Electrospun Template Directed Molecularly Imprinted Nanofibers Incorporated with BiOI NanoFlake Arrays as Photoactive Electrode for Photoelectrochemical Detection of Triphenyl Phosphate

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Abstract

Triphenyl Phosphate (TPhP), as a typical model of organophosphorus flame retardants (OPFRs), has been regarded as emerging environmental contaminants of health concern. In this study, a rapid and highly sensitive visible-light-response PEC sensor has been developed for the detection of Triphenyl Phosphate (TPhP) using electrospun template directed molecularly imprinted nanofibers modified BiOI nanoflake arrays (BiOINFs) as a photoactive electrode. The molecularly imprinted electrospun nanofibers ((labeled as MI-ESNFs) were carefully characterized by scanning electron microscopy (SEM), UV spectra, FTIR spectra measurements and various electrochemical techniques. Under the optimized experimental conditions, the photoelectrochemical response was linearly proportional to the logarithm value of TPhP concentrations in the range of 0.01 ng mL^{-1} to 500 ng mL^{-1} . Meanwhile, the sensor exhibited high selectivity and stability.

Keywords: Triphenyl phosphate; Photoelectrochemical sensor; Electrospinning;

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Electrospun template directed molecular imprinting technique.

1. Introduction

Triphenyl phosphate (TPhP), as a representative of organophosphate flame retardants (OPFRs), has been widely used in a variety of man-made industrial products such as electronic equipments, plastics, textiles, furniture, floor polishes, paints, lubricants, building and insulation materials (Isales et al., 2015; Wang et al., 2014; Liu et al., 2016; Zhao et al., 2016). Due to their extensive utilization in household items and consumer and baby products, their ubiquitous occurrence in all environmental matrices has always been detected (Wang et al., 2011; Veen et al., 2012; Wei et al., 2015). Exposure to TPhP has been proved to cause serious damage to the immune and endocrine system (Li et al., 2015; Mendelsohn et al., 2016; Morris et al., 2014). As a result, rapid determination and reliable quantification of TPhP has become increasingly important in environmental monitoring. The current available detection methods for OPFRs include gas chromatography (GC) (Veen et al., 2012; Wei et al., 2015; Santina et al., 2016) and liquid chromatography–tandem mass spectrometry (LC-MS/MS) (Veen et al., 2012; Wei et al., 2015; Maa et al., 2013). However, these methods often suffer from some issues such as complicated procedures, high cost, and lack of portability (Jin et al., 2015; Liu et al., 2015). Therefore, a simple, cheap and sensitive analytical method for fast screening of OPFRs residues is urgently desirable. Photoelectrochemical (PEC) sensor, a newly emerging analytical technique with desirable advantages such as remarkable sensitivity, portability, and easy integration, has received much interest (Zhao et al., 2015; Shi et al., 2016; Yan et al., 2015).

Recently, great efforts have been devoted to constructing a high-performance PEC sensing platform bearing tailor-made recognition properties. Various nanostructured semiconductor/quantum dots-based PEC immunosensors (Hu et al., 2013; Yu et al., 2015; Song et al., 2016; Ma et al., 2016; Zhu et al., 2016) (i.e. using antibody/antigen as the biosensing element) and enzyme biosensors (Barroso et al., 2016; Gong et al., 2012; Shen et al., 2015) have been progressed remarkably, focusing on biomolecules analysis. Molecular imprinted polymers (MIPs), termed as “artificial antibodies” have received much attention in PEC sensing (Zhang et al., 2016; Peng et al., 2014; Gong et al., 2015; Fang et al., 2016), in particular utilized for environmental analysis under extreme conditions. Here, for the detection of TPhP, the corresponding natural receptor doesn't exist. And moreover, owing to the rigid structure of TPhP, it is difficult for TPhP to be chemically bound with other host materials, resulting in failure of the formation of MIP (Du et al., 2015; Liu et al., 2016; Wolschke et al., 2016). Thus, currently, how to construct a high-performance PEC sensing platform with tailor-made recognition properties for the detection of TPhP still remains a significant challenge.

