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Highly sensitive electrochemical assay for Bisphenol A detection based on poly (CTAB)/MWCNTs modified pencil graphite electrodes

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ABSTRACT

In this work, we offered a cheap, effective and a rapid electrochemical detection of Bisphenol A (BPA) in a simple methodology. Cetyltrimethylammonium bromide (CTAB) and multi- walled carbon nanotubes (MWCNTs) were combined through electropolymerization onto pencil graphite electrode (PGE) surface by cyclic voltammetry to produce poly (CTAB)-MWCNTs composite. Electrochemical signal of BPA at poly (CTAB)-MWCNTs modified PGE was significantly enhanced. Scanning electron microscopy (SEM) and electrochemical methods were utilized to clarify the surface characterization. The limit of detection was calculated as 134 pM with a good regression between the concentration and peak current of BPA (R^2 = 0.993) by using square wave voltammetry within the range of 2–808 nM. A teether, bottle water and a baby's bottle, which were purchased from local markets, were used as real matrixes and this method was used efficiently for the detection of BPA with a maximal recovery. Poly (CTAB)-MWCNTs based sensor demonstrated perfect electrochemical performance for the detection of BPA and this platform can be used for the determination of various analytes.

1. Introduction

Bisphenol A (BPA) is known as one of the important endocrine disruptors which is commonly used in an intermediate step in the production of epoxy resins and polycarbonate plastics. Thus, polycarbonate plastics, especially the food and beverage containers (water and milk bottles, baby bottles), fire retardants and dental filling materials may contain BPA [1]. By virtue of its very wide field of use, humans may routinely be exposed to BPA in their daily lives. BPA, owing to its structure similar with estrogen hormone, imitates the hormonal activity and functions as an endocrine disruptor by binding estrogen receptors which results in many adverse effects on biological systems of both humans and animals.

Numerous studies showed that BPA displays induced enlargement in the number of fat cells and caused weight gain in both people and laboratory mice. In addition to this effect, it is known that BPA can lead to problems such as decrease in fertility, resistance to insulin, cardiovascular disorders, diabetes, cancer and thyroid disorder [2,3]. Consequently, to protect health, the use of BPA in baby bottles have been banned in many countries and its content of residue in food packages is limited to 3 mg/kg [3]. Thus, highly selective and sensitive analysis of BPA remains its significance due to the various potential sources for BPA contamination. Toxic effect of BPA has not fully been demonstrated. Many analytical methodologies based on colorimetric [4], spectroscopic [5,6], chemiluminescence [7], capillary electrophoresis [8] and chromatographic [9,10] methods have been developed for the analysis of BPA in literature. Although these methods provide highly efficient way for selective and sensitive analysis of BPA, they have some drawbacks such as high instrument cost, time consuming sample pretreatment processes and requirement of specialists for the operation of the systems. At this point, electrochemical methods have outstanding features emerging as an alternative way to the other methods mentioned above. However, at traditional working electrodes, BPA exhibit poor electrochemical response due to sluggish electrode kinetics and formation of electropolymerized film on the electrode leading problems such as electrode fouling, low sensitivity and reproducibility [11]. Hence, considerable attempts have been devoted to modify the electrode surfaces with selective recognition elements in order to improve the analytical performance in BPA sensing [1,2,12–23]. Also, there are only a few studies focused on disposable BPA sensors which were based on screen-printed electrodes (SPEs) [24–26]. Besides, disposable pencil graphite electrode (PGE) was used as a substrate modified with gold nanoparticle/polyviniylpyrolidone [27], an electrochemically pretreatment procedure [28] and also polyaniline (PANI)

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nanorods/multi-walled carbon nanotubes (MWCNTs) [29]. Surface passivation in which adsorption or polymerization of an oxidized molecule occur on the electrode surface is one of the major disadvantages of the modified electrodes. The use of disposable electrode materials (such as PGE) is an important solution to this handicap. PGE surface shows high electrical conductivity and serves as a suitable surface on which analyte can easily be adsorbed.

Furthermore, application of surfactants in electrochemistry is of particular interest. As they are surface active and amphiphilic molecules, they can greatly show influence on the characteristics of electrochemical processes [30–37]. Addition of polar surfactants in the solution may improve the aqueous solubility of molecules which results in significant change in redox properties and electroanalytical properties of the analytes [30–32]. Also, it was reported that surfactants adsorbed at the electrode surface may alter the electrode behavior and promote the electron transfer process between the electrode surface and analyte [37]. Cetyltrimethylammonium bromide (CTAB), is a cationic surfactant, which has been studied as an electrode modifier in some of these electrochemical sensor applications [30–36]. Only a few studies dealt with the electrochemical behavior or determination of CTAB molecule [38,39]. Recently, electropolymerization of CTAB in acidic medium and application of this polymer modified surface for the simultaneous determination of some biomolecules (dopamine, uric acid, tryptophan and theophylline) has been first time reported by Yang and Zhang [40].

