 Voltammetric Determination of Bisphenol A Based on Its Anodic Deposition at Chitosan-Graphene Modified Glassy Carbon Electrode under UV Irradiation

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Received: 19 October 2017 / Accepted: 6 December 2017 / Published: 28 December 2017

Bisphenol A (BPA) was successfully electrodeposited on glassy carbon electrode modified with the chitosan-graphene (Chit-GR/GCE) by multiple sweep voltammetry under ultraviolet (UV) irradiation. The experimental conditions of the BPA deposits and the probable oxidation mechanism were investigated. Two oxidation peaks (peakII=0.12 V, peakIII=0.20 V) appeared in a suitable potential range of 0.0V and 0.2V at the Chit-GR/GC electrode in the presence of UV light, and it could be seen that the oxidation peak current increased with the increase of UV irradiation time. The emerging peakIII was reported firstly in the work, which showed that the Chit-GR modified electrode had catalytic activity on the oxidation of BPA. Based on the oxidation peak (peakIII) of BPA oxidative products on the Chit-GR/GC electrode under UV irradiation, the electrochemical sensor was fabricated for determination of BPA. The calibration curve was obtained in the range of 5.0 to 200.0 μM with the limit of detection of 0.34 μM (S/N=3) and the response sensitivity of 0.33 μA μM⁻¹, which was higher than those of the method of determining BPA based on the direct oxidation of BPA (0.98 μM (S/N=3), 0.12 μA μM⁻¹). It was applied successfully for determination of BPA in lake, soil and plastic bottle samples. The new strategy, based on anodic electrodeposition and photocatalytic oxidation of BPA oxidation products, was provided for determination of BPA under UV irradiation. It was green, environmental and effective.

Keywords: Bisphenol A, Anodic deposition, Graphene, Ultraviolet irradiation

1. INTRODUCTION

Bisphenol A (BPA) has been a recognized environmental endocrine disruptor, which is harmful to the human endocrine, nervous system and the immune function and will lead to a variety of diseases, such as cancer and metabolic syndrome [1]. But it is widely found in mineral water bottles, medical devices, food packaging materials and so on, this is because BPA has been used as a stabilizer...
for plastic products and a raw material for polycarbonate and epoxy resins [2-4]. At present, BPA has become a universal environmental pollutant which was a direct threat to human health and safety [5].

It is of great practical significance to establish a rapid and simple method for detection of BPA [6-8]. Many kinds of methods for determination of BPA in wastewater and other phenolic pollutants had been reported, such as chemical methods [9-11], biodegradation methods [12-16], photochemical methods [17-21], and electrochemical methods [22-30] and so on. Electrochemical methods had been widely used for environment analysis because of the advantages of simplicity and low cost, and it will not cause secondary pollution to the environment. In previous reports, electrochemical methods for detection of BPA were mainly based on the direct oxidation of BPA, and the method of electrochemical oxidation degradation based on the oxidation of BPA oxidative products was few reported [31-34]. And there was no report on the method of BPA determination based on the oxidation of BPA oxidative products.

In this study, the GR-based redox-active electrode had been fabricated for determination of BPA based on the anodic deposition of BPA by the repetitive differential pulse voltammetry (DPV) on the Chit-GR/GC electrode. After the first cycle of DPV, two new oxidative peaks (peakII=0.12 V, peakIII=0.20 V) of BPA oxidative products appeared and they could be used to determine BPA. The emerging peakIII was reported for the first time in the paper. The two oxidative peaks were located in the double electrode layer range, which could increase the selectivity of the detection. Moreover, according to the reports, the BPA and its oxidation product intermediate could be photocatalytically degraded by UV with the TiO$_2$ [35-37]. In this work, the two oxidative peak heights were enhanced under the UV irradiation, which provided a good alternative for the electrochemical determination of BPA. Based on the oxidation of the oxidative products of BPA under UV irradiation, namely peakIII, a new method was developed and used successfully in real samples with satisfactory results. At the same time, the idea for photocatalysis degradation of BPA was promising.

