Molecularly imprinted polymer grown on multiwalled carbon nanotube surface for the sensitive electrochemical determination of amoxicillin

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ABSTRACT

We described a novel electrochemical sensor for amoxicillin (AMOX), which was constructed by multiwalled carbon nanotubes@molecularly imprinted polymer (MWCNTs@MIP), single walled carbon nanotube (SWCNT) and dendritic Pt-Pd nanoparticle (NP). Firstly, ionic liquid (IL, i.e. 3-propyl-1-vinylimidazolium bromide) was grafted onto MWCNTs surface to form MWCNTs@IL by using an ionic exchange strategy. Then, the resulting MWCNTs@IL was used as monomer to synthesize MWCNTs@MIP. Meanwhile, dendritic Pt-Pd bimetallic NP was prepared by using hexadecylpyridinium chloride and hexamethylenetriamine as synergetic structure-directing agents, and then it was dispersed into SWCNT suspension. After that, the hybrid suspension was dropped on a glassy carbon electrode, followed by coating with MWCNTs@MIP. Under the optimal conditions, the obtained sensor presented linear response to AMOX in the ranges of $1.0 \times 10^{-9} \sim 1.0 \times 10^{-6}$ mol L^{-1} and $1.0 \times 10^{-6} \sim 6.0 \times 10^{-6}$, respectively, and its detection limit was 8.9×10^{-10} mol L^{-1}. This sensor was used to detect AMOX in real samples with satisfactory results.

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1. Introduction

Amoxicillin (AMOX) belongs to β-lactam antibiotics of the penicillin group. It not only possesses antimicrobial activity against most gram-positive and gram-negative bacteria as other β-lactam antibiotics, but also presents higher absorption rate than other β-lactam antibiotics in humans and animals [1–3]. Thus, it is usually used for the treatment of infectious diseases caused by these bacteria in humans and animals, and remained in biological fluids and animals food production. However, AMOX can cause some side-effects on human beings as other β-lactam antibiotics [4]. Thus, it is important to detect its residue in food production and biological fluids.

At present, a number of analytical methods were used to determinate AMOX, such as spectroscopy [5,6], chromatography [7,8], surface plasmon resonance (SPR) [9] and electrochemical method [10–16]. Generally, molecularly imprinted polymer (MIP) was used as a recognition receptor to enhance the selectivity and/or sensitivity for these methods [17–19]. For instance, Beltran et al.

used MIP to extract AMOX from urine samples for high-performance liquid chromatography (HPLC) [17]. Wan et al. used MIP to construct a chemiluminescence sensor for AMOX [18]. Szultka et al. combined MIP with HPLC-mass spectrometry to selectively detect AMOX in human plasma samples [20]. Yola et al. applied MIP to prepare a SPR sensor for the sensitive determination of AMOX [9]. In addition, several modified electrodes were reported to detect its residue based on different voltammetric methods such as cyclic voltammetry [10,11], square wave voltammetry[12], chronoamperometry [13,15] and differential pulse voltammetry [14,16], including multiwalled carbon nanotube (MWCNTs) [11], MWCNTs/FeCr$_2$O$_4$ hybrid film [14] and polyglutamic acid/glutaraldehyde [12] modified glassy carbon electrodes (GCEs), nickel-curcumin complex [13] and polyaniline [15] modified carbon past electrodes and Au nanoparticles (NPs) modified indium tin oxide electrode [16]. However, their selectivity and/or sensitivity need to be further enhanced. For this purpose, MIP should be useful.

MIPs are artificially synthesized but popular and inexpensive recognition receptor [21,22]. They not only possess the desired selectivity for target molecules as natural receptors, such as enzyme, antibody and nucleic acid, etc., but also have higher chemical and physical stability in comparison with natural

receptors [22]. As a result, they were widely applied in various fields, including sensor, drug delivery, catalysis and separation [21,22], etc. However, MIPs were generally prepared by bulk or precipitation polymerization, which made many recognition sites be buried in polymeric matrix so that they presented slow mass transfer and low binding capacity. For these disadvantages, surface molecular imprinting technique was developed.

Surface imprinting technique makes polymer grow on supporting material surface, thus the imprinted sites situate at or near the material's surface, and the target molecules are more easily removed and rebound in comparison with traditional MIP [23–25]. Importantly, the supporting materials usually possess nano-structures, giving rise to high imprinted sites/volume ratio [23]. Thus, the binding capacity, mass transfer and binding kinetics are improved. Recently, several nanomaterials were chosen as supporting materials for surface imprinting, such as SiO_2 [26], Fe_3O_4 [27], $Fe_3O_4@SiO_2$ [28] and Au NP [29], quantum dot [30] and MWCNT [31] due to their large surface and easy functionalization. For electrochemical sensors, the conductive property of supporting material is a critical factor because it decides the electron transfer rate of MIP. Based on these criterions, MWCNT is a satisfactory supporting material and widely used in this field. In most reports, the functional monomer or initiator is firstly immobilized on MWCNTs surface by using covalent bonding before the preparation of MIP [32–38]. However, a few reports focus on no-covalent bonding [39–41]. For instance, Qian et al. reported the in situ chemical oxidative polymerization of pyrrole on MWCNT surface for the preparation of novel MWCNTs@MIP [40]. We also adopted a novel ionic liquid (IL, i.e. 3-hexadecyl-1-vinylimidazolium chloride) as monomer to directly prepare MIP on MWCNT [41]. Hence, the no-covalent bonding method is also promising, and is still in need of exploration.

