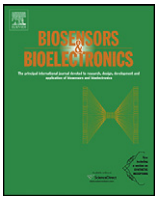
Biosensors and Bioelectronics 26 (2010) 868–871

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

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



Short communication

Electrochemical fabrication of molecularly imprinted porous silicate film electrode for fast and selective response of methyl parathion

Xiaohong Tan[a,b], Buhai Li[a], KongYong Liew[a,c], Chunya Li[a,*]

[a] Key Laboratory of Analytical Chemistry of the State Ethnic Affairs Commission, College of Chemistry and Materials Science, South-Central University for Nationalities, Minyuan Road 708#, Wuhan 430074, China
[b] School of Chemical and Environmental Engineering, Hubei Institute for Nationalities, Enshi 445000, China
[c] Faculty of Industrial Science and Technology, Universiti Malaysia Pahang, 26300 Kuantan, Malaysia

ARTICLE INFO

Article history:
Received 1 August 2009
Received in revised form 20 July 2010
Accepted 22 July 2010
Available online 30 July 2010

Keywords:
Molecularly imprinted
Methyl parathion
Electro-deposition
Silicate
Voltammetry

ABSTRACT

A methyl parathion-templated molecularly imprinted porous silicate thin film was electrodeposited onto a glassy carbon electrode using tetraethylorthosilicate sol as the silicon precursor and vinyltriethoxysilane as the functional monomer. The surface morphology and crystallinity of the imprinted film were characterized by scanning electron microscope and X-ray diffraction. The binding performance of the film with methyl parathion was examined with voltammetric techniques. The results show that the imprinted sol–gel film gives fast, sensitive and selective response to methyl parathion. The good selectivity of the film allows fine discriminations of methyl parathion from interferants, which including parathion, α-hydroxyl-4-nitrophenyl-dimethyl-phosphonate, *p*-nitrophenol and nitrobenzene. A linear range for methyl parathion determination was found from 1.0×10^{-8} to 1.0×10^{-5} mol l^{-1} with an estimated detection limit of 8.9×10^{-9} mol l^{-1} (S/N = 3). This imprinted sol–gel film electrode was proved to be a versatile sensing tool for the selective detection of methyl parathion in real samples.

1. Introduction

Molecularly imprinted technology is an attractive and revolutionary way to obtain artificial receptors due to its high specificity and selectivity to the templates (Arshady and Mosbach, 1981; Wulff and Sarhan, 1972; Zimmerman and Lemcoff, 2004). Compared with biological receptors, molecularly imprinted materials possess many advantages such as ease of mass production, high stability, and easily adapted for different compounds with specific binding sites. Therefore, molecularly imprinted materials have been extensively used in chromatographic separation (Qin et al., 2009), solid phase extraction (Fan et al., 2009), catalysis (Lettau et al., 2006), binding assays (Stephenson and Shimizu, 2007) and molecular sensing (Fang et al., 2009; Lakshmi et al., 2009; Li et al., 2005; Mazzotta et al., 2008).

Traditional methods for imprinted materials preparation are carried out under the polymerization conditions containing template molecules, monomers, functional monomers, and a high concentration of cross-linker (Arshady and Mosbach, 1981; Wulff and Sarhan, 1972; Zimmerman and Lemcoff, 2004). Unfortunately, the imprinted materials prepared through these approaches usually produce deeply embedded binding sites and suffer from certain limitations, such as slow mass transfer, moderate sensitivity and selectivity, incomplete template removal and broad guest affinity (Katz and Davis, 2000; Sallacan et al., 2002; Vlatakis et al., 1993). Formation of imprinted sites on a monolayer surface or a thin film was suggested as an alternative to eliminate the diffusion barriers (Chen et al., 2009).