2. EXPERIMENTAL

2.1. Reagents

GR was supplied from Nanjing Pioneer Nano Material Science and Technology Co., Ltd. 10.0 mM BPA stock solution was prepared with ethanol and stored in 4°C refrigerator. The chitosan solution was prepared with 1% acetic acid solution and adjusted to pH 5.0. The above reagents were purchased from Aladdin. All the experimental water was redistilled water.

2.2. Apparatus and measurements

Electrochemical experiments were performed on a CHI660E electrochemical workstation (Shanghai Chenhua Co., Ltd, China) with a conventional three-electrode system. A bare or modified GC electrode (3mm diameter, CHI) was used as working electrode, a silver/silver chloride electrode and platinum wire were used as reference electrode and auxiliary electrode, respectively. Differential
pulse voltammetry (DPV) scans were performed in a 0.1M NaCl solution (pH7.0) containing BPA at different concentrations in the potential range from -0.2 to 1.0V. A Zeiss Ultra55 field emission scanning electron microscope (SEM, Germany) was employed to analyze the surface appearance of Chit-GR and BPA/Chit-GR. Electrochemical impedance spectroscopy (EIS) was recorded on an Autolab PGSTAT-30 electrochemical system under open-circuit conditions between 100 kHz and 0.1 Hz with an amplitude of 10 mV. Unless otherwise noted, all the experiments were performed at room temperature (26-28°C).

2.3. Chit-GR/GC electrode preparation

Glassy carbon electrode was polished on the polishing pad with 0.3 μm alumina powder, then cleaned ultrasonically for 10 min with ethanol and distilled water, respectively, and air-dried at room temperature. 3.0 mg of GR was weighed and added into 3 ml chitosan solution (0.5g/100ml), then sonicated for 1 h to obtain a uniform black suspension. 5 μl suspensions were droped to the surface of the treated glassy carbon electrode using a microinjector. The Chit-GR/GC electrode was prepared by evaporating the solvent at room temperature.

3. RESULTS AND DISCUSSION

3.1. Characterization of Chit-GR/GC electrode

The morphologies of Chit-GR and BPA/Chit-GR composites were investigated by SEM. The layered structure of GR was visible and the edge of GR was transparent (Fig. 1A), which indicated that the GR could be dispersed by Chit solution. When the BPA was electrodeposited, the lamellar structure of GR become blurred and the entire surface appeared flat (Fig. 1B), which showed that a thin film had been formed on the surface of Chit-GR/GC electrode by anodic deposition of BPA.

![Figure 1. SEM images of Chit-GR (A) and BPA/Chit-GR (B).](image-url)

The electrochemical characterization of the modified electrodes were further investigated by cyclic voltammetry (CV) and EIS using K₃[Fe(CN)₆] and K₄[Fe(CN)₆] as the electrochemical redox
probes. As can be seen from the Figure 2B, the electron transfer impedance (Ret) on the bare GC electrode was 698 Ω by the equivalent circuit simulation. When the GC electrode surface was modified with the non-conductive chitosan, the Ret increased more significantly (3568.5 Ω), reflected by a larger semi-circle at higher frequencies. When the Chit-GR was immobilized on the GC electrode surface, the Ret decreased to 408.4 Ω, which was ascribed to GR. The GR could improve the conductivity of the GC electrode and promote the transfer of electrons between the solution and the electrode surface. Therefore, the Chit-GR/GC electrode was used as the working electrode in the study. The results had been verified by the CVs (Fig. 2A).

Figure 2. CVs (A, 0.1 V s$^{-1}$) and Nyquist plots (B, 0.1-10$^5$ Hz) of GC electrode (1), Chit/GC electrode (2) and Chit-GR/GC electrode (3) in 5 mM [Fe(CN)$_6$]$^{3/-4}$ (1:1)/0.1 M KCl.

