Sensors and Actuators B 260 (2018) 388–395

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Photoelectrochemical endocrine-disrupting chemicals aptasenor based on resonance energy transfer between SnSe/GR and AuNPs along with GSSG for signal amplification

Shanshan Wang, Xu Hun*, Xiliang Luo*

Key Laboratory of Rubber-Plastics of Ministry of Education/Shandong Provincial Key Laboratory of Rubber Plastics, Key Laboratory of Sensor Analysis of Tumor Marker, Ministry of Education, State Key Laboratory Base of Eco-chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

ARTICLE INFO

Article history:
Received 31 July 2017
Received in revised form 2 January 2018
Accepted 3 January 2018
Available online 4 January 2018

Keywords:
PEC
Aptasensor
SnSe/GR
GSSG
Bisphenol A

ABSTRACT

The continued expansion of the fields of photoelectrochemical (PEC) aptasensor has guided the development of photoactive materials that can generate electron-photo pairs to emerge photocurrent. However, only such an improvement has an insatiable appetite for the application of molecular level for PEC aptasensor due to the limited quantity of the bioprobes immobilized on the working electrode. Here, we successfully synthetized SnSe/graphene (SnSe/GR) nanohybrids as a photoactive material with a strong photocurrent signal. The constructed bioprobe, DNA/gold nanoparticles/glutathione disulfide (DNA/AuNPs/GSSG), decreased photocurrent effectively. GSSG, an electron acceptor, was designed as a quencher in the bioprobe to overcome a part of shortcomings of DNA/AuNPs in a way. This was owing to the resonance energy transfer (RET) between AuNPs and SnSe/GR, and GSSG to accept photoelectrons, so that the photocurrent response was obviously decreased comparing to the PEC response of SnSe/GR/CPE. Based on this, probe/SnSe/GR/CPE was built as a signal-on PEC aptasensor to detect endocrine-disrupting chemicals using bisphenol A as model. This signal-on PEC aptasensor showed a linear response in the range of 0.01–7 μM and a limit of detection of 3 nM for bisphenol A. And this method presented a promising prospect for sensitive and accurate analysis of other biological molecules between aptamers and corresponding targets at low levels.

1. Introduction

Endocrine-disrupting chemicals (EDCs) are a kind of chemical substances of exogenous endocrine disturbance, which can simulate natural hormone in combination with hormone receptor to affect the content of hormone in the body and induce the body to excessively effect on internal hormones. The most prominent feature of EDCs is that it can inhibit the action of hormones which are the crucial role in controlling development or alter the normal regulatory function of the immune, nervous and endocrine systems. It was not attached importance by people until 1991 when the expert scientists working on EDCs concluded that "Many compounds introduced into the environment by human activity are capable of disrupting the endocrine system of animals." Subsequently, the numerous documenting examples of adverse effects of EDCs were flooding on invertebrates, fish, wildlife, domestic animals and humans [1–4]. On the basis of substantial experiments, it has been affirmed that EDCs not only adversely impact environment, but also endanger human by altering the physiological control mechanism. The adverse effects of EDCs on human are that it can cause breast cancer and endometriosis in women, cryptorchidism and decreased semen quality in men, alteration in pituitary and thyroid gland functions, immune suppression and neurobehavioral effects [5–7]. EDCs can be divided into two categories: natural sources and anthropogenic occurring [8]. Therein, the latter, manmade organic compounds consisted of carbon and other elements such as hydrogen, nitrogen and chlorine, are more recalcitrant and brings greater risks to both health of human and environment. Examples of the second kind of compounds are the plasticizer bisphenol A (BPA), pesticides, phthalates, flame-retardant polybrominated diphenyl ether, heavy metals, dioxins, butyltins originating consumer products and personal care products [5,9,10]. Up to now, EDCs have attracted global attention, due to their propagation and collection by different routes into aquatic environment, the most vulnerable ecosystem. It is primarily the discharge of wastewater, including industries, agriculture and domesticities. Most of EDCs belong to persistent organic pollutants (POPs) which can survive for ages to be gotten rid of, based on its good stabilization and poor decompo-

* Corresponding authors.
E-mail addresses: hunxu@sohu.com (X. Hun), xiliangluo@qust.edu.cn (X. Luo).

https://doi.org/10.1016/j.snb.2018.01.074
0925-4005/

sition in environment. Varying concentrations of EDCs have been found not only in surface water, such as dams, rivers, and wastewaters, but also in other aquatic environment, including sediment and biota [11]. One of the EDCs, bisphenol A [2,2-bis (4-hydroxyphenyl) propane], as an intermediate, is widely applied in producing epoxy resins, polycarbonate, flameretardants and other special products. Most of baby bottles, foodcan linings, beverage containers and thermal papers are the plastic products and epoxy resins. Therefore, the humans may daily ingest trace amounts of BPA from these food containers [12].

Many detective methods have been applied to EDCs, such as gas chromatography (GC) [9], ultra-performance liquid chromatograph tandem mass spectrometer (UPLC-MS/MS) [13], ultra-violet soectroscopy (UV) [14], high performance liquid chromatography (HPLC) [15], gas chromatography coupled with mass spectrometry (GC–MS) [6], photoelectrochemical (PEC) [16], capillary electrophoresis (CE) [17], electrochemical (EC) [18]. Among these detective methods, PEC technique is outstanding due to its advantages of low cost, simple device, low background signal and desirable sensitivity, so that it has been rapidly developed in recent years [19]. For a PEC sensor, under the illumination, photocurrent variations of photoactive materials modified electrode are the detective object, which will either increase via hole oxidation or decrease via electron reduction during the addition of analytes [16].

