Thin Solid Films 520 (2012) 4459–4464

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

# Voltammetric detection of bisphenol a by a chitosan–graphene composite modified carbon ionic liquid electrode

Qingxiang Wang [a], Yuhua Wang [b], Shengyun Liu [b], Liheng Wang [a], Feng Gao [a], Fei Gao [a], Wei Sun [b,*]

[a] *Fujian Province University Key Laboratory of Analytical Science, Department of Chemistry and Environment Science, Zhangzhou Normal University, Zhangzhou 363000, PR China*
[b] *College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China*

## ARTICLE INFO

*Article history:*
Received 9 October 2011
Received in revised form 15 February 2012
Accepted 16 February 2012
Available online 23 February 2012

*Keywords:*
Graphene
Bisphenol A
Differential pulse voltammetry
Carbon ionic liquid electrode

## ABSTRACT

In this paper 1-ethyl-3-methylimidazolium tetrafluoroborate based carbon ionic liquid electrode (CILE) was fabricated and further modified with chitosan (CTS) and graphene (GR) composite film. The fabricated CTS-GR/CILE was further used for the investigation on the electrochemical behavior of bisphenol A (BPA) by cyclic voltammetry and differential pulse voltammetry. A well-defined anodic peak appeared at 0.436 V in 0.1 mol/L pH 8.0 Britton–Robinson buffer solution, which was attributed to the electrooxidation of BPA on the modified electrode. The electrochemical parameters of BPA on the modified electrode were calculated with the results of the charge transfer coefficient ($\alpha$) as 0.662 and the apparent heterogeneous electron transfer rate constant ($k_s$) as 1.36 $s^{-1}$. Under the optimal conditions, a linear relationship between the oxidation peak current of BPA and its concentration can be obtained in the range from 0.1 μmol/L to 800.0 μmol/L with the limit of detection as $2.64 \times 10^{-8}$ mol/L ($3\sigma$). The CTS-GR/CILE was applied to the detection of BPA content in plastic products with satisfactory results.

## 1. Introduction

Bisphenol A (BPA) is commonly used to produce polycarbonate, epoxy resin, polysulfone resin etc. in chemical industry and also can be used as an additive in some products such as infant bottle, canned soft drinks and food package in order to make the products more colorless, transparent and durable. Also BPA is one of the endocrine disrupting compounds and mimics the action of hormone estrogen [1,2]. It has been proved that BPA can cause a decrease of sperm quality in humans [3], result in neural and behavioral changes in infants and children, led to any negative effects in pregnant women and their unborn children or in other adults [4,5], such as induce prolactin secretion [6,7]. Furthermore, many kinds of abnormalities, including the cancers and other diverse pleiotropic actions in the brain and cardiovascular system had been found with the longer contact to BPA [8]. So the safety of products containing BPA brought to the public attention in many countries [9–12].

At present many methods have been established to detect BPA, such as liquid chromatography–mass spectrometry (LC-MS) [13] and gas chromatography–mass spectrometry (GC-MS) [14], enzyme-linked immunosorbent assay [15], high performance liquid chromatography (HPLC) [16], molecular imprinting technique [17] and electrochemical methods [18–20], Among these detection techniques, electrochemical methods have attracted more attentions with the advantages of low cost, easy to preparation, fast response, bulk modification, convenience of surface renew, high sensitivity and selectivity, and real-time detection in situ condition. The working electrode is often modified to enhance sensitivity and selectivity. Brugnera et al. [18] illustrated the effect of cetyltrimethylammonium bromide as an anti-fouling and pre-concentrating agent for electroanalysis of BPA on a screen-printed carbon electrode. Kuramitz et al. [19] used a column type carbon fiber electrode to investigate the electrochemical removal of BPA. Yin et al. [20] constructed an amperometric biosensor for the determination of BPA based on tyrosinase immobilized onto multiwalled carbon nanotubes-cobalt phthalocyanine-silk fibroin films.