3.2. Anodic deposition of BPA on Chit-GR/GC electrode

The BPA was electrodeposited on the Chit-GR/GC electrode by the repetitive DPVs sweeping between -0.2 V to 1.0 V. As depicted in Figure 3, only an direct oxidation peak (I) was appeared after 1st DPV. As the scanning number increased from 1 to 10, two new anodic peaks (II and III) occurred (Fig. 3B, Fig. 3C) and increased gradually, indicating that the oxidation products of BPA obtained by anodic deposition was oxidized again. And the peak current of direct oxidation peak I decreased gradually with the increase of scan number because the deposition of oxidation products of BPA blocked the further direct oxidation of BPA on the Chit-GR/GC electrode surface. The two oxidation peaks (peak I, peak II) had been reported in the literature [31, 32, 38]. But the peak III was reported in the work for the first time. The emerging peak III might be due to the π-π stacking and hydrogen bonding between GR and BPA oxidative products, and BPA oxidative products can be adsorbed onto the GR surface [39]. Moreover, the adsorption oxidation peak of BPA appeared at a more negative potential than that of the direct oxidation peak, which indicated that the GR had a catalytical activity to the BPA oxidation. The UV adsorbance peak of BPA appeared at 278 nm and the excited state of BPA was easy to lose electrons and oxidized when it was exposed under the UV. The results showed that UV could improve the sensitivity of BPA determination and decrease the oxidation potential of BPA(Figure 3C), which were consistent with the reference reported [40]. An electrochemical method
for determination of BPA was developed based on the anodic electrodeposition and photocatalytic oxidation of BPA products on the Chit-GR/GC electrode.

Figure 3. DPVs of 0.1 mM BPA in the 0.2 M NaCl (pH7.0) on the GC electrode (A) and Chit-GR/GC electrode in the absence (B) and presence of UV light (C). Inset shows 10th DPV of 0.1 mM BPA on the Chit-GR/GC electrode in the absence (1) and presence of UV light (2).
3.3. Optimization of experimental conditions

The oxidative degradation reaction of BPA as phenol derivatives could be affected by the acidity. Therefore, the effects of different pH values on the deposition of BPA on Chit-GR/GC electrode were investigated in the paper. With the increase of the pH value, the oxidation peak current decreased and the peak potential shifted negatively. As shown in Fig. 4, the oxidation peak potentials of BPA had a linear relationship with the pH values with a linear equation of $E_{pa} (V) = -0.051pH + 0.4596$ (R=0.9970), which had indicated that the electron number and proton number was equal in BPA oxidation reaction. In addition, the oxidation peak current of BPA increased with the increase of the pH values from 5.0 to 7.0, and then decreased with a further increase of pH values (Fig. 4A).

![Figure 4](image)

**Figure 4.** Effects of pH value on the oxidation peak current (A) and effect of pH on the oxidation peak potential (B) of BPA.

The whole anodic electrodeposition process of BPA was divided into three steps. The first step (peak I) was the direct oxidation-electrodeposition process of BPA. The reaction of four-electron and four-proton in BPA led to the quinone-containing products [41, 42]. The second step (peak II) was defined as the quinone-based reaction. Anodic deposition of BPA on the Chit-GR/GC electrode was carried out by the following reaction. The reaction product with the “R” group in the first step represented the potential oxonium ion phenol and its polymers. The third step (peak III) was defined as the adsorption oxidation peak which was ascribed to the π-π stacking and hydrogen bonding between GR and BPA oxidative products, and the reaction process was similar to the second step.

\[
(2+x) \quad \text{OH} - \begin{array}{c} \rightleftharpoons \end{array} -4e^- - 4H^+ + 4e^- + 4H^+ \quad \text{OH} - \begin{array}{c} \rightleftharpoons \end{array} -O-R
\]
In the experiment, the concentrations of sodium chloride solution also affected the oxidation peak current of BPA. The results were shown in Fig. 5. With the increase of sodium chloride concentration from 0.05 to 0.20 M, the oxidation peak current of BPA increased gradually, but decreased when it was over 0.20 M.

