



Electrochemical sensor based on molecularly imprinted composite membrane of poly(*o*-aminothiophenol) with gold nanoparticles for sensitive determination of herbicide simazine in environmental samples

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ARTICLE INFO

Article history:

Received 15 October 2015

Received in revised form 24 January 2016

Accepted 16 February 2016

Available online 18 February 2016

Keywords:

Molecular imprinting

Electrochemical sensor

Gold nanoparticles

Herbicide simazine

o-Aminothiophenol

ABSTRACT

A novel electrochemical sensor based on molecularly imprinted polymer membranes (MIPM) as biomimetic molecular recognition element involved in *o*-aminothiophenol functionalized Au nanoparticles (ATP@AuNPs) modified gold electrode was constructed for sensitive and selective detection of herbicide simazine (SMZ). The nano-scaled MIPM, with high specific surface area, was prepared by self-assembly of *o*-aminothiophenol (ATP) and electrodeposition of ATP@AuNPs in the presence of template SMZ. Cathodic current of SMZ was measured by cyclic voltammetry and the results exhibited that the proposed sensor possess a high electrocatalytic activity at a negative potential and a fast rebinding dynamics towards the reduction of SMZ in 0.01 M H₂SO₄ solution (pH 1.7). Linear dependency of peak current on SMZ concentrations was observed from 0.03 to 140 μM and detection limit was estimated to be 0.013 μM (3S/N). The enhancement of sensitivity was attributed to the presence of gold nanoparticles (AuNPs) which decreased the electron-transfer impedance and increased imprinting sites, lead to the superior enrichment effect of the trace amount of SMZ in aqueous solvent. The developed SMZ imprinted sensor exhibited excellent long-term stability and acceptable repeatability. In addition, the proposed method was successfully applied to measure SMZ in several real samples with the spiked recoveries changing from 91.4% to 96.8%, showing a promising potential in practical application.

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1. Introduction

Simazine (SMZ, 6-chloro-*N,N*-diethyl-1,3,5-triazine-2,4-diamine), an usual *s*-triazine herbicides, is distributed in soil or natural water, and may be spread to adjacent areas due to drift, runoff or evaporation [1]. Serious environmental problems can originate from SMZ persistence due to its low solubility in water and strong sorption on carbonous materials or clays. So SMZ is suspected of being an endocrine disrupting chemical and has potentially hazardous to human health [2]. Several methods such as thin-layer chromatography [3], surface plasmon resonance [4,5], high-performance liquid chromatography [6,7], gas chromatography–mass spectrometry [8] and immunosensor [9,10]

have been developed for SMZ quantification. Unfortunately, some of these methods require sophisticated equipment, advanced technical expertise, high cost, and time-consuming. So they are difficult for in situ or online monitoring. Particularly, a biosensor fabricated by using biological receptors is generally expensive and unstable [11]. Consequently, the development of a simple, rapid, inexpensive, stable and sensitive analytical method for routine SMZ screening is of particular significance and necessity.

Molecularly imprinted polymers (MIP), recognized for their versatile adsorption and catalytic properties, is a promising material as the recognition element or modifying agent in the preparation of sensors. MIP has been regarded as good candidate to replace biological receptor and investigated intensively [12,13], owing to their high selectivity, chemical stability, moderate cost and easy preparation [14]. The molecularly imprinted electrochemical sensor (MIECS), however, typically suffers from drawbacks such as poor binding sites resulting in low sensitivity, slow binding kinetics leading to long analysis time, and the reported difficulties related to the integration of the MIP with the transducer [15,16]. To over-

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come these situations, electropolymerization with the advantages of simplicity and speed of preparation, thickness and morphology controlling, high reproducibility and the possibility of preparation and operation in aqueous solutions [17,18], is utilized to directly prepare rigid, uniform, and compact MIP films on transducer surfaces [11]. A drawback of electropolymerization is that fewer imprinted sites form on the surfaces of electrode because of the relatively high density of polymers [19], which subsequently decrease the selectivity and sensitivity of MIECS. Fortunately, the nanoparticle-based amplification platforms and amplification processes have been reported to dramatically enhance the intensity of the electrochemical signal and lead to ultrasensitive assays [20]. Thus the integration of various nanoparticles with MIP polymers films have been proposed to overcome the mentioned defects of MIECS [21,22]. In particular, AuNPs have caused considerable interest and been extensively applied in fabrication of MIECS because of their excellent conductivity, good catalytic activity, high effective surface area, easy to be functionalized and quite stable in aqueous environment [23,24].

Previously, we implemented the AuNPs-based amplification platforms to improve the conductivity of MIP films via adsorption of AuNPs to the prepared ATP polymer (PATP) film, which enhanced effectively sensitivity of MIECS and constructed a novel method for indirect detection of tolazoline with ferrocyanide/ferricyanide redox probe [25]. The objectives of this study were (a) to investigate a new design of the MIECS modified by *o*-aminothiophenol functionalized gold nanoparticles (ATP@AuNPs) to prevent from AuNPs aggregation and enhance the immobilized amounts of template per unit surface area, and (b) to apply the as-prepared MIECS for direct and ultrasensitive electrochemical determination of herbicide SMZ in environmental samples using cyclic voltammetry (CV) technique. ATP@AuNPs was prepared firstly as a substrate. Then the electro-polymerization process was implemented on PATP modified gold electrode, in the presence of template molecule SMZ, to form a porous and rigid three-dimensional (3D) SMZ imprinted film. Which contribute to the MIECS exhibited fast rebinding dynamics, high selectivity, excellent sensitivity and prominent stability for ultrasensitive determination of SMZ.