Electrospun template directed molecular imprinting technique has been demonstrated to be a viable approach allowing the creation of robust, molecularly imprinted nanofibers with highly selective recognition and easy encapsulation of exotic target molecules (Zhao et al., 2015; Chronakis et al., 2006; Moein et al., 2015; Awokoya et al., 2013). In the present work, we first present a facile approach to synthesize molecularly imprinted electrospun nanofibers (MI-ESNFs) using TPhP as the template

molecule and exploit its PEC sensing for the detection of TPhP using MI-ESNFs incorporated with photoactive BiOI nanoflake arrays (BiOINFs). Molecularly imprinted electrospun nanofibers were prepared with a simple electrospinning method using TPhP and functional polymer of chitosan as the starting materials. The smart integration of MI-ESNFs with visible-light-responsive BiOINFs (Zhao et al., 2013; Gong et al., 2012; Yan et al., 2015) yields a novel MI-ESNFs@BiOINFs nanohybrid as a photoactive electrode. Upon visible-light irradiation, the efficient separation of electron-hole pair could be initiated on the as-prepared photoactive nanohybrid. With the addition of the template molecules TPhP, the specific recognition and rebinding event would occur, thus leading to a strong steric hindrance effects toward the diffusion of electron donors, and consequently a decrease in photocurrent (Scheme 1). On the basis of the effect of TPhP on the PEC responses, a new rapid and sensitive PEC sensor is developed for TPhP sensing. To the best of our knowledge, this is the first report on utilizing MI-ESNFs incorporated with visible-light-responsive BiOINFs for PEC sensing TPhP. The resulting composite of MI-ESNFs@BiOINFs exhibits fine applicability for the determination of TPhP in real water samples.

2. Experimental section

2.1. Chemicals

Triphenyl Phosphate (TPhP), Tris(2-chloroethyl) phosphate (TCEP), Tributyl phosphate (TBP), Tris(2-butoxyethyl) phosphate (TBEP) and Tricresyl phosphate (TCP) were obtained from Aladdin Industrial Co. (Shanghai, China). The FTO (fluorine-doped tin oxide glass) was purchased from NSG, Japan. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KI

(AR, $\geq 98.5\%$), chitosan (BR, deacetylation degree of 80~95%, $M_w \approx 600,000$, Sinopharm Chemical Reagent Co., Ltd), trifluoroacetic acid (TFA, CF_3COOH), dichloromethane (DCM), acetonitrile and other reagents were of analytical grade and were used as received without further purification. Ultrapure water (resistivity $\geq 18 \text{ M}\Omega$) was used during the experiment process. Measurements were performed in 0.1 M Tris (hydroxymethyl) aminomethane hydrochloride buffer solution (Tris-HCl) with 2mM ascorbic acid (AA). The whole experiments were carried out at room temperature.

2.2. Apparatus

The general morphology of the products was characterized by scanning electron microscopy (SEM, JSM-5600). FTIR spectra of the adsorbents were obtained on the Perkin-Elmer PE-983 spectrometer. Ultraviolet–visible (UV–vis) absorption spectra were recorded on a UV-2550 (Daojin) spectrophotometer. The electrospinning setup contains a high-voltage power supply (Tianjin Dongwen, DWLP303-1ACFO) and a syringe pump (Baoding longer, LSP02-1B). Electrochemical and photoelectrochemical measurements were performed on a CHI 660D electrochemical workstation (CHI, USA) with a conventional three electrode system comprising platinum wire as auxiliary electrode, a standard $\text{Hg}/\text{Hg}_2\text{Cl}_2$ in saturated KCl solution as the reference electrode, and the as-prepared MI-ESNFs@BiOINFs or NI-ESNFs@BiOINFs onto FTO electrode as the working electrode. Electrochemical impedance spectra (EIS) were measured in the frequency range from 0.1 Hz ~ 100 kHz with a signal amplitude of 5 mV at CHI 660D. A 500W Xe lamp (Shanghai

LanSheng Electronic Co., China) equipped with a monochromator was used as the irradiation source ($\lambda = 420$ nm).