![Diagram](image1.png)

**Figure 5.** Effects of ionic strength on the oxidation peak current of BPA.

In addition, the effect of the irradiation time of the UV light on the experiment had been examined and the results were shown in Fig. 6. It could be seen that the oxidation peak current of BPA increased with the increase of irradiation time. So it was necessary to be irradiated with UV light throughout the experiment. The time of UV irradiation lasted for 25 minutes because the process of the repetitive DPVs needed 25 minutes.
Figure 6. Effects of UV irradiation time on the oxidation peak current of BPA.

3.4. Voltammetric determination of BPA

Under the optimum experimental conditions, the voltammetry response of different concentrations of BPA in 0.2 M NaCl (pH 7.0) solution on Chit-GR/GC electrode was studied by DPV. The results of the 10th cycle DPV were obtained for determination of BPA. Fig. 7A showed the DPV response of BPA at various concentrations from 5.0 to 200.0 μM on a Chit-GR/GC electrode. As can be seen, the oxidation peak (peakIII) current of electrodeposited product of BPA had a good linear relationship with its concentration from 5.0 to 200.0 μM. The regression coefficient was 0.9954 and the detection limit was 0.34 μM, respectively. So the electrochemical determination of BPA based on the oxidation of BPA oxidative products had been developed. At the same time, when the BPA concentration increased from 5 to 200 μM, the peak I current in the first DPV increased linearly and the regression coefficient of 0.9937 was obtained as shown in Fig. 7B. The response sensitivity were 0.33 μA μM⁻¹ (peakIII) and 0.12 μA μM⁻¹ (peak I), respectively. And the detection limit of the peak I was 0.98 μM. By comparison, the method based on the oxidation of BPA oxidative products was
superior to the method based on the direct oxidation of BPA. The linear calibration range and detection limit for BPA determination at this modified electrode were compared to other modified electrodes (Table 1).

Table 1. Comparison of the response characteristics of different modified electrodes for BPA detection

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Method</th>
<th>Linear range (μM)</th>
<th>LOD (μM)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-CD polymer/PVC/optical fiber sensor</td>
<td>Amperometry</td>
<td>6–1000</td>
<td>1</td>
<td>[43]</td>
</tr>
<tr>
<td>Tyr-SWCNT/PE</td>
<td>Amperometry</td>
<td>0.1–12</td>
<td>0.02</td>
<td>[44]</td>
</tr>
<tr>
<td>CYP2C9-PAM/GCE</td>
<td>I-t</td>
<td>1.25–10</td>
<td>0.58</td>
<td>[45]</td>
</tr>
<tr>
<td>Ordered mesoporous silica (SBA-MIP)/CPE</td>
<td>Amperometry</td>
<td>1–500</td>
<td>0.32</td>
<td>[46]</td>
</tr>
<tr>
<td>Tyrosinase/boron-doped diamond electrode</td>
<td>FIA</td>
<td>1–100</td>
<td>1</td>
<td>[47]</td>
</tr>
<tr>
<td>Chit-GR/GCE</td>
<td>DPV</td>
<td>5–200</td>
<td>0.34</td>
<td>This work</td>
</tr>
</tbody>
</table>

Tyr: tyrosinase;  
PE: paste electrode;  
CYP2C9: cytochrome P4502C9;  
I-t: amperometric I-t;  
MIP: surface molecularly imprinted electrode;  
CPE: carbon paste electrode;

3.5. Interference experiment

Figure 8. Effect of the interferences on the determination of 0.1 mM BPA
Based on the possible metal ions and organic compounds in the experiment, the selectivity of Chit-GR/GC electrode was studied. A suitable amount of interfering agent was added during the test of 0.1mM BPA and the measurement error was allowed to be within ± 5%. The results were shown in the Fig. 8. It was found that 100-fold concentration of p-nitrophenol, phenol, o-phenylenediamine, 20-fold resorcinol and 10-fold hydroquinone had no effect on 0.1mM BPA signal. Some ions, such as Cu$^{2+}$, Pb$^{2+}$, Ca$^{2+}$, Fe$^{3+}$, Cl$^{-}$ and Br$^{-}$, have no effect on BPA determination.

