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Electrochemical bisphenol A sensor based on core–shell multiwalled carbon nanotubes/graphene oxide nanoribbons

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ABSTRACT

Bisphenol A (BPA) can disrupt endocrine system and cause cancer. It has been considered as an endocrine disruptor. It is important and necessary to develop a sensitive and rapid method for detection of BPA. In this study, graphene oxide nanoribbons (GONRs) were synthesized from the facile unzipping of multiwalled carbon nanotube (MWCNT) with the help of microwave energy. MWCNT/GONRs and chitosan (CS) were used to prepare electrochemical BPA sensor. Compared with graphene, MWCNT/GONRs have favorable adsorption capacity, electron transfer ability and electrocatalytic property, which could enhance the response signal toward BPA. CS also exhibits excellent film forming ability and improves the electrochemical behavior of MWCNT/GONRs modified electrode. The sensor displays a sensitive response to BPA within a wide concentration range (0.005–150 μg/L). The proposed electrochemical sensor shows low detection limit (1 ng/L), good reproducibility (RSD = 5.2%), selectivity, and acceptable stability. This proposed sensor was successfully employed to determine BPA in water samples with satisfactory results.

1. Introduction

Bisphenol A (BPA), is one of the highest volume chemicals in the world [1,2] and extensively used in the plastic industry, dental fillings, and the lining of food cans [3,4]. Global demand for BPA grew from 3.9 million tonnes in 2006 to about 5 million tonnes in 2010. The extensive use of BPA-based polymers has led to wide spread environment contamination. BPA concentrations in the ranges 5–320 ng/L in river waters and 20–700 ng/L in sewage effluents have been reported [5–8]. BPA shows estrogenic potential [9] and acute toxicity toward aquatic organisms [10] and human cultured cells [11]. In addition, BPA is postulated to cause reproductive disorders including decrease of sperm quality in humans, birth defects due to its fetal exposure and various kinds of cancers, such as prostate, testicular, and breast cancer [12]. Therefore, it is very important to establish a sensitive and simple method for the determination of BPA.

Various analytical methods such as enzyme-linked immunosorbent assay (ELISA) [13], high-performance liquid chromatography (HPLC) [14], liquid chromatography–mass spectrometry (LC–MS) [15], gas chromatography–mass spectrometry (GC–MS) [16], have been reported for determination of BPA. By comparison, electrochemical sensor is preferred because of its reliability, fast response, cheap instrument, low cost, simple operation, short analysis time, high sensitivity, good selectivity, the potential for miniaturization and the possibility of in situ analysis. BPA is electrochemical active, but direct determination of BPA using electrochemical sensor is rare due to the poor response of BPA at traditional electrochemical sensor. To solve this problem, novel sensing material with high stability, good catalytic activity and excellent conductivity must be developed [17–19].

To increase the sensitivity and selectivity for the detection of BPA, various modified electrode such as thionine-tyrosinase and cobalt phthalocyanine modified carbon paste electrode, Mg–Al layered double hydroxide modified glassy carbon electrode, poly(thionine)-tyrosinase modified GCE, Ni(II) tetraamino metallophthalocyanine polymer modified Au electrode have been developed [20,21,3,22,23]. Carbon nanotubes (CNTs) have been widely utilized in the electrochemical detection [24–26]. Recently, platelet graphite nanofibers were found to exhibit faster electron transfer rates than CNTs because of their graphene sheet

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orientation. Graphene-based nano-materials have also attracted attention for electrochemistry applications, including energy storage and sensing [27,28]. In order to enhance the sensitivity of the sensor, graphene oxide nanoribbons (GONRs) fabricated by the microwave-assisted facile unzipping of multiwalled carbon nanotubes (MWCNTs) were introduced during the modification of electrochemical sensor owing to their unique properties involving large surface area, strong excellent conductivity, subtle electronic property catalytic ability and adsorption ability.

Chitosan (CS), a naturally occurred biopolymer product, is derived from chitin via deacetylation with alkali. Its superiority including excellent film forming, high permeability toward water, adhesion ability, nontoxicity together with satisfying biocompatibility, has gained growing interests in electrochemical sensor [29].

Herein, a new electrochemical sensing platform based on MWCNT/GONRs modified electrode was first constructed to develop for the determination of BPA. It was found that the response signal of BPA remarkably enhanced, suggesting that MWCNT/GONRs may be excellent sensing materials for BPA sensor. The parameters such as the concentration of MWCNT/GONRs and pH value were optimized. This sensitive and convenient electrochemical sensor was used for determination of BPA in river water samples with satisfactory results.

2. Materials and methods

2.1. Apparatus and reagents

Bisphenol A (BPA, 97%) was purchased from Acros (NJ, USA). Chitosan was acquired from Aladdin Reagent Database Inc. (Shanghai, China). All other chemicals and solvents were of analytical grade. All the chemicals were used directly without further purification. Phosphate buffered solutions (PBS) were prepared using 0.067 mol/L Na_2HPO_4 and 0.067 mol/L KH_2PO_4 stock solution. Ultrapure water was used throughout the experiments.

