



High sensitive visible light photoelectrochemical sensor based on in-situ prepared flexible Sn₃O₄ nanosheets and molecularly imprinted polymers



Juan Wang^a, Qin Xu^{a,*}, Wei Wei Xia^b, Yun Shu^a, Dangqin Jin^c, Yang Zang^a, Xiaoya Hu^{a,*}

^a School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China

^b College of Physics Science and Technology & Institute of Optoelectronic Technology, Yangzhou University, Yangzhou 225002, China

^c Department of Chemical Engineering, Yangzhou Polytechnic Institute, Yangzhou 225127, China

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ABSTRACT

This work described the construction of a novel photoelectrochemical platform with Sn₃O₄ which was in-situ decorated on a carbon fiber paper (Sn₃O₄@CFP) as the visible light-active species, and molecularly imprinted polymers (MIPs) as the recognition element. This is the first attempt to apply Sn₃O₄ in the field of photoelectrochemical sensors. Sn₃O₄ nanoplates were directly grown on CFPs by a simple hydrothermal process. The MIP layer with special selectivity for 2,4-dichlorophenoxyacetic acid (2,4-D), a kind of carcinogen, was prepared on the Sn₃O₄@CFP by electropolymerizing pyrrole in the presence of 2,4-D. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) techniques were used to characterize the as-prepared Sn₃O₄@CFP. Benefiting from the structural advantages of Sn₃O₄@CFP and selectivity of MIP, the binder-free PEC sensor affords a linearity from 5.0×10^{-11} to 1.0×10^{-7} M for 2,4-D and the detection limit was down to 1.08×10^{-11} M. This PEC platform demonstrates excellent stability, reproducibility, remarkably convenience, and cost-effective advantages, as well as low detection limit. The successful detection of 2,4-D in bean sprout samples has been acquired. Furthermore, the flexibility of the Sn₃O₄@CFP offers an easy integration of PEC sensor onto different non-planar shape and size surfaces which extends its applications for sensors construction.

1. Introduction

Photoelectrochemical (PEC) technique is now in its rapid development stage because of its low cost, easy miniaturization, high sensitivity, rapid turnaround time and simple instruments [1–3]. Under the irradiation of light, the intensity of photocurrent generated from a PEC sensor is in proportion to the concentration of the analyte, which can be used for the quantification analysis. Photoactive materials and recognition elements are two crucial factors that determine the sensitivity and selectivity of the PEC sensors. TiO₂ [4] and ZnO [5] et al. have been firstly used as the photoactive materials. However, these semiconductors can only be activated by ultraviolet (UV) light because of their wide bandgaps.

Over the past twenty years, researchers have paid much attention to look for efficient visible-light-driven photoactive materials. Progresses have been made on semiconductors such as semiconducting organic-inorganic nanodots heterojunctions [6], polyaniline-sensitized 3D inverse opal TiO₂ [7], BiOI [8], graphene quantum dots/3D bismuth oxyiodine (NFGQDs/3D BiOI [9], MoS₂ [10], and C₃N₄ [11], etc. However, some of them could not be prepared for large-scale and

applied in some biological systems because some of the metal sources were toxic or expensive. There has been a strong push to develop alternatives that could be produced from abundant metals such as iron or tin, and some successes have been achieved with tin oxides.

Tin oxides have been widely applied in the areas of transparent electrodes, sensors [12] and lithiumion batteries [13] because they have the advantages such as excellent optical and electrical properties, natural abundance, non-toxicity and a strong resistance against acidic/alkali solutions. SnO₂ and SnO are the common existence status for tin based oxides. However, heterovalent tin oxides, including Sn₅O₆, Sn₃O₄ and Sn₂O₃, are taking increasing attentions and have been demonstrated to possess special performances compared to both SnO₂ and SnO. As the firstly identified non-stoichiometric tin oxide, Sn₃O₄ is a thermodynamically stable intermediate composition in the Sn-O phase diagram [14]. It has attracted a great deal of attention for its good photocatalytic performance in energy conversion and remediation under visible light irradiation. Recent studies have introduced the photocatalytic and photoelectric properties of Sn₃O₄ for the production of hydrogen and degradation of dyes [15], but few work has shed light to its potential for PEC sensors.

