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An electrochemical sensor for the determination of bisphenol A using glassy carbon electrode modified with reduced graphene oxide-silver/poly-L-lysine nanocomposites

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ABSTRACT

Bisphenol A (BPA) is an effective endocrine-disrupting compound (EDC) that causes adverse effects on human health and environment. Therefore, it is indispensable to construct efficacious methods for evaluating the level of BPA to enhance the quality of life. In this study, a facile electrochemical sensor based on reduced graphene oxide-silver/poly-L-lysine nanocomposites (RGO-Ag/PLL) modified glassy carbon electrode (GCE) is proposed for the detection of BPA. The synthesized RGO-Ag/PLL nanocomposites displays high electrocatalytic activity towards the electrochemical oxidation of BPA. Differential pulse voltammetry (DPV) is used as an analytical method for the quantitative determination of BPA, and the fabricated electrochemical sensor exhibits a linear response to BPA in the range of 1–80 μM with the limit of detection (LOD) of 0.54 μM at a signal-to-noise ratio of 3. Additionally, the developed RGO-Ag/PLL/GCE sensor is applied to detect the BPA in drinking water, and obtains satisfactory results.

1. Introduction

In chemical applications, bisphenol A (4, 4′-(propane-2, 2-diyl) diphenol, BPA) is typically applied as monomer for synthesis of polycarbonate (PC) and epoxy resins. Besides, BPA is extensively used in food packaging materials and has been widely favored [1]. However, it was discovered that BPA could be diffused from polycarbonate plastic bottles due to the thermal treatment. Additionally, some related reports that the BPA in food packaging containers or plastic film can penetrate into the food or beverage have been proposed by researchers successively [2]. Consequently, BPA as a kind of migratory pollutant in food packaging materials has been stepping into the horizon of the public gradually, which contaminates both biological and abiotic environments. Simultaneously, bisphenol A is also an effective endocrine-disrupting compound (EDC) that can imitate or interfere with endogenous estrogen, causes adverse effects towards organism reproduction, growing development, nervous system, immune system and so on [3,4].

Considering the seriously detrimental influences of BPA on human beings and environment, thus it is indispensable to construct efficacious methods for evaluating the level of BPA and enhance the quality of life. Up to now, a number of approaches have been brought forward in literatures, such as the enzyme linked immune sorbent assay (ELISA) [5], liquid chromatography–mass spectrometry (LC–MS) [6], gas chromatography–mass spectrometry (GC–MS) [7], fluorescence (FL) [8], surface-enhanced Raman scattering (SERS) [9] and high-performance liquid chromatography(HPLC) [10]. However, most of the forementioned detection approaches need complicated pretreatment due to its higher requirements for the extraction and purification of the sample. In addition, some shortcomings such as exorbitant implement, time-consuming and unsuitability for onsite detection further limit its application [4]. By comparison, electrochemical sensors access to a great research enthusiasm due to their portability, credibility, onsite inspection, fast response and low cost. However, the response signal of conventional sensors towards BPA detection is quite weak, which makes it very difficult to achieve accurate measurements of BPA [11]. Therefore, in order to improve the response signal of the BPA determination, electrochemical sensors modified with advanced materials such as molecularly imprinted polymer, quantum dots, metal nanoparticles based composites, carbon based materials and aptamer based probes have been ceaselessly fabricated for the detection of BPA. Generally, the oxidation potential of BPA is high, which results in low selectivity. Another problem is the poor sensitivity of the conventional electrodes that have less active-sites for BPA oxidation. Therefore, advanced materials with good adsorption, large surface area, good electrical conductivity and excellent electron-transfer ability are essential for the practical application of the BPA sensors [12–19].

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In the field of electrochemical analysis and catalysis, carbon materials have been widely studied and applied [20]. Graphene, an emerging carbon material, is a two-dimensional sheet of carbon atoms arrayed into honeycomb lattice [21], which has attracted a large number of attention due to its varieties of unique and charming properties, such as the superior thermal conductivity [22], excellent carriers mobility [23] and high theoretical specific surface area [24]. Up to now, a number of methods have been developed to prepare graphene, including epitaxial growth [25], micromechanical exfoliation [26], chemical reduction of graphene oxide and chemical vapour deposition (CVD). Compared with the graphene obtained from other methods, the chemically reduced graphene oxide (RGO) has inspired a great deal of enthusiasm because of its scalability, feasibility and liable chemical modification [27]. However, the deoxygenation of graphene oxide will eliminate most of oxygen-containing functional groups and cause the restacked graphene sheets due to the strong π-π bonds and vander Waals interactions [28,29]. The aggregation of graphene will deteriorate the properties of graphene and limit its application. Therefore, modification of graphene with functional materials is utilized to overcome the reunion problem of RGO and endow the novel properties of composites [30,31].

Recently, great progress has been made in the fabrication of noble metal nanostructures and the exploration of its potential application in various fields such as in catalysis, sensors, and electronics [32]. Ag is known to researchers for its excellent conductivity, whereas a series of particular characteristics about it have been excavating gradually with the deep research on Ag, for instance the catalytic activity, sensing and so on [33–35]. Additionally, Ag nanoparticles can be utilized as catalysts in various oxidation reactions [36]. Therefore, the incorporation of Ag nanoparticles in graphene for synthesis of nanocomposites provides strategies for manufacturing innovative materials that combine the merits of silver and grapheme, and play a synergistic effect [28].