2. Experimental

2.1. Reagents and materials

o-Aminothiophenol (ATP, 99%), *p*-aminobenzenesulfonic acid (ABS) and dodecanethiol (DDE) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Simazine (SMZ), picloram (PL), acetochlor (AC) and terbutylazine (TL) were obtained from Shanghai Pesticide Research Institute (Shanghai, China). Sodium borohydride (NaBH_4) and gold chloride (HAuCl_4) were purchased from Sigma Chemical Co. (St. Louis, MO, USA). All chemicals and solvents used were of analytical grade and used as received. Ultrapure water obtained from a Millipore water purification system ($\geq 18 \text{ M}\Omega$, Milli-Q, Millipore) was used throughout the experiments. Solutions of either sulfuric acid, for $\text{pH} < 2$, or 0.1 M in both acetic and phosphoric acids, for $2 < \text{pH} < 6$, were used as supporting electrolytes. The ionic strength was adjusted to 0.3 M with solid NaCl and the pH was adjusted with 0.2 M NaOH. Phosphate buffered solution (PBS, $\text{pH} 6.8$) was prepared using 0.2 M Na_2HPO_4 and 0.2 M KH_2PO_4 .

2.2. Apparatus

Electrochemical experiments were carried out with a CHI 660D electrochemistry workstation (Shanghai CH Instruments, China). The AC impedance of the MIP film was measured with the

Autolab PGSTAT302 electrochemical analyzer (Metrohm, Switzerland). Scanning Electron Microscope (SEM) images were obtained using a S-4800 Scanning Electron Microscope (Hitachi, Japan). Transmission Electron Microscope (TEM) images were performed on a JEM-2000FX II Transmission Electron Microscope (JEOL, Japan). And Atomic Force Microscope (AFM) images were obtained using a Veeco Introduces Dimension Edge Atomic Force Microscope System (Bruker, USA). All the pH measurements were performed with a MP 230 pH meter (Mettler-Toledo Switzerland).

2.3. Synthesis of the ATP functionalized Au nanoparticles

The ATP@AuNPs was synthesized referring to the method reported elsewhere [26] with slight modifications. Briefly, 10 mL solution containing 197 mg of HAuCl_4 in ethanol was added quickly to a 5 mL solution containing 51.1 mg of ABS and 8 mg of ATP in methanol. The mixture solution was stirred in the presence of 2.5 mL of glacial acetic acid in an ice bath for 1 h. Subsequently, 7.5 mL 1.0 M NaBH_4 aqueous solution was added dropwise, resulting in a rapid color change from pale yellow to deep red that indicated the formation of AuNPs. The solution was stirred for an additional 1 h in an ice bath and then for 12 h at room temperature (a dark solid confirmed that the AuNPs were coated with ATP). The black solid was separated by centrifuging at a speed of 10000 rpm for 15 min, washed and centrifuged successively (twice in each solvent) with methanol, absolute ethanol and acetone, and then dried in a vacuum oven overnight at 80°C . The obtained ATP@AuNPs was stored at 4°C prior to use.

2.4. Fabrication of SMZ imprinted sensor

Prior to modification, gold electrode ($\Phi = 2 \text{ mm}$) was polished to a mirror-like surface repeatedly by applying 1.0, 0.3 and 0.05 μm alumina slurries on the chamois, respectively. Then it was chemically cleaned by immersing into a freshly prepared mixture of "piranha" solution (a 3:7 mixture of 30% H_2O_2 and conc. sulfuric acid) for 10 min and successively sonicated with ethanol and distilled water for 10 min and then dried in air. Finally the electrode was electropolished via a CV process, with the potential scanning from -0.2 to 1.4 V in 0.5 M H_2SO_4 until a stable cyclic voltammogram was obtained at 50 mV s^{-1} vs. SCE.

The schematic diagram of the preparation of SMZ imprinted sensor is shown in Scheme 1. Firstly, PATP/Au electrode was prepared by immersing the cleaned electrode for 20 h into deoxygenated 0.01 M H_2SO_4 solution ($\text{pH} 1.7$), with a 20% volume of ethanol solution to ensure the solubility, containing 2 mM ATP and 0.5 mM SMZ. Secondly, PATP/Au electrode was implemented CV scan for 10 cycles in aqueous dispersion of 1.0 mg mL^{-1} ATP@AuNPs and 0.5 mM SMZ under nitrogen atmosphere, at a scan rate of 100 mV s^{-1} between -0.4 V and 0.8 V . Thirdly, the resulting electrode was soaked in 5% DDE ethanol solution for 5 h to seal the blank surface where did not form imprinted PATP film. Finally, the obtained electrode was immersed in 0.01 M H_2SO_4 supporting electrolyte to remove non-polymeric ATP@AuNPs and named as SMZ@MIP/ATP@AuNPs/ATP/Au electrode. As control, non-imprinted polymer modified electrode, was prepared under the same experimental conditions without adding SMZ, both the self-assembly and electrodeposition process, to check the reliability of the measurements.

2.5. SMZ removal from electrode surface

There are electrostatic interactions and hydrogen bonding between ATP monomer and polar groups of SMZ molecules. In order to break the interactions, we used methanol/acetic acid (7:3 v/v) solution in water as a desorption agent. The

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