2.3. Preparation of Molecularly Imprinted Electrospun Nanofibers (MI-ESNFs)

The MI-ESNFs were prepared by electrospinning at room temperature at a high voltage of 15 kV. Briefly, according to the previous reports (Ogunlaja et al., 2014; Teng et al., 2009), 0.6 g of chitosan was first dissolved in 30 mL of trifluoroacetic acid/dichloromethane ($V/V = 7/3$). And then 1 mL of TPhP (0.2 g in acetonitrile) as template was added into the dissolved chitosan solution. After that, the mixture was stirred overnight until a homogeneous electrospinning solution was observed. The resulting solution (5 mL) was loaded in a 20 mL syringe with an 18 gauge needle. An aluminum foil was used as a collector and was positioned 15 cm away from the tip of the needle. After electrospinning, the nanofiber mats were placed in a vacuum chamber for 2 h at 60 °C. To improve the stability and realize the actual usefulness of the as-spun imprinted chitosan nanofibers, a neutralization treatment was carried out by immersing the as-spun nanofibers in 5 M Na_2CO_3 aqueous solution for 3 h (Sangsanoh et al., 2006). After the immersion, the imprinted nanofibers were washed with distilled water until neutral pH was received, then removed the template of TPhP by ethylacetate, and further dried in an oven at 60 °C overnight (labeled as MI-ESNFs). For comparison, non-imprinted polymers were also prepared in the same way but without TPhP templates in the solution while electrospinning (labeled as NI-ESNFs).

2.4. Design and Fabrication of PEC Sensor

Prior to use, the FTO substrates were cleaned by ultrasonication in distilled water and ethanol, respectively. The BiOI modified FTO (BiOINFs/FTO) were prepared according to a successive ionic layer adsorption and reaction (SILAR) approach (Peng et al., 2014; Gong et al., 2012). Briefly, the pre-treated FTO was first immersed in 5 mM $\text{Bi}(\text{NO}_3)_3$ aqueous solution, followed by a subsequent washing step, and then immersed in the 5 mM KI solution. The immersion time for each solution and washing process was set ~ 10 s, respectively. After certain cycles of SILAR, the as-prepared BiOINFs/FTO was dried at room temperature, followed by casting an optimized amount of MI-ESNFs dispersion ($100\ \mu\text{L}$, $2.0\ \text{mg mL}^{-1}$) onto the surface of BiOINFs/FTO and dried at room temperature to obtain an electrode of MI-ESNFs@BiOINFs/FTO. As a control, the electrode of NI-ESNFs@BiOINFs/FTO was also fabricated under the same conditions without using template molecules.

2.5. PEC Measurement

All PEC measurements were performed using a conventional three-electrode system in a quartz cell linked with the electrochemical workstation. Photocurrents were recorded in 0.1 M pH 7.0 Tris-HCl with 2 mM AA before and after the incubation of MI-ESNFs@BiOINFs into different concentration of TPhP aqueous solution for an optimized time of 15 min, respectively.

3. Results and discussion

3.1. Characterization of Molecularly Imprinted Electrospun Nanofibers (MI-ESNFs)

The typical SEM images for the as-formed BiOINFs and MI-ESNFs@BiOINFs onto the FTO substrate are shown in Fig. 1A and 1B, respectively. Free-standing

nanoflakes were observed to be uniformly distributed over the whole FTO with each a lateral dimension in the micrometer size (Fig. 1A). After the subsequent casting process, one can see that the smooth and uniform as-spun imprinted fibers with an average diameter of ~ 50 nm were interlaced layout onto the surface of BiOINFs (Fig. 1B). The generated MI-ESNFs were homogenously dispersed in the framework of crossed BiOI nanoflakes, constructing a 3D interconnected network.

