Reagentless Electrochemiluminescence Sensor for Triazophos Based on Molecular Imprinting Electropolymerized Poly(Luminol-\(p\)-Aminothiophenol) Composite-Modified Gold Electrode

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Abstract
Combining high recognition selectivity with excellent electrochemiluminescent (ECL) performance, the imprinted poly(luminol-\(p\)-aminothiophenol) was prepared by the electrochemical copolymerization of luminol and \(p\)-aminothiophenol onto the gold electrode surface in the presence of triazophos. The recognition selectivity and ECL of the imprinted poly(luminol-\(p\)-aminothiophenol) were studied using triazophos as analyte. It was found that the imprinted poly(luminol-\(p\)-aminothiophenol) presented better ECL emission to triazophos than that of the polyluminol. On this basis, a reagentless ECL sensor based on the imprinted poly(luminol-\(p\)-aminothiophenol) as recognition elements is established for the detection of ultra-trace triazophos residues in the environmental water samples under near neutral condition. The resulting reagentless ECL sensor shows wide linear ranges from \(1.0 \times 10^{-10}\) to \(1.0 \times 10^{-6}\) M with lower detection limit of \(5.8 \times 10^{-11}\) M for triazophos.

Keywords Poly(luminol-\(p\)-aminothiophenol) · Polyluminol · Electrochemical polymerization · Electrochemiluminescence · Triazophos · Molecularly imprinted polymer

1 Introduction
Triazophos is an organophosphorus pesticide widely used on a variety of crops, such as paddy, cotton, maize and vegetables in China [1]. Therefore, the detection of triazophos residues in agricultural and environmental samples is of great significance to human health and ecological protection. Many methods have been utilized in the triazophos residues analysis, including electrochemistry [2], gas chromatography [3], ultra-performance liquid chromatography [4,5], immunoassay [6–8], and chemo/biosensor [9,10]. Among these methods, chemo/biosensors have been paid more and more attentions in the residue analysis due to the advantages of fast response, simple operation, high sensitivity and selectivity. However, because of the extremely low residue and much high interference in the residues, to develop more efficient recognition elements is very important in the chemo/biosensors.

The molecularly imprinted polymer (MIP), a synthetic antibody, has been widely used as recognition element in chemo/biosensors because of its advantages of specific recognition, good chemical stability and easy preparation [11,12]. Generally speaking, the efficiency of MIP-based sensor depends mainly on the selectivity and sensitivity of MIP to target analyte and the approaches of signal readout [13]. However, traditional bulk MIPs produced by traditional imprinting techniques usually exhibit some shortcomings, such as low binding capacity, poor site accessibility and slow binding kinetics because a large number of imprinting sites embedded in highly cross-linked bulk polymers [14–16]. To overcome these drawbacks, conducting imprinted polymeric thin films (such as polyaniline), which are synthesized by electropolymerization techniques at the various electrode surfaces, have become popular recognition elements due to their easy preparation, good stability, thickness controllability and strong adherence [17–20]. On the other
hand, traditional bulk MIPs also exhibit poor signal-output responses to analyte binding events, which limit their applications as recognition elements and lead to relatively low sensitivity in MIP-based sensor [21,22]. As a highly sensitive luminescence method, ECL has attracted much attention due to its the significant advantages of wide dynamic range, excellent sensitivity and simplified optical setup [23,24]. Among various ECL-active reagents, luminol is one of the most widely used ECL luminophores because of its high emission quantum yield and low reagent cost [25,26]. However, during the luminol ECL processes, luminol suffers from several problems: (i) luminol ECL is usually required under a high pH condition because the ECL emission of luminol is very weak in neutral or acidic solution; (ii) luminol ECL is generally required for the addition of the luminol in solution phase, resulting in poor analytical reproducibility because the sensor surface is readily contaminated [27,28]. Therefore, to develop a reagentless ECL sensor, that avoids the addition of luminol into the solution phase, the immobilization of luminol onto a electrode surface appears attractive. One alternative for immobilizing luminol technique is electropolymerized luminol to form polyluminol film onto the surface of electrode [29–31]. However, polyluminol suffers from some drawbacks, such as low conductivity, bad mechanical properties and little reusability [32]. Therefore, for further improving the mechanical and ECL properties of the polyluminol, some aromatic amine compounds were mixed with luminol for the preparation of copolymeric composites [33].