Graphene (GR) is a kind of $sp^2$ hybridized two-dimensional honeycomb lattice, which has attracted enormous attention for its properties such as high thermal conductivity, high electrical conductivity and electron transfer rate [21]. Due to its specific advantages, GR can be used in electrochemical sensors. Stankovich et al. [22] provided a path to a broad class of GR-based materials and their use in a variety of applications. Wang et al. [23] prepared a GR-modified electrode for selective detection of dopamine. Wu et al. [24] constructed GR-based modified electrode to sense cytochrome c and enlarged the application of GR in the field of biosensor.

Carbon ionic liquid electrode (CILE) is prepared by incorporating ionic liquid into the traditional carbon past electrode, which has been proved to be an efficient working electrode in the field of electroanalysis with the advantages such as easy to prepare, high ionic conductivity, wide electrochemical windows and good electrocatalytic activity [25–27]. Sun et al. [28] investigated the direct electrochemistry of herring sperm double-stranded DNA on CILE. Safavi et al. [29] studied the electrochemical behavior of hemoglobin based

---

* Corresponding author. Tel./fax: +86 532 84023927.
*E-mail address:* sunwei@qust.edu.cn (W. Sun).

0040-6090/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2012.02.069

on its direct immobilization on CILE. Zhu et al. [30] constructed a single-walled carbon nanotubes modified CILE for electrochemical detection of rutin.

In the present paper, a CILE was prepared by using 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) as binder and modifier. Then the composite film prepared by GR and chitosan (CTS) was cast on the surface of CILE to get a modified electrode, which exhibited an improved electrochemical response due to the presence of GR. CTS is a positively charged alkaline polysaccharide with nontoxicity, well biocompatibility and excellent film-forming ability, which has been used in the chemically modified electrodes. The electrochemical behaviors of BPA were investigated on CTS-GR/CILE carefully with the electrochemical parameters calculated. Furthermore, the fabricated sensor was applied to determine trace amounts of BPA in plastic samples with satisfactory results.

## 2. Experimental details

### 2.1. Instruments and reagents

Electrochemical experiments such as cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and differential pulse voltammetry were carried out on a CHI 750B electrochemical workstation (Shanghai CH Instruments, China). A three-electrode system was used with a CTS-GR/CILE as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as counter electrode. All the potentials reported in this work had been measured versus SCE reference electrode. HPLC was performed on an Agilent model 1100 series with a photodiode array detector. The analytical column used was a Phenomenex ODS column (200 × 4.6 mm, I.D. 5 μm) and the mobile phase was consisted of acetonitrile–water (50:50) at a flow rate of 1.0 mL/min.

$1.0 \times 10^{-2}$ mol/L Bisphenol A (BPA, Tianjin Damao Chemical Reagent Factory) was prepared with anhydrous ethanol and used as the stock solution. Graphite powder (average particle size 30 μm, Shanghai Colloid Chemical Company), ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$, Lanzhou Greenchem ILS, LICP. CAS. China), chitosan (CTS, Dalian Xindie Limited Company, China), graphene (GR, ≥98.3%, Sinocarbon Technology Limited Company, China) were used as received. 0.1 M Britton–Robinson (B-R) buffer solution with various pH values were used as the supporting electrolyte. All the other chemicals used were of analytical reagent grade and doubly distilled water was used in all the experiments.

### 2.2. Preparation of CILE and CTS-GR/CILE

CILE was fabricated by hand-mixing 3.2 g graphite powder, 850 μL liquid paraffin, and 150 μL $EMIMBF_4$ thoroughly in a mortar to form a homogeneous carbon paste. A portion of the ionic liquid modified carbon paste was packed firmly into one end of a glass tube (internal diameter of 4.0 mm), and a copper wire was inserted through the opposite end to establish an electrical contact. Prior to use, the surfaces of the CILE were smoothed on a piece of weighing paper. Equal volume of 1.0 mg/mL GR suspension solution and 1.0 mg/mL CTS (in 1.0% HAc) solution were mixed together and ultrasonicated for 30 min. Then with a microinjector, 9.0 μL of CTS-GR mixture solution was cast on the surface of CILE and left it to dry at room temperature to form a stable film. The resulted electrode was denoted as CTS-GR/CILE. For comparison, CTS/CILE was fabricated with the similar procedure.