In general, it can be divided into two types according to mechanism, signal-on and signal-off. By constructing a PEC biosensing, the detection of target analytes is making a greater progress, such as ions [20,21], biomarkers [22,23], cancer cells [24], toxic mycotoxin [25] and other small molecules [26]. For a PEC sensor, the mechanism is that a photocurrent variations as signal emerges by modifying photoactive materials on working electrode to achieve biological interactions between the biosensing elements and their corresponding target analytes [27]. So, among all of the structures of PEC biosensing, photoactive materials play a vital role based on its determinant on the sensitivity of the biosensor by changing the photocurrent. With the prolongation of photoactive materials, nano-semiconductor materials have raised in the world, such as nanoTiO_2, nanoZnO, nanoCdS, nanoCdSe. SnSe is a p-type semiconductor [28]. The layered SnSe has shown several of advantages, such as its anisotropic carrier mobility due to its special layered orthorhombic crystal structure at room temperature. Nevertheless, only few studies about the applications and researches of PEC properties of SnSe in analytical detection have been reported.

So far, depending on steric-hindrance effects [29], enzymatic reactions [30], sensitization effects [31], and resonance energy transfer (RET) [27], several popular strategies have been applied to PEC biosensor with biorecognition events occurring. Among them, RET is a popular and promising theory for the sensitive detection of various biomoleculars, as well as easy to be achieved. To some extent, when the overlap of the absorption and emission spectral is excited and the distance of the energy donors and the energy acceptors is suitable, energy could transfer between energy donors and acceptors. Usually, nano-semiconductor materials act as energy donor because the electron could be excited from valence band (VB) to conduction band (CB). Based on the strong surface plasmon resonance (SPR), as well as high extinction coefficient and broad absorption spectra of metallic nanoparticles (NPs), AuNPs were the most popular to be used as photoelectrochemical energy acceptors [27]. Thus, AuNPs were used to label aptamer DNA to form bioprobes to achieve the detection of targets by the specific recognition between aptamer DNA and target. Yet, because of the limited quantity of the bioprobes immobilized on the electrode, the changes of signal are not very obvious [27]. On the basis of this, we found that glutathione disulfide (GSSG), one of amino acids, could effectively extinguish the photocurrent signal.

Herein, taking BPA as one of EDCs for instance, we reported a sensitive signal-on PEC aptasensor based on RET between SnSe/GR and AuNPs. SnSe/GR nanohybrids were prepared by one step synthetic method, and it was served as PEC substrate of the sensing electrode. Then, AuNPs were modified by GSSG and aptamer DNA as probe to be combined the surface of electrode. At this time, the RET occurred between SnSe/GR and AuNPs among probe, and the photocurrent signal obviously reduced. When BPA was present, the probe could affect on it to be pulled away from the surface of the electrode so that the RET between SnSe/GR and AuNPs was interfered to a great degree and the photocurrent signal obviously recovered. This signal-on PEC aptasensor showed the advantages of high sensitivity and selectivity comparing to signal-off PEC aptasensor. And it also showed a promising prospect for sensitive and accurate analysis of other biological molecules between aptamers and their targets at low levels.

2. Experimental

2.1. Reagents and apparatus

Graphene power was purchased from JCNANO. Glutathione disulfide (GSSG) and glutathione (GSH) were purchased Aladdin Chemistry Co. Ltd. Chloroauric acid ($HAuCl_4{\cdot}4H_2O$), bisphenol A (BPA) and dopamine (DA) were purchased from Sigma-Aldrich (St. Louis, MO). Tin (II) chloride dihydrate ($SnCl_2{\cdot}2H_2O$), selenium (Se) powder and sodium citrate were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Phosphate buffer solution (PBS) was prepared by mixing the stock solutions of 0.2 M NaH_2PO_4 and 0.2 M Na_2HPO_4 containing 0.1 M KCl. All chemicals were of analytical reagent grade and used as received without further purification. All aqueous solutions were prepared with ultrapure water from an Aquapro ultrapure water system (Ever Young Enterprises Development. Co., Ltd., Chongqing, China). BPA aptamer was purchased from Sangon Biotech Co. Ltd (Shanghai, China) with the following sequence: 5′-SH-CCG GTG GGT GGT CAG GTG GGA TAG CGT TCC GCG TAT GGC CCA GCG CAT CAC GGG TTC GCA CCA-3′. 5 mM $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl was used as the electrolyte in the electrochemical impedance spectra (EIS) characterization process.

PEC measurements were performed with a homemade detection system [32]. A white 10 W LED lamp was used as irradiation source. Photocurrent was performed on a CHI 660D electrochemical working station (CHI instrument, USA) with a conventional three-electrode cell. A carbon paste electrode (CPE) or modified CPE was used as the working electrode, saturated calomel electrode (SCE) as reference electrode and a platinum wire as auxiliary electrode.

2.2. Preparation of CPE electrode

The CPE electrode was prepared by mixing graphite powder and paraffin in the mass ratio of 1:3 into a mortar to thoroughly form a homogeneous carbon paste, then transferred into a baking box at 80 °C for 30 min, repeated above process for three times. Next, a portion of the carbon paste was filled into the end of a 7 cm glass tube with a 6 mm diameter, while a copper wire was inserted through the opposite end to establish an electrical contact. A propriate packing was achieved by pressing the surface against a bond paper and polishing on an abrasive paper until a smooth surface was obtained.

2.3. Synthesis of SnSe/GR nanohybrids

SnSe/GR was grown in a 50 mL Teflon liner autoclave from stoichiometric Se, $SnCl_2{\cdot}2H_2O$ and graphene power by a solvothermal route. 0.01 mol Se (0.789 g) and 0.01 mol $SnCl_2{\cdot}2H_2O$ (2.256 g) were