* Corresponding authors.

E-mail addresses: xuqin@yzu.edu.cn, yz_xiner@163.com (Q. Xu), xyhu@yzu.edu.cn (X. Hu).

An ideal photoactive electrode should have controllable morphology and surface structure and a uniform dispersion of the active sites. The conventional process for the fabrication of a photoactive electrode is to cast the photoactive materials on a conductive substrate such as ITO or glassy carbon electrodes (GCE). A binder, such as nafion or chitosan, was used to improve the stability of the electrode. A major drawback of the casting process is that it usually induced the agglomerations of the nanomaterials and decreased the active surface area. Furthermore, the use of binders adds complexity to the fabrication process, and the degradation of binders would result in the undesired loss of photoactive materials and subsequent decrease in catalytic performance. In addition, GCE is not a miniaturized electrode, and requires tedious polish procedure between experiments, which are not suitable for fast analytical procedure. Therefore, the in-situ preparation of the visible-light photoactive material on a conductive substrate is highly needed. This preparation process could avoid undesirable effect coming from dropping process and improve the electrical conductivity between diffusion layer and catalyst supports. Using in situ synthesis method also avoids the use of a binder, which eliminates over-potential and other side reactions, and enhances the photoelectrochemical performance.

Recognition element is the other important parts of the PEC sensors. liposome [16], DNA [17], cells, peptide [18], enzyme, antibody [19,20], aptamer [21] and molecularly imprinted polymers (MIPs) [22,23], etc., have always been introduced to achieve this objective. Compared with the biomolecular recognition elements, MIPs have lots of advantages, such as potential reusability, resistance to microbial spoilage, good stability for long-time storage and custom synthesis without inoculating laboratory animals. To date, MIPs have been successfully used with different types of transducers [24]. However, only few work reported the integration of MIP with PEC transducers. It may be due to the reason that PEC sensor is a recently developed technique. Zhao [25], Yu [23] and Gong [26] groups did a great deal of pioneering work in this area. TiO_2 [27,28], BiOI [8], AgI-BiOI [26] and CdTe [29] photoactive materials were used.

Given the above status of PEC sensor research, there appear considerable scopes for developing simple, inexpensive but high performance PEC sensors. With above objective, Sn_3O_4 was used as the photoactive material of a PEC sensor in the present study. 2,4-Dichlorophenoxyacetic acid (2,4-D) was selected for analysis because it was regarded as one of the “probably carcinogenic compound to humans” (Group 2B) [30]. Scheme 1 illustrated the PEC sensor construction (panel A) and 2,4-D detection procedures (panel B). A facile hydrothermal method was used for the direct growth of Sn_3O_4 on a conductive carbon fiber paper (CFP). This approach simplifies the nanoparticle preparation process and post-electrode modification steps into one overall route by assembling Sn_3O_4 directly onto a CFP support. This process is beneficial to maintain the electrode stability. Furthermore, the flexibility or bendability of CFP offers an easy integration of PEC sensor onto different non-planar shape and size surfaces. The 2,4-D imprinted film was prepared on the Sn_3O_4 @CFP by electropolymerization of pyrrole in the existence of 2,4-D. After removing 2,4-D, the tailor-made cavities serving as specific recognition sites were left throughout the polypyrrole (PPy) film. In the presence of 2,4-D, the photocurrent was decreased owing to the specific capture of 2,4-D by MIP. Furthermore, the proposed detection method could effectively exclude the interferences because of the selectivity of MIP. Through the combination of the merit characteristics of Sn_3O_4 @CFP and MIP, the sensitivity and selectivity of the sensing platform toward 2,4-D detection are significantly improved. We also demonstrated that the established 2,4-D photoelectrochemical sensor can be used to detect 2,4-D directly in food samples. To our best knowledge, this study is the first time to use Sn_3O_4 for the construction of PEC sensor and develop the flexible photoelectrochemical sensor by a simple one-step process.