Sol–gel technique was also used to construct molecularly imprinted sensors with dip-coating and spin-coating (Kunitake and Lee, 2004; Marx et al., 2004; Wang et al., 2006). Dip-coating usually produces thick films, which suffer from slow diffusion kinetics, long response time and low sensitivity (Kunitake and Lee, 2004). Thin film prepared with spin-coating (Li et al., 2005; Marx et al., 2004) also needs long incubation time for rebinding of templates. In addition, the film thickness is relatively difficult to be controlled. Recently, electro-assisted deposition was proposed to coat a thin sol–gel film on a solid electrode surfaces (Nadzhafova et al., 2007; Rozhanchuk et al., 2009; Sayen and Walcarius, 2003; Zhang et al., 2006). This method shows a number of advantages, particularly the ease of film-thickness control, fast mass transfer and rapid response to templates.

The aim of this study is to construct a highly sensitive and selective sensor for methyl parathion (MP) detection. MP, a typical organophosphorus pesticide, has been widely used in the past few years (Akhtar et al., 2009; De Souza and Machado, 2006). Unfortunately, its high toxicity generates serious health problems to both

---

* Corresponding author. Tel.: +86 27 67842752; fax: +86 27 67842752.
E-mail address: lcychem@yahoo.com (C. Li).

0956-5663/$ – see front matter
doi:10.1016/j.bios.2010.07.085

human and animals. Therefore, a methodology for rapid determination and quantification of trace MP residues becomes more and more important for homeland security and health protection. Electrochemical techniques based on chemically modified electrode have proved to be the sensitive and advantageous methods for MP determination (Bian et al., 2010; Du et al., 2008; Zen et al., 1999). Nevertheless, these methods suffer from some interferents, which possess similar electroactive groups. In order to improve its selectivity, we developed a MP-imprinted sol–gel film electrode by electro-deposition using tetraethylorthosilicate sol as the silicon precursor and vinyltriethoxysilane as a functional monomer. The MP-imprinted electrode performances such as stability, sensitivity and selectivity towards MP were evaluated.

2. Material and methods

2.1. Reagents

The compounds used in this study are listed in Fig. S1. Tetraethylorthosilicate and vinyltriethoxysilane were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). MP and parathion were purchased from Shanonda Corporation (Shashi, China). The stock solutions ($0.01\ \mathrm{mol\,l^{-1}}$) were prepared in ethanol and stored at 4 °C. Sample solutions were prepared freshly by the dilution of stock solutions with a phosphate buffer solution (KH_2PO_4 and Na_2HPO_4). Other chemicals were of analytical grade. All compounds were used without further purification. All solutions were prepared with ultrapure water purified by a Milli-Q water purification system.

2.2. Apparatus

Cyclic and square wave voltammetric (SWV) measurements were performed on EC 550 electrochemical workstation (Gaoss Union Technology Co., Ltd., Wuhan, China), which is a three-electrode system consisting an imprinted film working electrode (3 mm in diameter), a saturated calomel reference electrode (SCE) and platinum wire auxiliary electrode. For electrochemical analysis of MP, the imprinted film electrode was dipped into a 10 ml electrochemical cell containing a known concentration of MP for 80 s with stirring. Square wave voltammetric measurements were performed from −0.80 to 0.40 V. Cyclic voltammograms were recorded between −0.85 V and +0.40 V. The imprinted film electrode was washed with ethanol and ultrapure water successively before taking measurement. The solution was purged with nitrogen for 5 min before electrochemical measurements. All electrochemical experiments were carried out at room temperature (about 25 °C).

JEOL JSM-7400 F field emission scanning electron microscope (JEOL Ltd., Japan) was used for morphology analysis. X-ray powder diffraction (XRD) was performed on a Bruker D8 X-ray diffractometer (Bruker, Germany) employing Cu $K\alpha$ radiation.

