Photoelectrochemical sensor based on molecularly imprinted film modified hierarchical branched titanium dioxide nanorods for chlorpyrifos detection

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ABSTRACT

A photoelectrochemical (PEC) sensor based on hierarchical branched titanium dioxide nanorods (B-TiO$_2$ NRs) modified with molecularly imprinted polymer (MIP) was constructed for sensitive and efficient detection of chlorpyris (CPF). B-TiO$_2$ NRs were grown directly on fluorine doped tin oxide substrate by the hydrothermal method and employed as matrix for immobilization of MIP. P-aminothiophenol (ATP) and CPF were assembled on the surface of B-TiO$_2$ NRs by formation of hydrogen-bonding interactions through electropolymerization in the MIP preparation process. The MIP was characterized by scanning electron microscopy, and further confirmed by cyclic voltammetry to prove the successful synthesis. In the proposed sensing platform, the photocurrent response is inversely proportional to the CPF concentration because the insulating layer hinders the harvesting of light and electron transfer with increasing of CPF concentration. Moreover, the MIP based B-TiO$_2$ NRs (MIP-B-TiO$_2$ NRs) had an excellent recognition capacity for specific detection CPF over other pesticides. The PEC sensing platform is developed for the detection of CPF in the linear range from 0.01 ng mL^{-1} to 100 ng mL^{-1} with a low detection limit of 7.4 pg mL^{-1}. The proposed sensor offered a promising platform for application in detecting pesticide residuals and other environment deleterious chemicals with excellent sensitivity and selectivity, low interference and high stability.

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1. Introduction

The application of pesticides is becoming more and more extensive in agricultural products to combat pests [1]. Nevertheless, their excessive use to keep fruits and vegetables from pests may result in air, water, soil and crop pollution, eventually harm to human through enrichment of food chain [2]. Chlorpyrifos (CPF), as one of the most important organophosphorus pesticides, is widely utilized for insect control [3]. In addition, CPF residues will harm to human health because of its high toxicity as an inhibitor of acetylcholinesterase which is an indispensable substance for normal function of nervous system [4]. Therefore, monitoring the behavior of CPF residues is important for human health. Nowadays, a variety of analytical method have already been developed to detect organophosphorus pesticides by using of complicated techniques, such as gas chromatography-mass spectrometry [5] and high-performance liquid chromatography [6]. However, these above-mentioned analytical methods often require expensive equipment, time-consuming and troublesome sample pretreatment [7,8].

Recently, photoelectrochemical (PEC) as a promising analytical method has been developed for detection of various target analyte [9–11], although other methods have been applied [12]. Owing to the separation of excitation source and detection signal [13–15], the background signal of PEC sensor is reduced. In addition, the PEC sensor offering the advantages of low cost [16] and high sensitivity [17,18], which is promising for detecting low concentration of organophosphorus pesticides in the environment [19]. As we all know, one important aspect for preparing PEC sensor is to find photoactive materials that can be used to convert a light input into a current signal. Driven by this aim, branched titanium dioxide nanorods (B-TiO$_2$ NRs) has been proved to be excellent semiconductor material due to their high photoelectric activity under UV irradiation attributed to morphology and specific features such as low density, high surface-to-volume ratio [20] and the effect of void space [21–26]. Compared with bare TiO$_2$, B-TiO$_2$ NRs have

higher charge transport rate and excellent light absorption properties [27,28]. Moreover, B-TiO$_2$ NRs as a substrate material for constructing PEC sensor could effectively overcome the disadvantage of slow mass transfer in the polymers [29]. In this work, we choose fluorine-doped tin oxide (FTO) as a substrate to fix B-TiO$_2$ arrays. FTO exhibits high optical transparency and high electrical conductance simultaneously [30]. Although some sensors have been reported to immobilize materials on indium-tin oxide (ITO) [31,32], the FTO is more stable than the ITO in acid condition [33]. In addition, FTO glasses are superior to ordinary glassy carbon or platinum electrode from the cost consideration [34]. Although the application of TiO$_2$ has been widely studied in PEC sensor [35–37], its selectivity in PEC for detection of harmful low-level pollutants is poor.

Recently, many techniques have been developed to improve the selectivity of PEC sensor such as molecular imprinting technique, which is a promising strategy to provide specific recognition sites for detecting pesticides [38,39]. Molecularly imprinted polymer (MIP) is considered to be specific polymers with a high chemical stability, easy synthesis and low cost [40,41], polymer such as polypyrrole have been reported [42]. Traditionally, the preparation of MIP is performed in radical copolymerization of functional monomer in the presence of template. However, this way suffers from some intrinsic limitations such as exhausting template removal and the low amount of effective imprinted sites [43]. Herein, surface molecular self-assembly strategy which involves the self-assembly of template molecule and functional monomer has attracted much attention because of the total amount of effective imprinted sites enhanced by forming simultaneously surface imprinted sites and interior imprinted sites [44–46]. After the removal of template molecules from the polymer, complementary cavities generated to the shape, size of the target analyte leaves in the film onto the surface of B-TiO$_2$ NRs [47] and then B-TiO$_2$ NRs were exposure to exciting light to generate the photocurrent [48]. Consequently, photocurrent change can be observed owing to MIP could specifically recognize template [49].

