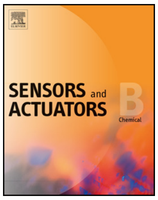
Sensors and Actuators B 259 (2018) 394–401

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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



A self-powered sensor based on molecularly imprinted polymer-coupled graphitic carbon nitride photoanode for selective detection of bisphenol A

Kai Yan, Yaohua Yang, Jingdong Zhang*

Key laboratory of Material Chemistry for Energy Conversion and Storage (Ministry of Education), School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Luoyu Road 1037, Wuhan 430074, PR China

ARTICLE INFO

Article history:
Received 10 August 2017
Received in revised form
17 November 2017
Accepted 13 December 2017
Available online 14 December 2017

Keywords:
Self-powered sensor
Photofuel cell
Graphitic carbon nitride
Molecularly imprinted polymer
Bisphenol A

ABSTRACT

A visible light-induced self-powered sensor for selective detection of bisphenol A (BPA) based on photofuel cell (PFC) was proposed. The PFC was constructed with a Pt cathode and a photoanode which was prepared by modifying fluoride doped tin oxide (FTO) electrode with graphitic carbon nitride (g-C_3N_4) and molecularly imprinted polymer (MIP). The MIP/g-C_3N_4/FTO photoanode possessed high photoelectrocatalytic activity of g-C_3N_4 and binding ability of MIP towards BPA. Under visible light illumination, the PFC generated different output power densities towards varied concentrations of BPA, and thus it was proposed as a self-powered sensor for BPA. The maximum output power density of the sensor was linearly proportional to the logarithm of BPA concentration ranging from 5 to 100 μmol L^{-1}. Moreover, the proposed self-powered sensor exhibited good selectivity, reproducibility and stability for BPA detection.

1. Introduction

Bisphenol A (BPA), namely 4,4′-(1-methylethylethylidene) bisphenol, is an important organic compound widely used as a monomer in the production of polycarbonate and epoxy resin [1,2]. However, the release of BPA from plastic products into the environment has threatened the human beings' health [3]. It has been reported that BPA could interact with estrogen receptors [4] and act as a typical estrogenic endocrine interferon [5]. Human exposure to BPA is linked to cardiovascular diseases, liver abnormalities, adverse effects on the reproductive system, and obesity [6]. Thus, it is of great significance to develop highly sensitive and selective strategies to detect BPA in water samples. Different methods such as high performance liquid chromatography (HPLC) [7], gas chromatography coupled with mass spectrometry (GC–MS) [8], capillary electrophoresis [9], enzyme linked immunosorbent assays (ELISA) [10], electroanalysis [11] and photoelectrochemical sensing [12] have been developed for BPA detection.

Photocatalysis is a representative advanced oxidation process for effective degradation of BPA and other organic pollutants [13–15]. Since photocatalytic oxidation process could generate electricity, photofuel cell (PFC) using organic compounds as fuel has been considered as a promising device for simultaneous pollutant removal and electricity generation [16–19]. Recently, our group has successfully fabricated PFC devices for developing self-powered sensors which could directly provide the responsive signal for sensing without using external electric source [20,21]. Compared to previously reported enzymatic self-powered sensors [22], the PFC-based sensor can effectively avoid the drawbacks of enzyme such as short durability and instability. However, unlike the high specificity of enzyme, photocatalyst can induce the reactions of many compounds [23], which limits the selectivity of PFC-based sensor.

Molecularly imprinted polymers (MIPs) are artificial recognition materials which have been extensively introduced in various sensing platforms to improve the selectivity of detection [24–26]. Compared with biological recognition elements such as antibodies, aptamers and enzymes, MIPs have several advantages including low cost, high storage stability, easy preparation and applicability in harsh chemical media [27]. So far, BPA-binding MIPs have been successfully synthesized and employed to fabricate fluorescent [28], electrochemical [29], and photoelectrochemical [30] sensors for selective detection of BPA.

In the present work, we proposed a novel self-powered sensor for selective detection of BPA based on MIP-coupled PFC.

---

* Corresponding author.
E-mail address: zhangjd@mail.hust.edu.cn (J. Zhang).

https://doi.org/10.1016/j.snb.2017.12.075

Recently, we have proposed an enzyme-free self-powered sensor for glucose detection based on a glucose-H_2O_2 PFC consisting of a $Ni(OH)_2/CdS/TiO_2$ photoanode and a hemin-graphene nanocomposite coated cathode [20]. Furthermore, to simply the configuration of electrodes, we have designed a glucose-air PFC constructed with a $Ni(OH)_2/TiO_2$ photoanode and a Pt cathode [21]. However, both sensors were developed for glucose sensing by utilizing the catalytic activity of $Ni(OH)_2$ toward the oxidation of glucose. In the present work, in order to broaden the PFC-based self-powered sensors to detection of environmental pollutants represented by BPA, we synthesized graphitic carbon nitride (g-C_3N_4), a metal-free semiconductor with narrow band gap, to serve as visible light-responsive material for construction of PFC. Actually, due to its eco-friendly preparation and superior photoelectric properties [31,32], g-C_3N_4 has been intensively explored as outstanding photocatalyst for degradation of pollutants and photoelectrochemical sensing [33–35]. Herein g-C_3N_4 was incorporated with MIP to fabricate a PFC possessing good selectivity, which could generate suitable power output under visible light illumination to drive the sensing process of BPA.