The capability of electron transfer of different electrodes was investigated by electrochemical impedance spectra (EIS) analysis (Fig. 1C). It can be seen that EIS of the bare FTO is composed of a semicircle and a straight line featuring a diffusion-limiting step of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ processes (curve a). With the formation of the crossed BiOINFs onto FTO, the semicircle increases significantly as compared to the bare FTO, suggesting the hindrance effect to the interfacial charge transfer, caused by the formation of the BiOI thin film on the electrode surface (curve b). After the modification of the imprinted TPhP MI-ESNFs on BiOINFs/FTO, the semicircles further increased distinctively (curve c). Obviously, the nonconductive properties of chitosan and TPhP would obstruct electron transfer, resulting in the increased resistance. After removing the template of TPhP, the semicircles decreased (curve d). It may be attributed that removal of TPhP left a lot of cavities in MI-ESNFs, and thus reduced the mass-transfer resistance of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ through MI-ESNFs film, confirming the successful preparation of MI-ESNFs modified BiOINFs.

To get the direct evidence for the successful entrapment of TPhP in the MI-ESNFs, UV spectra and FTIR measurements were carried out (shown in Fig. 2A and Fig. 2B).

As shown in Fig. 2A, the as-prepared TPhP-imprinted ESNFs exhibited a characteristic absorbance peak at 255 nm (curve c), corresponding to the maximum absorbance ($\lambda_{\max}$) of original TPhP solution (curve d). In contrast, after removing the target molecule of TPhP, the characteristic adsorption peak of the TPhP molecule almost disappeared (curve b), similar with that of the NI-ESNFs composite (curve a). Fig. 2B showed the FTIR spectra measurements. The characteristic absorption peaks of chitosan were observed in the FTIR spectra of the as-spun NI-ESNFs and MI-ESNFs, respectively (curve a & b), corresponding to 3459 cm^{-1} (O–H and N–H stretching vibrations), $\sim 2920\text{ cm}^{-1}$ (C–H stretching mode of the alkyl chain), $\sim 1650\text{ cm}^{-1}$ (N–H bending mode), $\sim 1390\text{ cm}^{-1}$ (C–H symmetric bending vibration) and $1000\text{--}1200\text{ cm}^{-1}$ (C–O–C stretching vibrations) (Goyala et al., 2016; Ogunlaja et al., 2014). With the entrapment of TPhP by MI-ESNFs (curve c), there appears several characteristic absorption bands of TPhP: at 3060 cm^{-1} assigned to the C-H stretching vibrations of the aromatic ring in TPhP; 1589 cm^{-1} and 1489 cm^{-1} (the phenyl rings in aromatic compounds); 1294 cm^{-1} (P=O stretching vibrations); and $\sim 950\text{ cm}^{-1}$ from P–O–C in phosphates (Zhang et al., 2015, Alejo-Molina et al., 2016). For the free TPhP, the characteristic absorption peak of P=O was observed at 1298 cm^{-1} (curve d); In contrast, the band at 3459 cm^{-1} , mainly due to the N-H stretching vibrations, shifted to the lower wavenumber of 3422 cm^{-1} . The shift of P=O and N-H stretching vibration to the lower wavenumber implies that the hydrogen bond could be formed between P=O groups of TPhP and N-H groups of chitosan. After removing the target molecule of TPhP, the characteristic peak of the TPhP molecule disappeared and the FTIR

spectrum became identical to that of the NI-ESNFS composite. UV and FTIR measurements further demonstrated the successful entrapment of TPhP in the MI-ESNFs.

3.2. Optimization of detection conditions

To get high-performance visible-light-responsive PEC responses for TPhP detection, the experimental parameters were optimized. As shown in Fig. 3A, the photocurrent of BiOI rises at first up to 30 cycles and then decreases upon increasing the SILAR cycles. With the (BiOI)_n layer increased, the amount of photoactive material increased, resulting in the increase of the photocurrent. On the other hand, due to the increase of self-assembled layers, the barrier effect for the charge transfer became dominate. Thus, 30 cycles is optimal. As the recognition element, the amount of MI-ESNFs dispersed onto the BiOINFs/FTO sharply influenced the PEC response of TPhP. The final PEC response of TPhP at MI-ESNFs@BiOINFs /FTO first increased up to 100 μL as a function of different volumes of MI-ESNFs dispersion (2.0 mg L^{-1}) onto BiOINFs/FTO, and then decreased at higher amounts (Fig. 3B).