Herein, the imprinted poly(luminol-p-aminothiophenol) was prepared by the electrochemical copolymerization of luminol and p-aminothiophenol. Combining high recognition selectivity with excellent ECL, a reagentless ECL sensor based on the imprinted poly(luminol-p-aminothiophenol) as recognition elements is established for the detection of ultra-trace triazophos residues in the environmental water.

2 Experimental

2.1 Reagents and Apparatus

Luminol, p-aminothiophenol and triazophos were purchased from Fluka. 0.1 M phosphate buffers solution (PBS, pH 6.0) was prepared from KH₂PO₄ and K₂HPO₄ with 0.1 M KCl solution. Cyclic voltammetry and ECL response were recorded using a model MPI-B ECL analyzer systems, equipped with a three-electrode system, consisting of the imprinted polymeric composite-modified gold electrode (2-mm in diameter), an Ag/AgCl/saturated KCl electrode and platinum wire as working, reference and auxiliary electrodes, respectively. The morphology of the imprinted poly(luminol-p-aminothiophenol) composite was examined by an SU-8000 field emission scanning electron microscope (SEM).

2.2 Preparation of Triazophos-Imprinted Poly(Luminol-p-Aminothiophenol) Composite-Modified Gold Electrode

Figure 1 shows the preparation processes of the triazophos-imprinted poly(luminol-p-aminothiophenol)-modified gold electrode. First, a gold electrode was carefully polished with 5.0, 1.0, 0.3 µm alumina aqueous slurry and then successively washed with water and alcohol, respectively. Then, the gold electrode was immersed in the 0.1 M PBS (pH 6.0) containing 0.1 mM luminol, 0.1 mM p-aminothiophenol and 10 µM triazophos. Further, the electrochemical copolymerization was completed by 10-cyclic scans in the potential range of 0–0.6 V at a scanning rate of 50 mV s⁻¹. Finally, triazophos-imprinted poly(luminol-p-aminothiophenol)-modified gold electrode was immersed with 0.05 M NaOH in 90% methanol to completely remove triazophos templates and successively washed with water and alcohol, respectively. As a comparison, triazophos-imprinted polyluminol- and poly(p-aminothiophenol)-modified gold electrodes were also produced. The non-imprinted poly(luminol-p-aminothiophenol)- and non-imprinted polyluminol-modified gold electrodes were prepared in the same way except omitting triazophos templates in electropolymerization stage.

2.3 Measurement of Electrochemical and ECL Properties

To realize ECL sensing of triazophos, the imprinted poly(luminol-p-aminothiophenol)-modified gold electrode was first immersed into 10 mL of 0.1 M PBS (pH 6.0) containing the desired concentration of triazophos for 10 min and then transferred to an ECL cell containing 15 mL of 0.1 M PBS (pH 6.0) solution. The ECL response to triazophos at the imprinted poly(luminol-p-aminothiophenol)-modified gold electrode was recorded between −0.6 and 0.6 V at a scan rate of 100 mV s⁻¹. The quantitative assay for triazophos was carried out by calculating the net ECL intensity (∆F = F₅ − F₀), which F₅ and F₀ were ECL intensity (F₅) to the triazophos and the background ECL intensity (F₀) to the blank solution, respectively.

3 Results and Discussion

3.1 Preparation of the Imprinted Poly(Luminol-p-Aminothiophenol) Composite

The imprinted poly(luminol-p-aminothiophenol)-modified gold electrode was prepared by the electrochemical copoly-