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Electrochemical sensor for bisphenol A determination based on MWCNT/melamine complex modified GCE

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ABSTRACT

Based on the unique electronic properties and high adsorption capacity of carbon nanotubes as well as the electrostatic attraction between protonated melamine and negatively charged bisphenol A (BPA), a novel electrochemical sensor for the determination of BPA in water was fabricated by immobilization of multi-walled carbon nanotubes (MWCNTs)/melamine complex onto the surface of glassy carbon electrode. The cyclic voltammetry results showed that the sensor exhibited strong catalytic activity toward the oxidation of BPA with a well-defined cyclic voltammetric peak at 0.56 V. Moreover, the electrochemical sensor exhibited a wider linearity range from 10.0 nM to 40.8 μM BPA with a detection limit of 5.0 nM (S/N = 3). The enhanced performance of the sensor can be attributed to the combination of the excellent electrocatalytic property of MWCNTs and the electrostatic attraction of the protonated melamine to the negatively charged BPA. This novel sensor was successfully applied to determine BPA leached from real plastic samples with good recovery, ranging from 96% to 102%.

1. Introduction

Bisphenol A (BPA, 2,2′-bis(4-hydroxyphenyl)propane) has been listed as a typical endocrine disruptor, which can mimic the body's own hormones and may lead to negative health effects [1]. The first study of health effects on humans associated with BPA exposure was reported in 2008 by Lang and coworkers [2], in which they found that higher BPA levels increased risk of heart disease, coronary heart disease, and diabetes. A later study at Tufts University Medical School concluded that BPA might increase cancer risk [3]. In recent years, the concern over the effect of BPA on humans has been heightened by the fact that infants and children are estimated to have the highest daily intake of BPA, because it is a key monomer in production of epoxy resins and polycarbonate plastics (PC). As we know, PC is used to make a variety of common products including baby bottles and water bottles, medical and dental devices, eyeglass lenses, and household electronics, and BPA-based epoxy resins are usually used as coatings on the inside of almost all food and beverage cans. Unfortunately, BPA has been known to be leached from these plastics, especially those that are cleaned with harsh detergents or those that contain acidic or high-temperature liquids. A recent Health Canada study found that the majority of canned soft drinks it tested had low, but measurable levels of BPA [4]. In September 2010, Canada became the first country to declare BPA as a toxic substance and banned the use of BPA in baby bottles [5]. Therefore, the development of new sensors for the detection of BPA at trace concentrations has become one of the most attractive subjects of investigation in analytical chemistry.

Various analytic methods have been developed and used for the determination of BPA. Such methods include liquid chromatography (LC), liquid chromatography–mass spectrometry (LC–MS), gas chromatography–mass spectrometry (GC–MS), liquid chromatography with electrochemical detector (LC-ECD), chemiluminescence, enzyme-linked immunosorbent assay (ELISA), and electrochemical techniques [6–13]. Among them, electrochemical method has great potential for environmental monitoring because of its inherently advantages such as fast response speed, ease of miniaturization, low cost, timesaving, high sensitivity, excellent selectivity, and in vivo real-time determination. However, a major obstacle encountered in the detection of BPA by electrochemical method is the relatively high overpotential together with poor reproducibility although BPA can be oxidized at electrode surface due to containing phenolic hydroxyl group [14]. Additionally, bare electrode often suffers from a fouling effect, which causes rather poor selectivity and sensitivity [15]. An effective way to overcome these barriers is electrode modification, of which is capable of reducing the overvoltage and overcoming the slow kinetics of many electrode processes. Enzymes [13], polymers [16], nanoparticles [17], and carbon materials, especially one-dimensional carbons,

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such as carbon nanotubes [18] and carbon fibers [19], have been successfully used to modify bare electrode.

Owning to their high electrical catalytic properties, high chemical stability and extremely high mechanical strength, multi-walled carbon nanotubes (MWCNTs) have been focused on the field of electrode modification [20,21]. However, the intrinsic van der Waals interactions between the pristine tubes make MWCNT bundles in scale and insoluble in routine solvents [22]. Therefore, MWCNT bundles are required to disperse in solvent prior to the electrode modification. Several approaches to the functionalization of MWCNTs, including covalent sidewall coupling reactions [21,23,24], and noncovalent exohedral interactions [20,25,26], have been developed to disperse MWCNTs. Recently, independent research groups in China [27,28] have reported the determination of BPA by electrochemical method using MWCNTs modified electrode with a detection limit of 0.03 μM and 7.5 nM, respectively. However, it is still a challenge to fabricate new electrochemical sensors based on familiar carbon materials with higher sensitivity through incorporation of interaction sites onto the surface of MWCNTs.