Recently, more and more attention has been gained in using polymers for functional modification of the working electrodes by virtue of their brilliant adhesion, remarkable specific selectivity and the ability to provide more active sites [37,38]. As the carboxyl groups could enrich the BPA molecules, thus L-lysine is used to modify the electrode by electrochemical polymerization [39,40]. Besides, hydrogen bonds could be formed between BPA and poly-L-lysine (PLL) due to the presence of hydrogen bond acceptors and donors in BPA and PLL, which leads to a reduced contact resistance of the composites material and an improved rate of electron transfer.

In this study, a facile electrochemical sensor based on reduced graphene oxide-silver/poly-L-lysine nanocomposites (RGO-Ag/PLL) modified glassy carbon electrode (GCE) is proposed for the quantitative determination of BPA. The RGO-Ag nanocomposites is synthesized by electrostatic force-directed assembly (ESFDA) technique [32], and the RGO-Ag/PLL nanocomposites is prepared by electrochemical polymerization in phosphate buffer solution (PBS) containing L-lysine. It has been demonstrated that the RGO-Ag/PLL nanocomposites displays high electrocatalytic activity towards the electrochemical oxidation of BPA. Additionally, the developed RGO-Ag/PLL/GCE sensor is applied to detect the BPA in drinking water, and obtains satisfactory results.

2. Experimental

2.1. Reagents and apparatus

BPA (> 99.0%) was purchased from Aladdin Reagent Co (Shanghai, China), which was dissolved in ethanol with 0.1 M for storage. Nafion solution and L-Lysine were purchased from Sigma-Aldrich (St. Louis, USA). Graphite powder (325 mesh), silver nitrate (AR, 99.8%), hydroquinone, p-(tert-octyl)phenol, nonylphenol, $NaH_2PO_4{\cdot}12H_2O$, and $Na_2HPO_4{\cdot}12H_2O$ were purchased from Aladdin Reagent Co (Shanghai, China). A series of PBS with different pH were prepared by mixing the solutions of $NaH_2PO_4{\cdot}12H_2O$ and $Na_2HPO_4{\cdot}12H_2O$, and then adjusted the pH with H_3PO_4 and NaOH. Double deionized water used throughout the experiment was supplied by Watsons (Guangdong, China). All of the other reagents used were at least of analytical grade without further purification.

Phase analysis was implemented on D/max 2500PC high-resolution X-ray diffractometer (Rigaku, Japan) with Kα radiation. Raman spectra were recorded on a Renishow Invia Reflex micro-confocal spectrometer (Renishaw, Britain) with 514.5 nm laser excitation. X-ray Photoelectron Spectroscopy (XPS) measurements were performed on Sigma probe XPS (Thermo VG Scientific). Scanning electron microscopy (SEM) images were operated with S4700 Field emission scanning electron microscope (Hitachi, Japan). Transmission electron microscopy (TEM) and selected-area electronic diffraction (SEAD) were performed on a TECNAI F30 TEM (FEI, USA). Electrochemical examinations were performed on CHI660E electrochemical workstation (Shanghai Chenhua Co., China) with a normal conventional three-electrode cell.

2.2. Synthesis of reduced graphene oxide-silver nanocomposites (RGO-Ag)

Graphene oxide (GO) was synthesized from natural graphite powder (325 mesh, Aladdin Reagent Co.) by an improved Hummers method [41]. RGO-Ag nanocomposites was synthesized according to literature with a little modification [42]. Briefly, GO (50 mg) and $AgNO_3$ (50 mg) were mixed in 50 mL deionized water and treated with sonication for 1 h at low temperature with moderate ultrasonic power. After that, 5 mL hydrazine hydrate was slowly added to the reaction by peristaltic pump with magnetic stirring. Then, the temperature of the mixture was elevated and kept at 95 °C for 1 h. Eventually, the obtained solution was washed with deionized water and absolute ethanol for three times. After centrifugation, the as-fabricated samples were processed via freeze-drying for 24 h and annealed at 700 °C under argon atmosphere for 2 h.

2.3. Fabrication of the BPA electrochemical sensor

Prior to modification, the GCE was conducted with mechanical polish using 1.0 μm, 0.3 μm and 0.05 μm α-alumina powder in succession and washed with deionized between each polishing step. After that, for purpose of obtaining a smooth, clean and fresh electrode surface, the GCE was sonicated three times in deionized water and ethanol, respectively, and dried in air. The construction of electrochemical sensor consisted of two steps. First, 2.5 μL (8 mg/mL) of the RGO-Ag nanocomposites suspension was dropped on the surface of GCE and dried in air, which was marked as RGO-Ag/GCE. Second, the functional modification of L-lysine on RGO-Ag/GCE was conducted by cyclic potential scanning from − 1.0–1.2 V for 10 cycles with a scan rate of 100 mV/s through immersing the above RGO-Ag/GCE into PBS buffer solution (pH 9.0) containing 10 mM L-lysine. The final obtained electrode was marked as RGO-Ag/PLL/GCE.

2.4. Electrochemical measurements

The electronic properties of the modified electrodes were characterized by electrochemical impedance spectroscopy (EIS) using $Fe(CN)_6^{3-/4-}$ as the redox probe in the frequency range from 0.1 to 10^5 Hz. The optimization of the experimental conditions was completed by cyclic voltammetry (CV). DPV was performed in phosphate buffer solution (pH 8.0) with different concentrations of BPA from 1 to 80 μM. The electrochemical signal was recorded from 0 to 1.0 V, and the oxidation peak of BPA was also measured.

3. Results and discussion

3.1. Characterization of RGO–Ag

Fig. 1 displays the XRD patterns of the natural graphite (a), GO (b),