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An electrochemical bisphenol A sensor based on one step electrochemical reduction of cuprous oxide wrapped graphene oxide nanoparticles modified electrode

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ABSTRACT

Bisphenol A (BPA), as an important industrial material, has been widespread concerned in recent years as its endocrine disrupting effect. This study reported a novel bisphenol A sensor via a facile one step electrochemical reduction of graphene oxide (rGO) and cuprous oxide (Cu_2O) nanocomposite modified glassy carbon electrodes. The characterization of the fabricated sensor was performed by scanning electron microscopy and X-ray spectroscopy. The prepared Cu_2O-rGO electrode presented fast response, high sensitivity and low background current. The response of BPA on prepared electrode was 2.15 times higher than reduced graphene modified electrode. Under the optimized experimental parameters, the detection range of the modified electrode was from 1×10^{-7} to 8×10^{-5} M and the limit of detection was 5.3×10^{-8} M (S/N =3). The prepared Cu_2O-rGO modified electrode has been successfully used for detecting BPA in environmental water samples.

1. Introduction

Bisphenol A (BPA) is a monomeric compound for producing plastics and resins, but also is an important environmental hormone due to its strong interference to the normal working hormones and metabolisms [1]. BPA is highly resistant to chemical degradation and it has been frequently detected in lots of environmental samples. Although European Food Safety Authority (EFSA) panel asserted that there is no health concern for any age group from dietary exposure and low health concern from aggregated exposure [2], the potential health risk of BPA are still a unresolved disputation between related toxicological researchers [3,4]. Recently, BPA has been found widely in natural waters, not only from the migration of BPA-based products, but also through effluent of wastewater, e.g., 568 ng/L of BPA in bottled water [5], 16 μg/L of BPA in the wastewater from an industrial park located in southern Taiwan [6]. From 2008, in order to avoiding the potential toxic effects of BPA to infants, Canada, European Union, most states of America and China successively impose restrictive measure on production and sale of milk bottles containing BPA. The dissolved BPA from food contact materials in the European Union (EU) should follow Regulation 10/2011/EU, i.e., specific migration limit (SML)≤0.6 mg/kg [7]. The oral reference dose (RfD) for BPA proposed by United States Environmental Protection Agency (EPA) is 50 μg/kg body weight day. Therefore, accurately and efficiently detecting BPA is particularly important.

In recent years, a large number of methods have been developed for detecting BPA, such as chromatography [8], spectrophotometry [9], immunoassay [10,11] and electrochemical sensor, etc. These methods have provided variously alternative strategies for studying environmental behaviors and physiological toxicities of BPA. Because BPA is an electrochemical active compound, and the advantages of electrochemical sensors, e.g., the high sensitivity, simple operation and on-site detection, developing and applying of electrochemical methods for BPA detection are attractive for the researchers. However, the signal to noise of bare electrode is insufficient to determine the trace level of BPA. Therefore, lots of efforts have been done by modifying the surface of bare glassy carbon electrode using various types of nanomaterials to improve the sensitivity of the electrode [12,13].

The reduced graphene oxide (rGO) characterized as the thinnest material in the world, and showed a bright future owing to its excellent properties [14–16]. The structural integrity of graphene is a single layer of carbon atoms with extremely stable six-membered ring in two-dimensional crystal. The unique property of graphene results in fast electron transportation, high thermal conductivity, excellent mechanical stiffness and good biocompatibility. The electrodes modified with rGO have been proposed and prepared for detecting BPA. Generally,

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these materials are often dominated by noble metal particles, such as Ag [17], Au [18], Pt [19], and Pd [20]. These modified electrodes usually suffered from high cost, multiple-step and time-consuming processes. Therefore, it is necessary to seek novel candidates to improve the properties of rGO-based modified electrodes.

Cu_2O is an important *p*-type transition-metal oxide semiconductor with a low cost and a high hole mobility. It has already been widely used as the electrode because of its superior performance in heterogeneous catalysts sensors [21]. As a potential alternative of noble metals, Cu_2O has been employed for attempting to prepare graphene-based electrodes. Zhang et al. [22] have prepared an electrochemical sensor of Cu_2O/graphene by solvothermal reactions for detecting dopamine. Liu et al. [23] have synthesized cubic Cu_2O nanocrystals and graphene hybrid by chemical reduction method at low temperature. Its electrochemical stability was highly improved as a non-enzymatic amperometric sensor for H_2O_2 and glucose. Murugan et al. [24] using facile two-step chemical methods have successfully synthesized $Co(OH)_2$ enfolded Cu_2O nanocubes on rGO for cafferne sensing. These composite nanoparticles are generally prepared by chemical reduced method, but their morphologies (e.g. cubic and porous) and electrochemical properties show differently due to their specific synthesized procedure. To date, the Cu_2O-rGO nanocomposite has not been used for the detection of BPA. In this paper, a novel electrochemical sensor based on sphere structure of Cu_2O nanospheres wrapped by rGO (Cu_2O-rGO) was prepared using electrochemical reduced method, which was carried out by one pot synthesis of Cu_2O nanocomposites and rGO by cyclic voltammetry (CV). The sensor was successfully evaluated to detect BPA in real environmental water sample.

