical strength (Xi et al., 2008; Tangkuaram et al., 2007). Also, it has a large number of reactive amino and hydroxyl functional groups. Due to its rare combination of physicochemical properties, CS has been widely applied in many fields such as food, agriculture, biology and pharmacy (Zou et al., 2008). During these decades, CS has been extensively used as an immobilization matrix for the construction of amperometric biosensors (Fan et al., 2007).

Graphene (GR) is a single-atom-thick sheet of sp2-bonded carbon atoms (Li et al., 2011). Since the discovery of GR, it has attracted considerable attention because of its unique and novel properties such as high surface area, high electrical conductivity, strong mechanical strength and good chemical stability (Du et al., 2011). Therefore, it has received more and more interest for applications in many technological fields such as nanocomposites, nanoelectronics, bioelectronics and biosensing (Sun et al., 2011; Chen et al., 2011).

During these decades, metal nanoparticles have been widely applied to the fabrication of nanocomposites. They have many excellent properties such as large surface-to-volume ratio, good electrical properties, strong adsorption ability, high surface reaction activity, small particle size and good surface properties (Singh et al., 2011). These excellent properties are helpful for the immobilization of biomolecules. Recently, Pt nanoparticles (PtNPs) and gold nanoparticles (AuNPs) have been widely used in many applications because of their unique optical, physical and chemical properties (Upadhyay et al., 2009; Luo et al., 2005). PtNPs have large specific surface area, good biocompatibility, and high conductivity (Yuan et al., 2011). AuNPs have good conductivity and biocompatibility. They also can form covalent bonds and combine with materials containing many functional groups, such as CN, NH_3, or SH (Du et al., 2007). Therefore, in this work, we used PtNPs and AuNPs to prepare nanocomposites to fabricate electrochemical sensor to improve the electrical conductivity of the sensor.

In this article, we constructed a novel imprinted electrochemical sensor based on chitosan–platinum nanoparticles (CS–PtNPs)/graphene–gold nanoparticles (GR–AuNPs) for sensitive detection of erythromycin. CS–PtNPs and GR–AuNPs were introduced to improve the electrochemical response and the effective surface area of the electrode. Erythromycin and MNA were used as template molecule and functional monomer, respectively. They were first assembled on the surface of GR–AuNPs/CS–PtNPs/gold electrode by the formation of Au–S bonds and hydrogen-bonding interactions. Subsequently, the polymers membrane was formed by electropolymerization of $HAuCl_4$, MNA and erythromycin. After electropolymerization, $HAuCl_4$ was reduced into gold nanoparticles (AuNPs) and it could improve the conductivity of MIPs. Erythromycin was removed by washing with ethanol repeatedly. The sensor was characterized by cyclic voltammetry (CV), scanning electron microscope (SEM), UV–visible (UV–vis) absorption speactra and amperometry. The selectivity, reproducibility, and stability of the sensor have also been investigated. This electrochemical sensor was successfully applied to the detection of erythromycin in real samples.

2. Materials and methods

2.1. Reagents and chemicals

Erythromycin, graphene (GR), kanamycin sulfate, neomycin sulfate, spiramycin and chloroplatinic acid (H_2PtCl_6) were purchased from Jingchun Co., Ltd. (Shanghai, China). Chitosan (CS) and 2-mercaptonicotinic acid (MNA) were purchased from Sangon Biotech Co., Ltd. (Shanghai, China). Chloroauric acid ($HAuCl_4$) and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the solutions were prepared with deionized water.

2.2. Apparatus

In this work, electrochemical measurements were performed using a model VersaSTAT 3 electrochemical workstation (Princeton Applied Research, USA). We used a three electrode system in 5.0 mmol/L $K_3[Fe(CN)_6]$ solution containing 0.2 mol/L KCl at room temperature (RT, 25 °C) to measure electrochemical response, which composed of platinum wire as auxiliary electrode, Ag/AgCl electrode as reference electrode and modified gold electrode as working electrode. Before use, the surface of the gold electrode was polished by 0.3 mm and 0.05 mm alumina slurry. Then the gold electrode was washed and sonicated in deionized water for 5 min. After drying at RT, it was subjected to sweep cyclically in 0.05 mol/L $K_3[Fe(CN)_6]$ solution between −0.20 V and +0.60 V to judge the quality of the pretreatment process. Scanning electron microscope (SEM) images were obtained using field emission SEM (ZEISS, Germany). UV–visible spectra were recorded using a Lambda 35 Spectrometer (PerkinElmer, USA) in the wavelength range from 200– 800 nm.

2.3. Synthesis of CS–PtNPs

CS–PtNPs composites were prepared according to previous method (Yang et al., 2008). First of all, we dissolved 50 mg CS into 10 mL of 1.0% (V/V) acetic acid solution and then stirred them for 2 h at RT until it was completely dispersed. The pH was adjusted to 3.0–4.0 using a concentrated NaOH solution. Thus we got 0.5 wt% CS. Secondly, we added 15 mL of 0.01 mol/L H_2PtCl_6 into the prepared CS. Then the mixture was stirred for 1 h at RT and sonicated for 20 min to get a well-dispersed solution. At last, H_2PtCl_6 was reduced to PtNPs after the addition of 0.05 mL of 5% $NaBH_4$.

In this work, we used UV–vis absorption spectroscopy method to verify the successful synthesis of CS–PtNPs. As shown in Fig. S1B, the absorption peak of the mixture of CS and H_2PtCl_6 (CS–H_2PtCl_6) was observed at 262 nm. It was derived from H_2PtCl_6. After the addition of $NaBH_4$, H_2PtCl_6 was reduced to PtNPs and CS–PtNPs was obtained. Therefore, the absorption peak of H_2PtCl_6 at 262 nm disappeared as shown in Fig. S1A. Thus CS–PtNPs was successfully synthesized.

2.4. Preparation of GR–AuNPs

The synthesis of GR–AuNPs nanomaterials consisted of the following three steps according to previous methods (Shan et al., 2010; Su et al., 2011): firstly, we prepared graphite oxide, which was synthesized from graphite. We added 1 g graphite powder to a big beaker containing 0.5 g sodium nitrate and 23 mL 98% H_2SO_4, and the mixture were stirred for 30 min in an ice-salt bath at 0 °C. Then 3 g $KMnO_4$ was slowly added into the solution at 20 °C. After being stirred for 2 h, the solution temperature was raised gradually to 35 °C in a water bath and remained for more than 30 min. Then 46 mL deionized water was added to the

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