Herein, we demonstrated a highly sensitive electrochemical sensor for the determination of BPA in aqueous solution by using MWCNT/melamine (MAM) complex (MWCNT–MAM) modified glassy carbon electrode (GCE). We choose MAM (1,3,5-triazine-2,4,6-triamine) as the modifier because it is cheap, and commercially available. Moreover, the amino groups of MAM can be protonated in pH 7.0 due to the fact that the pK_a of MAM is 8.0 [29,30]. The protonated MAM can thus interact with the negatively charged BPA through electrostatic attraction. In the present work, pristine MWCNTs were firstly modified with MAM following a procedure reported by Prado et al. [31], yielding MWCNT–MAM. Subsequently, GCE was coated with MWCNT–MAM film. The as-fabricated sensor, MWCNT–MAM/GCE, was further used to determine BPA by using cyclic voltammetry and amperometry. To the best of our knowledge, there is no report on the modification of GCE with MWCNT–MAM for BPA determination. This electrochemical sensor will combine the electrocatalytic property of MWCNTs and the electrostatic attraction of protonated MAM, thus exhibit an attractive ability for highly sensitive detection of BPA in real samples. The sensitivity, linear range, detection limit, and stability of the prepared electrochemical sensor in the detection of BPA were investigated.

2. Experimental

2.1. Reagents and apparatus

MWCNTs with the external diameter of 20–30 nm and length of 5–15 μm were obtained from Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China), which was prepared by the chemical vapor deposition (CVD) method. MAM (Aldrich) was used without further purification. BPA was purchased from Aldrich. 5.0 mM BPA stock solution was prepared with anhydrous ethanol and kept in darkness at 4 °C. A series of phosphate buffer solutions (PBSs) with different pH were prepared by mixing the solutions of 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4, and then adjusting the pH with H_3PO_4 or NaOH. All other reagents were analytical reagent grade and used as received. All solutions were prepared with doubly distilled water. Thermogravimetric analysis (TGA) was carried out on a STA 449C instrument under a flowing nitrogen atmosphere. The morphologies of the MWCNT–MAM and the MWCNT/MAM blended mixture were observed by scanning electron microscope (SEM) measurement, which was carried out with a field-emission microscope (Hitachi S-4800) operated at an acceleration voltage of 15 kV. Electrochemical experiments were performed with a CHI760D electrochemical workstation (Shanghai Chenhua Co., China) with a conventional three-electrode cell. A bare GCE or modified GCE was used as working electrode. A saturated calomel electrode and a platinum wire electrode were used as reference electrode and auxiliary electrode, respectively. The pH measurements were carried out on pHS-3C exact digital pH meter (Shanghai Rex Co. Ltd., China). All the measurements were carried out at room temperature.

2.2. Preparation of MWCNT–MAM

MWCNTs (50 mg) and dry ethanol (10 mL) were stirred in a three-necked round-bottomed flask equipped with reflux condenser at room temperature for 24 h. After 30 min sonication, MAM (100 mg) was added to the dispersion. This mixture was heated under reflux for 16 h. After cooling to room temperature, the resulting suspension was filtered through a 220 nm PTFE membrane under *vacuum*. The product was washed thoroughly with water at 80 °C (5 × 50 mL), and ethanol at ambient temperature (3 × 50 mL) to remove the excess MAM, and then dried in a *vacuum* overnight.

2.3. Preparation of MWCNT–MAM/GCE

The GCE was polished sequentially with sandpaper and 0.05 μm alumina slurry on polishing cloth to produce a mirror-like surface, and then sonicated for 1 min in HNO_3/water (1/1, v/v), ethanol/water (1/1, v/v), and distilled water in an ultrasonic bath, respectively. Subsequently, it was dried under IR lamp. For preparation of modified electrode, 1.0 mg mL^{-1} of MWCNT–MAM suspension in *N*,*N*-dimethylformamide (DMF)/water (1/2, v/v) was prepared, and then 15 μL of the suspension was deposited on the freshly treated GCE surface with a pipette. After the solvent was evaporated, the electrode surface was thoroughly rinsed with doubly distilled water and dried under ambient condition. For comparison, MWCNTs modified GCE (MWCNT/GCE) and MWCNTs/MAM blended mixture modified GCE (MWCNT/MAM/GCE) were fabricated with similar procedures.

3. Results and discussion

3.1. Electrode modification

In the present study, GCE was modified with MWCNT–MAM prior to use. The preparation of MWCNT–MAM was performed following a procedure reported by Prado and coworkers [31]. Pristine MWCNTs were modified with MAM to attach amino groups onto their surface via Diels–Alder heterocyclization reaction as well as π–π interaction between graphene layer of the MWCNTs and the aromatic ring of MAM. The content of MAM attached onto the surface of MWCNTs was analyzed by TGA. The TGA plots of MWCNTs before and after modification are shown in Fig. 1A, a mass loss of approximately 5.5%, due to MAM decomposition was observed for the MWCNT–MAM sample, indicating that the amino group incorporation density is about 1.31 mmol g^{-1} of neat MWCNTs. Elemental analysis further demonstrated the presence of nitrogen in the MWCNT–MAM sample with the amino group incorporation density of around 0.99 mmol g^{-1} of neat MWCNTs. It is important to note that this result is somewhat lower than that of 1.31 mmol g^{-1} neat MWCNTs, as measured by TGA analysis. This discrepancy may come from the dissimilarity of the measurement techniques.

The morphologies of MWCNT–MAM and MWCNT/MAM blended mixture were imaged by SEM as depicted in Fig. 1B. As expected, separated nanotubes were observed for MWCNT–MAM (Fig. 1B, a) in contrast to densely entangled nanotubes that existed in MWCNT/MAM blended mixture (Fig. 1B, b). Furthermore, some nanotubes were buried in the solid MAM as indicated by arrows for