Transmission electron microscope (TEM) image was obtained from H-800 microscope (Hitachi, Japan). Raman spectroscopy was analyzed at a laser wave length of 633 nm by a Raman spectrometer NEXUS 670 (Thermo Nicolet, United States). Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded at room temperature in the spectral range of 4000–400 cm^{-1} using the Perkin-Elmer Spectrum One FTIR spectrometer (Perkin-Elmer, United States). All electrochemical measurements were performed on a CHI760E electrochemical workstation (Chenhua Instrument Shanghai Co., Ltd., China). A conventional three-electrode system was used for all electrochemical measurements: a glassy carbon electrode (GCE, 4 mm in diameter) as working electrode, a platinum wire electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

2.2. Synthesis of MWCNT/GONRs

According to Sun et al. [30], MWCNTs (0.05 g) were suspended in 9:1 H_2SO_4/H_3PO_4 and treated with a microwave reactor with the power set 140 °C for 2 min. After the addition of $KMnO_4$ (0.25 g) to the solutions, the solutions were treated with the same microwave power at 65 °C for 4 min. The solutions were filtered through a Millipore membrane (0.1 μm pore size), and the solid products (MWCNT/GONRs) were washed with water several times.

2.3. Preparation of the BPA electrochemical sensor

A GCE was polished with 1.0, 0.3 and 0.05 μm alumina powder sequentially and then washed ultrasonically in ethanol and water for a few minutes, respectively. To prepare the BPA sensor, 6 μL of MWCNT/GONRs (1.0 mg/mL) was dropped onto the electrode and dried. Then, 3 μL of chitosan (0.5%) was added onto the electrode surface. After dried and washed, the CS/(MWCNT/GONRs)/GCE modified electrode was ready to measure.

2.4. Characterization of the electrochemical sensor

The electrochemical impedance technique is employed to detect impedance change during electrode modification process. The fabrication processes were characterized by using electrochemical impedance spectroscopy (EIS). It was carried out in the presence of 2.5 mmol/L $Fe(CN)_6^{4-/3-}$ as a redox probe.

The pH 7.40 PBS was used for all the electrochemical measurements. Cyclic voltammetry (CV) was recorded in PBS at 100 mV/s. For amperometric measurement of the sensor, a detection potential of 0.5 V was selected. BPA was added into the buffer and the current change was recorded. PBS (pH 7.40) as used as the determining medium for BPA. The differential CV from −0.60 to 0.60 V was recorded, and the oxidation peak current was measured for BPA.

3. Results and discussion

3.1. Characterization of MWCNT/GONRs

Transmission electron microscopy (TEM) images of MWCNTs and MWCNT/GONRs are shown by Fig. 1(a) and 1(b), respectively. Graphene sheet structures were found on both sides of the nanotubes in Fig. 1(b), and the central cores of nanotubes remained slightly dark and tubelike. This type of core-shell heterostructure is termed a MWCNT/GONRs nanomaterial. Raman spectroscopy is often taken as a useful tool to study carbon materials. Herein Raman spectroscopy was used to further analyze the structure of MWCNT/GONRs. It is obvious that D band (1300 cm^{-1}) and G band (1580 cm^{-1}) were identified for MWCNTs and MWCNT/GONRs from Fig. 1(c), which was in accordance with [31]. The average size of the sp^2 carbon domain is proportional to the intensity ratio of the D and G lines (I_D/I_G ratio). Comparing with MWCNTs, MWCNT/GONRs showed higher I_D/I_G ratio which indicated MWCNT/GONRs suffered a decrease in the size of the sp^2-hybridized carbon domain by the unzipping procedure [32]. Samples were also characterized by Fourier transform infrared spectroscopy (FTIR). In Fig. 1(d), the increase of the COO—H/O—H stretching region (3600–2800 cm^{-1}) implies an increase in the number of carboxyl and hydroxyl functional groups because of the oxidation procedure.

3.2. Characterization of the BPA sensor

The responses of different modified electrodes in same concentration of BPA (25 μg/L) were shown in Fig. 2(A). The oxidation current of BPA on MWCNT/GONRs modified GCE (curve c) was higher than that on bare GCE (curve a), indicating that MWCNT/GONRs had obviously catalytic activity toward BPA oxidation. The oxidation current of BPA on CS modified GCE (curve b) was higher than that on bare GCE (curve a). When CS was immobilized on the surface of MWCNT/GONRs modified GCE, a higher current response for the oxidation of BPA was observed (curve d) compared with CS modified GCE (curve b) and MWCNT/GONRs modified GCE (curve c). The results may be attributed to two factors: first, MWCNT/GONRs can be fixed by CS, which can maintain the electrochemical activity of MWCNT/GONRs; second, CS can adsorb BPA due to its excellent biocompatibility and film-forming, increasing the signal response.

In the nyquist diagram, the semicircle diameter of electrochemical impedance spectroscopy (EIS) is equal to R_{et}. EIS was used