The PEC responses of MI-ESNFs@BiOINFs /FTO also depend on the pH. Fig. 3C shows the variations of the photocurrent at MI-ESNFs@BiOINFs with the solution pH. Considering the stability of the MI-ESNFs, we start from the pH 6.5. Obviously, the maximum peak current was obtained at pH 7.0 in the pH range from 6.5 to 8.5. Immersion time is another influential parameter in PEC analysis. With prolonging the immersion time in TPhP solution, the photocurrent was decreased greatly during the initial time for 15 min and then became stable (Fig. 3D). When the immersion time

was longer than 15 min, the binding interactions (recognition process) reached saturation. Thus, the optimum incubation time is 15 min for the PEC determination of TPhP.

3.3 Analytical performance for the detection of TPhP

Under optimized experimental conditions, the photocurrents of MI-ESNFs@BiOINFs modified electrode were recorded in 0.1 M Tris-HCl (pH = 7.0) buffer solution containing different concentrations of TPhP (shown in Fig. 4A). With increasing concentrations of TPhP in the immersion solution, the produced photocurrent of MI-ESNFs@BiOINFs /FTO decreased successively, indicating that increasing amount of TPhP entrapped on MI-ESNFs enhanced the steric hindrances for the diffusion of AA to the sensing interface. It can be found that the relative change of the photocurrent ($\Delta i/i_0$, Δi equals i_0-i , where i_0 and i is the photocurrent before and after incubation in TPhP) is linear proportional to the logarithm value of TPhP concentrations in the range of 0.01 to 500.0 ng mL⁻¹ (Fig. 4B), with a correlation coefficient of $R = 0.9965$. The corresponding linearization equation is the relative change of the photocurrent $(i_0-i)/i_0 = 0.3994 + 0.1694 \log c/\text{ng mL}^{-1}$. The detection limit (S/N=3) is estimated to be 0.008 ng mL⁻¹ (i.e. 0.008 ppb) based on the response of three times the standard deviation of zero-dose response ($n = 6$). The achieved detection limit is significantly lower than the reported values: 0.032 ppb from SPE-LC-MS (Rodil et al., 2005), 0.01 ppb obtained using GC-MS (Andresen et al., 2004), and also comparable with those obtained using SPE-UHPLC-UV (0.008 ppb) (Maciej Mazur, 2014) as well as SPE-LC-MS/MS (0.006 ppb) (Wang et al., 2011).

Compared with these well-established methods, the cost of the present PEC sensor is greatly reduced because of much simpler and more commonly employed instruments used with more suitability for in situ and on-site measurements of TPhP.

3.4. Selectivity of the PEC sensor

To investigate the selectivity of the as-prepared PEC sensor towards TPhP, some representative OPFRs including TCEP, TBP, TBEP, and TCP, as well as PO_4^{3-} were selected as the interfering substances, respectively (Fig. 5). The selectivity of the PEC sensor for TPhP in a two-component system with the coexistence of TPhP (10 ng mL^{-1}) and each of the interference compounds (200 ng mL^{-1}) was evaluated, displaying that the photocurrent deviations are all less than 7%. These data adequately reveals that this MI-ESNFs@BiOINFs photoelectrode possess high selectivity. Evidently, the superior selectivity toward the detection of TPhP can be mainly due to the shape identification and the hydrogen bond identification from the as-spun imprinted ESNFs.