2.3. Preparation of MP-imprinted film electrode

A solution containing 2.00 ml of $0.2\ \mathrm{mol\,l^{-1}}$ KCl, 1.40 ml of ethanol, 0.50 ml of tetraethylorthosilicate, 0.10 ml of vinyltriethoxysilane, and 1.00 ml of $0.01\ \mathrm{mol\,l^{-1}}$ MP was sonicated for ca. 60 min until a transparent sol was observed. A glassy carbon electrode (GCE) was polished carefully to a mirror-like surface with alumina slurry. And then it was rinsed and sonicated with HNO_3 (1:1), ethanol and water for 3 min. Electrochemical fabrication of MP-imprinted film was carried out in the pretreated sol with constant potential at −1.80 V for 30 s. This potential is sufficient to increase the pH on the electrode surface because the reduction reaction (protons to H_2, as shown below) produces hydroxyl anions (OH^-):

$$2H_2O + 2e \rightarrow 2OH^- + H_2$$

The electrochemically generated OH^- destabilizes the silica sol and a thin gel film is then deposited on the electrode surface (Shacham et al., 1999). The mechanism for the electrochemical modulation of pH and gel film formation on the electrode surface was illustrated in Fig. S2. The template (MP) in the imprinted films was completely removed by repeated extraction in ethanol. This can be confirmed by disappearance of the redox peaks for MP in cyclic voltammetry. The parathion imprinted film electrode and the non-imprinted film electrode were prepared by the same procedure.

3. Results and discussion

3.1. Characterization of MP-imprinted film electrode

The surface morphology of the MP-imprinted film electrode was characterized using scanning electron microscope. As shown in Fig. 1A, the electrode surface is obviously covered with a porous reticulated silicate film. These reticulations and nano-cavities significantly enhance the rebinding rate of MP to the imprinted sites. A scheme for the construction of the imprinted film and the selective recognition of MP is depicted in Fig. S3.

The XRD spectrum of the molecularly imprinted silicate film on a glassy carbon electrode, shown in Fig. 1B, gives three broad peaks in a range of 10–90°. This finding indicates that the molecularly imprinted silicate film was a predominantly amorphous state, when it was deposited at low temperature.

3.2. Voltammetric behaviors of MP at the imprinted film electrode

Fig. 2A shows the cyclic voltammograms of MP at the imprinted (a) and the non-imprinted film electrode (b) in a phosphate buffer solution (pH = 5.9). For the imprinted film electrode, MP exhibits well-defined voltammetric peaks. These signals come from the irreversible reduction of the nitrophenyl group to hydroxylamine via a four-electron reduction process at −0.65 V (Epc_2), and then oxidized to nitroso compounds at −0.053 V (Epa_1). Under subsequent cycling, the nitroso group was reversibly reduced to the corresponding hydroxylamine at −0.085 V (Epc_1). The reversible peaks (pa_1 and pc_1) increase slightly under continuous cycling, while the irreversible wave (pc_2) decreases significantly. Similar electrochemical behavior was also observed for methyl parathion (Du et al., 2008; Liu and Lin, 2005). The electrochemical reactions of MP ($Ph\text{-}NO_2$) can be described as following:

$$Ph\text{-}NO_2 + 4e^- + 4H^+ \rightarrow Ph\text{-}NHOH + H_2O \qquad (1)$$

$$Ph\text{-}NHOH \underset{+2e^-,\,+2H^+}{\overset{-2e^-,\,-2H^+}{\rightleftharpoons}} Ph\text{-}NO \qquad (2)$$

A control experiment was performed under the same conditions with the non-imprinted film electrode. The peak potential (Epc_2), which is corresponding to the irreversible reduction of the nitrophenyl group to hydroxylamine shifted to −0.68 V. The oxidation of hydroxylamine to nitroso compound was taken place at 0.037 V (Epa_1) and the subsequent reduction of nitroso group to the corresponding hydroxylamine was found at −0.13 V (Epc_1). Compared to the redox peaks at the imprinted film electrode, the value of peak-to-peak potential separation (ΔEp) becomes larger and both of the peaks get broadened. In addition, the current response for MP at the non-imprinted film electrode was obviously lower than that at the imprinted film electrode. This result suggests that the rebinding ability of MP to the electrode surface is able to improve by the