## 3. Results and discussion

### 3.1. Characteristics of the modified electrodes

The $[Fe(CN)_6]^{3-/4-}$ redox couple is used for the electrode characterization and the electrochemical response from $Fe^{3+}/Fe^{2+}$ redox couple can reflect the conductivity of the electrode interface. The electrochemical behaviors of different modified electrodes were investigated in the $1.0 \times 10^{-3}$ mol/L $K_3[Fe(CN)_6]$ and 0.5 mol/L KCl mixture solution with cyclic voltammograms shown in Fig. 1A. At a bare CILE (curve a), a pair of redox peaks appeared with the peak-to-peak separation (ΔEp) as 102 mV. After casting CTS on the CILE (CTS/CILE, curve b), the redox peaks increased a little, which could be attributed to the affinity of positively charged CTS to negatively charged $[Fe(CN)_6]^{3-/4-}$. When CTS-GR was fixed on the CILE surface, the redox peaks increased obviously with ΔEp value as 87 mV, which was due to the excellent electrical conductivity of GR present on the electrode surface. GR is a specific carbon material with big surface area and high conductivity, which can accelerate the electron transfer rate.

EIS is further used for the investigation on the modified electrodes, which can exhibit the impedance changes of the modification processes. The value of the electrode-transfer resistance (Ret) depends on the dielectric and insulating features at the electrode/electrolyte interface. Fig. 1B showed the EIS of different electrodes in 10.0 mmol/L $[Fe(CN)_6]^{3-/4-}$ and 0.1 mol/L KCl solution, in which Z′ and Z″ were the real variable and the negative value of the imaginary variable of impendence, respectively. On the CILE (a) the Ret value was got as 172.5 Ω. While on the CTS/CILE (b) the Ret value was decreased to 110.7 Ω, indicating that the presence of CTS on the electrode surface could accumulate more $[Fe(CN)_6]^{3-/4-}$ and accelerate the diffusion of ferricyanide toward the electrode surface. However, on the CTS-GR/CILE (c), the Ret value was greatly decreased to 15.61 Ω, which could be attributed to the presence of high conductive GR in the composite film that accelerated the electron transfer rate of $[Fe(CN)_6]^{3-/4-}$. The results also demonstrated that GR had been immobilized on the electrode surface.

### 3.2. Cyclic voltammetric behaviors of bisphenol A

Fig. 2 showed the electrochemical behaviors of 0.5 mmol/L BPA at different electrodes in 0.1 mol/L pH 8.0 B-R buffer solution at the scan

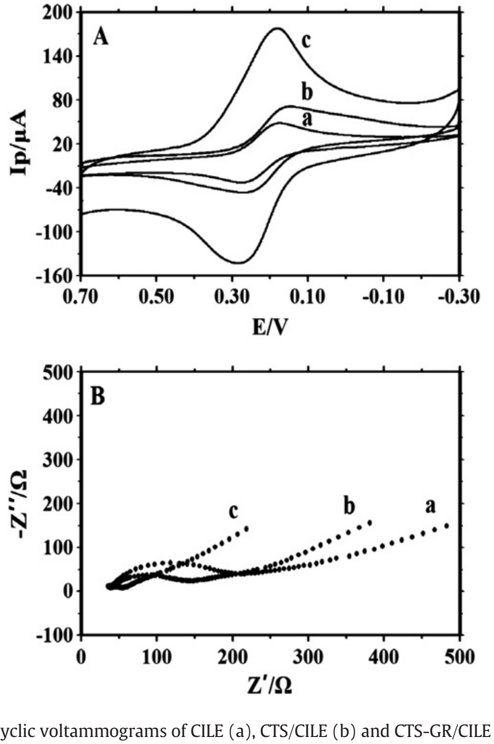

**Fig. 1.** (A) Cyclic voltammograms of CILE (a), CTS/CILE (b) and CTS-GR/CILE (c) in a solution of $1.0 \times 10^{-3}$ mol/L $K_3[Fe(CN)_6]$ and 0.5 mol/L KCl at the scan rate of 100 mV/s; (B) EIS for CILE (a), CTS/CILE (b) and CTS-GR/CILE (c) in 10.0 mmol/L $[Fe(CN)_6]^{3-/4-}$ and 0.1 mol/L KCl solution with the frequencies swept from $10^5$ to 0.1 Hz.