2. Experimental

2.1. Preparation of molecularly imprinted polymer

MIP was prepared according to previous reports [36,37]. Briefly, 0.228 g BPA and 430 μL 4-vinylpyridine (4-VP) were dissolved in 30 mL acetonitrile. The mixture was sealed and stirred for 60 min to assure the fully reaction of template molecule and the functional monomer. Then, 3.8 mL ethylene glycol dimethacrylate (EGDMA) as cross liker and 50 mg 2,2-azo-bis-iso-butyronitrile (AIBN) as radical initiator were added successively to the solution. Meanwhile, nitrogen gas was purged into the system for removal of oxygen. Subsequently, the reaction vessel was sealed and transferred to water bath at 60 °C. After polymerization for 24 h, the resulting polymer was dried and pulverized in a mortar. Regular-sized particles between 37.5 μm and 70.0 μm were obtained using different mesh sieves. Afterwards, the polymer particles were washed to remove template (BPA) molecules using an extraction solvent mixture of methanol and acetic acid (9:1 v/v) for 48 h in a Soxhlet apparatus. Then, the polymers were washed with methanol for 12 h and dried at 60 °C in a vacuum oven. Non-imprinted polymer (NIP) was prepared in the same way without the addition of the template molecule.

2.2. Static adsorption experiments

The static adsorption experiments were carried out in brown sample bottles containing 10 mL methanol solution of BPA at different initial concentrations (C_0). Then, 50 mg MIP was added into the each solution. After shaking for 12 h, the adsorption equilibrium was reached and the residual concentration (C_s) of BPA in the solution was determined using a TU-1900 UV–vis spectrophotometer (Beijing Purkinje General Instrument Company, China). The equilibrium adsorption capacity (Q) was calculated according to $Q = V(C_0 - C_s)/m$, where m is the mass of MIP and V is the volume of reaction solution. The adsorption capacity test time was 12 h. All the adsorption experiments were repeated three times. For comparison, the static adsorption experiments for NIP were also carried out using NIP instead of MIP.

2.3. Electrode modification

The water-dispersible g-C_3N_4 was synthesized according to our previous reports [38,39], and a g-C_3N_4 suspension was prepared by dispersing 6 mg g-C_3N_4 in 3 mL water under sonication.

Prior to modification, the fluoride doped tin oxide (FTO) glass substrate (NSG, Japan) was cleaned by sonication in acetone, mixed solution of ethanol and 2 mol L^{-1} NaOH (v/v, 1:1), and pure water for 20 min, respectively. After being dried with nitrogen gas, the electrode was sealed with Scotch tape with an exposed geometric area of 0.159 cm^2. Then, 20 μL of g-C_3N_4 suspension was dropped onto the exposed surface of FTO and dried at 60 °C to obtain a g-C_3N_4/FTO electrode. For preparation of MIP/g-C_3N_4/FTO, 6 μL of MIP suspension (1.0 mg/mL in DMF) was coated on the g-C_3N_4/FTO electrode surface and dried at 60 °C. The NIP/g-C_3N_4/FTO was prepared in the same procedure using the NIP suspension.

2.4. Construction of photofuel cell

The PFC was constructed with a prepared photoanode and a Pt cathode (Pt foil, 1 cm × 1 cm) in a two-compartment photoelectrochemical cell separated by a Nafion 117 membrane. In both chambers, 0.1 mol L^{-1} PBS (pH 7.4) served as the supporting electrolyte; whereas the analyte of BPA was only present in anodic chamber. Moreover, the anodic chamber of the cell had a quartz window to allow the illumination from the light source on the anode. A portable violet laser pen with a power of 20 mW at 405 nm and a diameter of *ca.* 3 mm for the illumination area served as the visible light source.

2.5. Apparatus

The surface morphology was characterized by a Quanta 200 field emission scanning electron microscope (FE-SEM) (FEI, The Netherlands). The crystalline phase was analyzed by X-ray diffraction (XRD, Bruker Instruments, Germany) using Cu K_α radiation. The UV–vis diffuse reflectance spectrum (DRS) was collected on a UV-2550 spectrophotometer (Shimadzu, Japan). Cyclic voltammetric (CV) and electrochemical impedance spectroscopic (EIS) measurements were carried out on a CHI 660A electrochemical workstation (Chenhua Instrument Co., Shanghai, China) in a conventional three-electrode cell. A modified electrode, a saturated calomel electrode (SCE), and a platinum wire were employed as the working, reference and counter electrodes, respectively.

3. Results and discussion

3.1. Characterization of g-C_3N_4 and MIP

The morphology of the synthesized g-C_3N_4 was characterized by SEM. As can be seen in Fig. 1A, g-C_3N_4 displays a typical stacked layered structure, consistent with the previous observation [35,38]. Meanwhile, the crystalline nature of g-C_3N_4 was analyzed by XRD. As shown in Fig. 1B, the prepared g-C_3N_4 exhibits two characteristic diffraction peaks at 13.0° and 27.3°, which can be assigned to the in-plane structural packing motif of tris-triazine units and interlayer-stacking of the conjugated aromatic groups, respectively [40]. Moreover, the UV–vis diffuse reflectance spectrum of g-C_3N_4 was recorded (Fig. 1C). The result indicates that the as-prepared g-C_3N_4 exhibits an absorption edge at *ca.* 460 nm, demonstrating that g-C_3N_4 could efficiently absorb visible light to induce photogenerated electron-hole pairs.

On the other hand, the prepared MIP was also characterized by SEM. As can be seen, MIP exhibits a morphological structure of porous film consisting of many particles in the sizes between 200 nm and 400 nm (Fig. 2A.) By comparison, the NIP film looks more compact than MIP film, although their morphological structures are similar (Fig. 2B). Furthermore, we investigated the adsorption capacity of MIP for BPA at different initial concentrations ranging from 0.25 mmol L^{-1} to 5 mmol L^{-1}. As shown in Fig. 2C, the adsorption capacity of MIP increases as the initial