3.5. Reproducibility, Stability, and Regeneration of PFOA PEC Sensor

To investigate the reproducibility of the as-fabricated sensor, the intraassay and interassay measurements were performed. The intraassay RSD is 2.75% for determining of 1.0 ng mL^{-1} TPhP with five replicate measurements, while the interassay RSD is 3.24% by measuring 1.0 ng mL^{-1} TPhP with five same PEC sensors made under the same conditions independently, indicating an acceptable reproducibility. The stability of the photoactive electrode is very essential for the in situ monitoring pollutant level in water. Time-dependent photocurrent responses of the

PEC sensor were recorded under visible light irradiation repeatedly (Fig. S1). It is clear that the photocurrent does not change. Furthermore, the long-term storage of the PEC sensor was also investigated in 0.1 M Tris-HCl (pH 7.0) containing 0.1 M AA. No obvious decrease in the response of TPhP was observed in the first 10-day storage. After a 30-day storage period, the sensor retained 95% of its initial current response, demonstrating a good stability of the PEC sensor. A good regeneration and recycle performance of the as-prepared PEC sensor was observed.

3.5 Analysis of the Real Samples

To further demonstrate the practicality of the present PEC sensor, it was evaluated by processing real water samples. Three samples were collected from Yangtze River (Wuhan, China), Eastlake (Wuhan, China) and tap water. Before measurements, all water samples were treated by filtering through a nylon film (0.45 μm). As shown in Table S1, different concentrations of TPhP (0, 10 and 100 ng mL^{-1}) were added in three river water samples. The average recoveries of PEC sensor were from 92.8% to 108.2%, showing an acceptable feasibility to detect TPhP in real water with high accuracy and reproducibility.

4. Conclusion

In summary, this work first exploited the use of molecularly imprinted electrospun nanofibers incorporated with BiOINFs for PEC sensing. Using the as-prepared MI-ESNFs as the recognition unit, the smart integration of electrospun MI-ESNFs and visible-light-responsive BiOINFs yields a new class of promising PEC sensing probe.

The resulting sensor showed good sensitivity, reproducibility and fine applicability for the detection of TPhP. We believe that the proposed PEC sensor would not only benefit the field monitoring of TPhP but also present a promising strategy for detecting other OPFRs in the environment.

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Figure Captions

Scheme 1. Schematic illustration of the formation process of (A) the MI-ESNFs, and (B) the principle of PEC determination of TPhP using MI-ESNFs@BiOINFs/FTO.

Fig. 1 Typical SEM images of (A) BiOINFs/FTO, (B) MI-ESNFs@BiOINFs/FTO, and (C) Electrochemical impedance spectra of (a) FTO foil, (b) BiOINFs/FTO, and MI-ESNFs@BiOINFs/FTO before (c) and after (d) removal of PFOA in 0.1 M PBS containing 2.5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) mixture. The applied frequency was from 0.1 Hz to 100 kHz.

Fig. 2 (A) UV spectra and (B) FTIR spectra of (a) NI-ESNFs, (b) MI-ESNFs, (c) TPhP imprinted MI-ESNFs, and (d) pure TPhP.

Fig. 3 Effects of (A) the cycle number of SILAR on the photocurrent responses of BiOINFs/FTO; (B) the amount of MI-ESNFs solution pre-cast onto BiOINFs/FTO in TPhP (10 ng mL^{-1}) solution; (C) The solution pH of 0.1 M Tris-HCl on the photocurrent responses of MI-ESNFs@BiOINFs/FTO; (D) The immersion time of MI-ESNFs@BiOINFs/FTO into TPhP (10 ng mL^{-1}) solution. Supporting electrolyte: 0.1 M pH 7.0 Tris-HCl with 2 mM AA.

Fig. 4 (A) Photocurrent responses of MI-ESNFs@BiOINFs/FTO toward TPhP at

increasing concentrations (from top to bottom, 0, 0.01, 0.02, 0.05, 0.5, 1.0, 10, 20, 100, 200 and 500 ng mL⁻¹) in the supporting electrolyte of 0.1 M pH 7.0 Tris-HCl with 2 mM AA. (B) Linear calibration curve. Error bars indicate the standard deviation of five repeated measurements.

Fig. 5 Relative photocurrents of MI-ESNFs@BiOINFs/FTO in the presence of 10 ng mL⁻¹ TPhP alone and with 200 ng mL⁻¹ each for TCEP, TBP, TBEP, TCP, and PO₄³⁻, respectively.