In the present study, PEC sensing platform for CPF detection was proposed by preparing hierarchical B-TiO$_2$ NRs modified with molecularly imprinted polymer. The desirable morphologies of B-TiO$_2$ NRs were introduced to improve the signal response and the effective surface area of the electrode. In addition, surface molecular self-assembly strategy was developed in order to improve the selectivity of senor. CPF and *p*-aminothiophenol were used as template molecule and functional monomer respectively in the preparation of molecularly imprinted polymers. Moreover, glucose was exploited as an efficient electron donor for scavenging photogenerated holes as the supporting electrolyte for photocurrent measurements. Finally, photocurrent decreases with increasing CPF concentration after removing template molecules and adsorbing CPF. This proposed sensing platform exhibited good stability, precision, and reproducibility, indicating its promising applications in future.

2. Experimental

2.1. Materials

Titanium butoxide and *p*-aminothiophenol (ATP) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Titanium trichloride (TiCl$_3$) and organophosphate pesticide chlorpyrifos (CPF) were obtained from Aladdin Bio-chem Technology Co. Ltd. (China). Other reagents were of analytical grade. Pesticide CPF was prepared in acetonitrile and stored at 4 °C in the dark while not in use. ATP was stored at 4 °C in a refrigerator and avoided exposure to light. Phosphate buffer solution (PBS 0.05 M, pH 6.86) was prepared from KH$_2$PO$_4$ and Na$_2$HPO$_4$ in ultrapure water. KCl (0.1 M) was used as the supporting electrolyte in electrochemical measurements. Ultrapure water ($\geq$18 MΩ cm) was used for the preparation of aqueous solutions.

2.2. Apparatus

The morphology of the molecularly imprinted polymer (MIP) modified on the B-TiO$_2$ NRs was observed using a scanning electron microscope (SEM, FEI Co., USA). Electrochemical measurement was performed using a CHI 760D workstation (Chenhua, Shanghai, China); a conventional three-electrode system was used for electrochemical measurement. A platinum wire was used as the auxiliary electrode and a silver-silver chloride (Ag/AgCl) electrode was used as the reference electrode.

2.3. Preparation of B-TiO$_2$ NRs

TiO$_2$ NRs were grown directly on fluorine-doped tin oxide (FTO) substrate with hydrothermal method according to previously reported with some modification [50]. Typically, the mixed solution was prepared with 1:1 ultrapure water and hydrochloric acid (HCl). Then the mixture was stirred at room temperature for 5 min before the addition of 0.4 mL titanium butoxide. After stirring for another 30 min, one piece of FTO substrate which has been ultrasonically cleaned in solution of acetone, ethanol and ultrapure water for 10 min respectively was placed at an angle against the wall of the teflon-liner with the conducting side facing down in a sealed teflon-lined stainless steel autoclave containing mixed solution. The hydrothermal synthesis was performed at 150 °C for 4 h in an electric oven. After the completion of the reaction, the autoclave was cooled to room temperature. Then the TiO$_2$ NRs modified FTO was taken out and rinsed thoroughly with ultrapure water and dry.

After synthesis of TiO$_2$ NRs, the branches were grown on surface of TiO$_2$ NRs. Firstly, 20 mL ultrapure water was mixed with 0.1–1 mL concentrated HCl with stirring for 5 min before the addition of TiCl$_3$. After stirring for another 5 min, the TiO$_2$ NRs were rinsed with mixed solution, placing in oven at 80 °C for 30–90 min. Then the FTO was taken out and rinsed with ultrapure water and dry in oven at 80 °C.

2.4. Fabrication of the molecularly imprinted based PEC sensor

The whole preparation process of the PEC sensor is shown in Scheme 1. Typically, this process could be summarized in three steps: (1) B-TiO$_2$ NRs grown vertically on FTO substrate; (2) electropolymerization of MIP on the surface of B-TiO$_2$ NRs and (3) removal of the template CPF molecules from MIP. The MIP modified electrode was prepared by methods that have been reported [51]. Briefly, the as-prepared B-TiO$_2$ NRs were immersed in an ethanol solution containing 10 mM ATP. After a reaction period of 24 h at room temperature, the electrode was taken out and rinsed with ethanol and ultrapure water to remove physically absorbed ATP. Then, the ATP modified B-TiO$_2$ NRs was immersed into a 1 mM solution of CPF in acetonitrile for 6 h. After that, the electrode was taken out, rinsed with ethanol to remove physically absorbed CPF, and then dried under nitrogen gas flow at the ambient temperature. CPF molecules accordingly assembled into the ATP modified B-TiO$_2$ NRs through hydrogen bond interactions between the amino groups (-NH$_2$) of ATP and the nitrogen/oxygen atom of CPF.

To further enhance the stability of polymer, these CPF molecules assembled onto the ATP-modified B-TiO$_2$ NRs surface and formed surface imprinted sites. The ATP and CPF modified B-TiO$_2$ NRs electrode was immersed in the aqueous electrolyte solution containing 5 mM ATP, 0.1 M KCl, 0.1 mM CPF and 0.05 M PBS (pH 6.86). After the solution was deoxygenated by bubbling nitrogen gas for about 15 min, the electropolymerization was performed by the applica-