2. Experimental

2.1. Chemicals and reagents

Bisphenol A (BPA), graphite powders, cupric sulfate ($CuSO_4 \cdot 5H_2O$), sodium hydroxide (NaOH), polyvinylpyrrolidone (PVP), potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4, 98%), sodium nitrate ($NaNO_3$) and phosphoric acid (H_3PO_4) were purchased from Sinopharm Group Chemical Regent Co. Ltd. (Shanghai, China). BPA was dissolved in ethanol (5×10^{-5} M) and kept at 4 °C. Phosphate buffer solution (PBS, 0.1 M, pH=6.5) was used as reduced and supporting electrolyte. All chemicals used were at least analytical grade. Ultrapure water (18.2 MΩ·cm, obtained by Milli-Q water purification system, Billerica, USA) was used for preparing of all buffers and standard solutions.

2.2. Instrumentation

Electrochemical measurements were performed on a CHI 660e electrochemical workstation (CH Instrument, Shanghai) in a conventional three-electrode system. The working electrode was a glass carbon electrode, the reference electrode was an Ag/AgCl electrode and the auxiliary electrode was a platinum wire. The morphology of nanocomposite was examined by scanning electron microscope (SEM) (Hitachi S-4800, Tokyo, Japan). The X-ray diffration (XRD) of the samples were carried out by using Bruker D8 Advance X-ray diffractometer.

2.3. Preparation of Cu_2O-rGO composite

The Cu_2O nanoparticles (Cu_2O NPs) were synthesized following a hydrothermal method [25]. Typically, 50 mg $CuSO_4 \cdot 5H_2O$ and PVP were dissolved in 20 mL H_2O to form a uniform solution under ultrasonic assistance. After 20 min, 2 mL of 0.2 M NaOH was added into the solution. Then, $N_2H_4 \cdot H_2O$ was introduced for reducing $Cu(OH)_2$. When the mixture turned to brick red suspension, the Cu_2O NPs was successfully prepared. The precipitates were washed with ethanol and ultrapure water for several times to remove the impurities, and then dispersed into water to form an aqueous solution of 1 mg/mL (Cu_2O NPs) for further use.

The graphite oxide was synthesized from graphite according to previous reports [26]. Graphite (0.5 g) and $NaNO_3$ (0.5 g) were successively added into concentrated H_2SO_4 (23 mL) in an ice bath. Then, another 3 g of $KMnO_4$ was added into the solution slowly, heated to 35 °C and kept for two hours. 40 mL of H_2O was thereafter added into the solution and heated to 95 °C. After 30 min, 100 mL H_2O and 20 mL of H_2O_2 was added sequentially into the solution. The final suspension was filtered, washed with 1 M of HCl and ultrapure water for three times. The product was dried at 60 °C to obtain graphene oxide (GO). Then, appropriate GO was dispersed into water to prepare 1 mg/mL GO solution.

2.4. Fabrication of Cu_2O-rGO nanocomposite based electrode

The details of the preparation of the Cu_2O-rGO composite are given as Fig. 1. The surface of glassy carbon electrode (GCE) was ultrasonically cleaned by ultrapure water and ethanol, and was mechanically

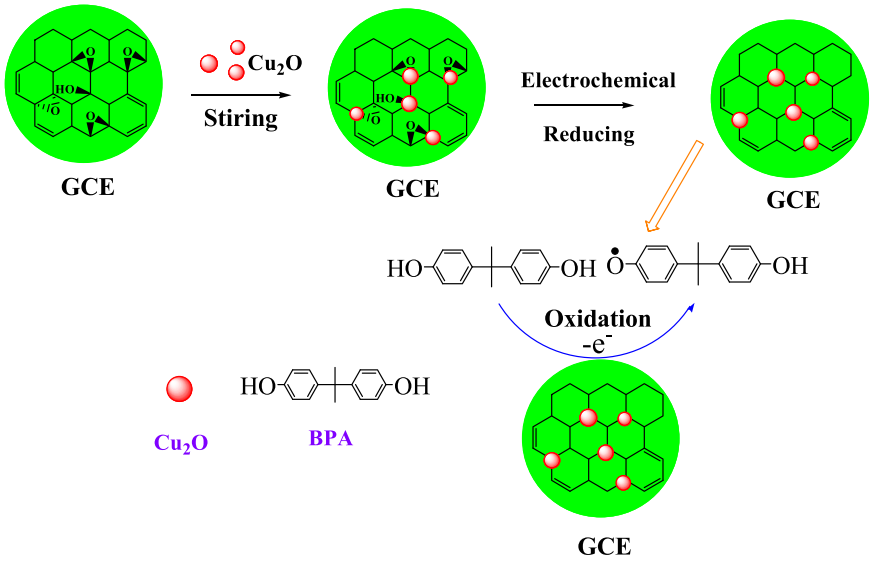

Fig. 1. Schematic diagram for one step electrochemical synthesis of Cu_2O-rGO electrode, and electrochemical oxidation process of BPA at Cu_2O-rGO/GCE.