On the other hand, multi-walled carbon nanotubes (MWCNTs) are known to be promising one dimensional nanomaterials which are widely used for the construction of biosensors for their unique properties such as high electron transfer ability, electro-catalytic effect, specific surface area and strong adsorption capability [41,42]. Modification of surfaces with MWCNTs do not only enhance the electrochemical reactivity of analytes but also decrease the electrolyte impedance. These properties make MWCNTs extremely attractive materials as a surface modifier for many electrochemical devices. Besides, incorporation of carbon nanotubes (CNTs) with polymer matrices for the development of hybrid structures with new electronic features have received significant interest because these composite materials possess the properties of each component in a synergistic effect. The preparation of composite structures of polymers and CNTs by chemical or electrochemical methods have been reported in a large number of publications including deposition of polymers on CNT-modified electrodes [43], self-assembly process [44], functionalization of CNTs with monomer units prior to polymerization [45] and by the co-electropolymerization of CNTs and monomers [46,47]. Among them, copolymerization of monomers and CNTs onto electrode surfaces by electrochemical method offers several advantages in which CNTs are first dispersed in monomer solution and then the suspension is in-situ electropolymerized. In this method, CNTs act as dopants during the polymer formation and the resulting composite films often show a porous structure which leads to a high surface area [46]. The physical, chemical properties and morphologies of the resulting films can be controlled simply by adjusting the parameters of electropolymerization so the resulting composites are more stable, uniform and controllable which is essential for the achievement of highly sensitive sensor surfaces [48]. Thus, such a preparation route offers efficient, rapid and reproducible preparation of high quality of nanocomposites due to enhanced polymer–nanotube interactions.

Herein, we present a facile approach for the electrochemical preparation of poly (CTAB)/MWCNTs nanocomposite on PGE and application for the electrochemical analysis of BPA. To date, electrochemical investigation of BPA using poly (CTAB)/MWCNTs/PGE has not been reported. The cationic surfactant based polymer film together with MWCNTs on the surface showed distinct structure and allowed good electro-catalytic activity and high sensitivity towards the oxidation of BPA. The surface characterization of PGEs was carried out by scanning electron microscope (SEM) and electrochemical impedance spectroscopy (EIS) to prove the formation of composite onto the surface. Furthermore, the developed sensor has been applied for the determination of BPA in water bottle, baby bottle and baby teether samples to show the applicability of this method to real matrices.

2. Experimental

2.1. Instruments and reagents

Electrochemical experiments were performed using Interface 1000 Potantiostat/Galvonastat/ZRA, Gamry and a three-electrode configuration including a disposable pencil graphite electrode which was used as working electrode, a platinum wire as auxiliary electrode and Ag/AgCl electrode as a reference electrode. The prepared composites were analyzed with a scanning electron microscope (Zeiss Evo 60 EP-SEM).

Bisphenol A (2,2-bis(4-hydroxyphenyl propane, BPA, >99%), carboxylic acid functionalized multi walled carbon nanotubes (MWCNTs) with a 95% purity, cetyltrimethylammonium bromide (CTAB) were purchased from Sigma Aldrich. Stock solutions of BPA were prepared in absolute ethanol. Sodium acetate and acetic acid from Merck were used to prepare 0.1 mol L^{-1} acetate buffer solution (ABS). $K_4Fe(CN)_6$ from Analar Analytical Reagent, $K_3Fe(CN)_6$ from Fischer Scientific Company and KCl from Merck were used to prepare the redox couple for EIS.

2.2. Preparation of the modified electrode

0.045 M of CTAB solution was prepared by dissolving appropriate amount of cetyltrimethylammonium bromide in 0.1 M H_2SO_4. The carboxylic acid functionalized MWCNTs (1 mg) were dispersed in 10 mL of 0.045 M CTAB solution and the mixture was agitated in an ultrasonic bath for 30 min to give a black suspension. 1 cm of pencil electrode leads were subsequently immersed into 0.045 M CTAB solution containing 0.1 mg mL^{-1} MWCNTs and cyclic voltammetry (CV) was employed in the potential range of − 0.8 V to 1.2 V (vs. Ag/AgCl) for 10 cycles at 100 mV s^{-1}, in which co-deposition of poly (CTAB) and MWCNTs was performed. The resulting electrode was dried overnight at room temperature and denoted as poly (CTAB)/MWCNTs/PGE.

2.3. Preparation of real samples

Plastic drinking bottle from a local supermarket was firstly cut into small pieces and washed with deionized water. After drying, about 1.0 g of plastic pieces were introduced into 30.0 mL of ethanol and sonicated at 50 °C for 4 h, as heating may increase BPA leaching levels. The solution was cooled to room temperature and sealed for a week. The mixture was then filtered through a cellulose acetate membrane (0.45 μm pore size) and then the solvent was evaporated. In order to extract BPA, the residue was dissolved in 3.0 mL ethanol and was diluted to 50 mL with acetate buffer solution. The pre-cleaned baby bottle (125 mL) was washed and filled with deionized water. The bottle was then heated at 70 °C for 1 h and at 30 °C for 4 h. The baby bottle was then kept at room temperature for a week by shaking occasionally. 1.0 mL of ethanol was added to the solution and filtrated. Finally, the sample was diluted with ABS (1:1). A baby teether was soaked into a beaker containing 20.0 mL of ethanol. The beaker was heated at 50 °C and stirred for 4 h. The mixture was filtered. The solvent was completely evaporated and the residue was then dissolved in 3.0 mL ethanol. Finally, the sample was diluted to 50.0 mL with ABS.