3.6. Reproducibility and stability

For investigating the fabrication reproducibility, 0.1mM BPA were measured by five modified electrodes and the RSD of the peak current was 2.1%, indicating that the method had excellent reproducibility. After the electrodes were stored at 4°C refrigerator for two weeks, the peak current of the electrodeposition product decreased to 92.7% of its original response with better stability.

3.7. Real sample analysis

In order to evaluate the analytical reliability and application potential of the proposed method. BPA in the soil, water and plastic bottles samples were determined by the standard addition method. Theses samples were prepared as follows: 10.0 g dry soil samples were transferred to a 100 mL volumetric flask with anhydrous ethanol to constant volume. After one hour, the soil sample was filtered and the collected filtrate was concentrated in 10 mL volumetric flask with absolute ethanol; The water sample was filtered through a 0.45 μm cellulose acetate filter and 1 mL of the filtrate was placed in a 10 mL volumetric flask and then filled with a buffer solution; 10.0 g of plastic product and 30 ml of distilled water were added to the beaker sealed with a cling film and allowed to stand at room temperature for 30 days.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured(μM)</th>
<th>Added(μM)</th>
<th>Found(μM)</th>
<th>RSD (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td></td>
<td>40</td>
<td>38.83</td>
<td>5.29</td>
<td>97.08</td>
</tr>
<tr>
<td>Soil</td>
<td>21.14</td>
<td>20</td>
<td>43.24</td>
<td>3.95</td>
<td>105.10</td>
</tr>
<tr>
<td>plastic bottle</td>
<td>12.82</td>
<td>20</td>
<td>31.77</td>
<td>4.39</td>
<td>96.80</td>
</tr>
</tbody>
</table>

The sample solution was filtered and the concentrated filtrate was transferred in a 50 ml volumetric flask. In addition, the spiked sample solutions were prepared by adding a known amount of BPA standard solution in the same manner. No BPA signal was observed in the water sample, possibly
due to the absence of BPA or too low concentration of BPA in the water below the detection limit. The results showed that the recoveries ranged from 94.4 to 105.1% and the corresponding RSD ranged from 3.72% to 5.47% (Table 2), which revealed that the developed method could be applied to the detect trace level BPA in soil, water and plastic bottles. The method was reliable in detecting the actual sample and had a certain practical application.

4. CONCLUSIONS

BPA could be deposited effectively on the Chit-GR/GC electrode by the simple multiple DPVs in the 0.2 M NaCl solution. A new strategy for determination of BPA based on anodic electrodeposition and photocatalytic oxidation was proposed in the paper. The reaction mechanism of BPA was discussed preliminarily. GR and UV could improve the sensitivity of determination of BPA to a certain extent. The oxidation peak (peakⅢ) of BPA oxidative product located in the range of double electrode layer, which can improve the selectivity of detection. The linear range was found to be between 5.0 μM and 200.0 μM and the limit of detection was 0.34 μM (S/N = 3). The experiment results showed that the oxidative degradation could be realized with the determination of BPA based on the direct oxidation of BPA. In principle, the strategy proposed in the paper provided a good alternative for photoelectrocatalysis degradation and determination of BPA based on the oxidation of BPA oxidative products.

ACKNOWLEDGEMENTS
This work was supported by the National Natural Science Foundation of China (Grant No. 81573678) and Natural Science Foundation of Guangdong Province, China (Grant No. 2015A030313584).

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