In this work, we grafted IL (i.e. 3-propyl-1-vinylimidazolium bromide, C3VimBr) on MWCNT surface by using ionic exchange strategy. Firstly, the carboxyl acid-functionalized MWCNT (HOOC-MWCNT) was transformed into KOOC-MWCNT, and then it reacted with IL to produce MWCNT@IL. After that, the resulting MWCNT@IL was used as a functional monomer to prepare MWCNT@MIP. At the same time, we prepared dendritic Pt-Pd bimetallic NPs with high ordered pore channels by using hexadecylpyridinium chloride (HDPC) and hexamethylenetetra-mine (HTM) as synergetic templates. Then, the suspension of Pt-Pd bimetallic NPs and SWCNTs was dropped on a GCE to obtain a three-dimensional porous modified interface. Finally, the obtained MWCNTs@MIP was coated on the above modified electrode to construct an electrochemical sensor for AMOX. To the best of our knowledge, it is first time to graft IL on MWCNTs surface by using ion exchange strategy for the preparation of MIP, and is also first time to adopt MIP for the electrochemical determination of AMOX. Meanwhile, we used HDPC and HTM as synergetic templates to reduce the scale and increase pore channel of dendritic Pt-Pd bimetallic NPs.

2. Experimental

2.1. Apparatus and reagents

A CHI 660D electrochemistry workstation (Shanghai CH Instruments Co., China) was used to perform electrochemical experiments. A three-electrode system was adopted, consisting of a modified glassy carbon electrode as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum foil as counter electrode. Transmission electron micros-copy (TEM) was recorded by using a JEM-2100, and scanning electron microscopy (SEM) was recorded by using a Zeiss (German). ^1H NMR spectra were obtained with a Varian Mercury 400 spectrometer and the used solvent was deuterated methanol (MeOD). Fourie transform infrared (FT-IR) absorption spectra were recorded with a model Nexus-6700 spectrometer (Nicolet, USA). High-angle annular darkeld scanning transmission electron micro-scopeenergy-dispersive-X-ray spectroscopy (HAADF-STEM-EDS) was recorded by using a FEI TITAN transmission electron microscopy.

Carboxylic acid-functionalized multiwalled carbon nanotubes (HOOCMWCNTs) and carboxylic acid-functionalized single walled carbon nanotubes (SWCNTs) were purchased from Nanjing XFNANO Materials Tech Co., Ltd. (Nanjing, China). Chloroplatinic acid (H_2PtCl_6), sodium tetrachloropalladate (Na_2PdCl_4), hexade-cylpyridinium chloride monohydrate ($C_5H_5N(Cl)(CH_2)_{15}CH_3 \cdot H_2O$, HDPC, 99.0%), hexamethylenetetramine ($C_6H_{12}N_4$, HTM), ascorbic acid ($C_6H_8O_6$, AA), amoxicillin (AMOX), ampicillin, cephalexin, 1-vinylimidazole, 1-bromopropane, 2,2-azobisisobutyronitrile (AIBN), ethylene glycol dimethacrylate (EGDMA) were purchased from Sigma (St. Louis, MO, USA). Unless stated otherwise, other reagents used were analytical grade. The milk samples and honey samples were purchased from local supermarket. The support electrolyte was 0.1 mol L^{-1} phosphate buffer solution (PBS, pH = 7.5), which was prepared with NaH_2PO_4 and Na_2HPO_4.
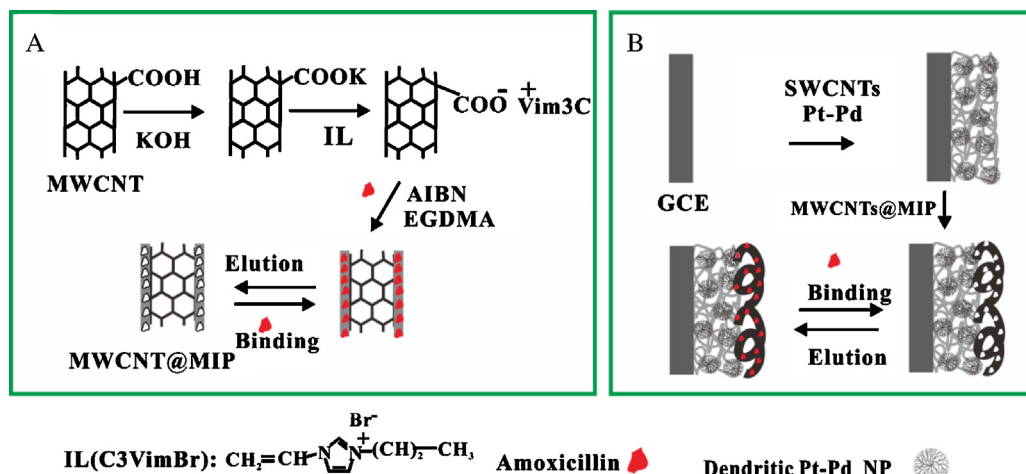
Scheme 1. Schematic diagram of the construction procedure of sensor.