2. Experimental

2.1. Chemicals

The carbon fiber papers (CFPs) used in this study were purchased from Toray, Japan. Tin(II) chloride dehydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), sodium citrate dehydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) were obtained from Sinopharm chemical Reagent Co., Ltd (Shanghai, China). 2,4-dichlorophenol (2,4-DCP), 4-(2,4-dichlorophenoxy)butyric acid (2,4-DB), 2,4-dichlorobenzoic acid (2,4-DCB) and 2,4-dichlorophenylacetic acid (2,4-DCPA) were all bought from Aladdin Reagent Company. 2,4-D was purchased from Chem. Service (American). 2,4-D powder was dissolved by ethanol to prepare the stock solution (0.1 M), and then was diluted to prepare a series concentrations of 2,4-D working solutions using 10% ethanol aqueous solution. The bean sprouts were bought from the local food markets.

2.2. Apparatus

A field emission scanning electron microscope (SEM) (Zeiss Supra 55, Germany) was used to characterize the morphologies of CFP, Sn_3O_4 @CFP and MIPPy/ Sn_3O_4 @CFP. The elemental analysis was done with energy dispersive X-ray spectroscopy (EDS) system attached to SEM. The phase and valence state analysis of Sn_3O_4 @CFP and MIPPy/ Sn_3O_4 @CFP were performed by powder X-ray diffractions (XRD, Bruker D8Advance, Germany) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB-250Xi, America), respectively. A PHS-25 model pH meter (Shanghai Leici Instruments) was used to adjust the pH. All the electrochemical experiments were recorded on a CHI 660D electrochemical analyzer (Shanghai Chenhua, China). The photoelectrochemical experiments were recorded on a CIMPS-2 workstation (Zennium, Zahner-Elektrik GmbH & Co. KG, Germany) by using a 500 W WLC02 (a type of white light source) (4300 k # 1522, Zahner-Elektrik) as the visible irradiation source. The wavelength of this light was in the visible-light spectral region ($564 \pm 60 \text{ nm}$). The photocurrent response (I-t) curves were recorded at the bias potential of 0.0 V. All the experiments were performed by a conventional three-electrode system at room temperature. The auxiliary electrode is a platinum coil electrode. The reference electrode is a commercial saturated Ag/AgCl electrode. Both of the auxiliary electrode and the reference electrode were obtained from Gauss Union Technology Co., Ltd (Wuhan, China). A bare or modified CFP electrode configuring with Sn_3O_4 , MIPPy@ Sn_3O_4 or NIPPy@ Sn_3O_4 was acted as the working electrode. The surface area of CFP working electrodes in this study was $1.0 \times 1.0 \text{ cm}^2$.

2.3. Preparation of Sn_3O_4 @CFP

Before the growth of Sn_3O_4 , CFP was firstly immersed in acetone and sonicated for 15 min to remove any surface organic impurities, and then washed with water and ethanol thoroughly [31]. The 3D cross-linked Sn_3O_4 nanoflakes were directly prepared on CFP through a one-step hydrothermal reaction [32]. The details for the preparation of Sn_3O_4 @CFP were as follows. Firstly, ethanol and deionized water with the same volume (20 ml) were mixed in a 100 ml beaker and stirred to ensure complete mixing. Then, 1.073 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 2.940 g $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ were dissolved into the mixture and agitated for approximately 1 h. The resulting mixture was poured into a Teflon-lined stainless-steel autoclave (50 ml), and a piece of CFP (3 cm \times 4 cm) was immersed vertically into the solution. Finally, a simple hydrothermal process was carried out at 180 °C for the growth of Sn_3O_4 . After 12 h, the autoclave was cooled down to room temperature naturally. By ultrasonically washed several times with water and ethanol, the product was dried at 60 °C overnight. The color of CFP changed from dark gray to dark brown after the reaction, suggesting the formation of Sn_3O_4 on CFP. The resulting sample was denoted as Sn_3O_4 @CFP, which was then

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