



# Electrochemical determination of bisphenol A in plastic bottled drinking water and canned beverages using a molecularly imprinted chitosan–graphene composite film modified electrode



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## ABSTRACT

Herein, a novel electrochemical sensor based on an acetylene black paste electrode modified with molecularly imprinted chitosan–graphene composite film for sensitive and selective detection of bisphenol A (BPA) has been developed. Several important parameters controlling the performance of the sensor were investigated and optimised. The imprinted sensor offers a fast response and sensitive BPA quantification. Under the optimal conditions, a linear range from 8.0 nM to 1.0  $\mu$ M and 1.0 to 20  $\mu$ M for the detection of BPA was observed with the detection limit of 6.0 nM ( $S/N = 3$ ). Meanwhile, the fabricated sensor showed excellent specific recognition to template molecule among the structural similarities and coexistence substances. Furthermore, this imprinted electrochemical sensor was successfully employed to detect BPA in plastic bottled drinking water and canned beverages.

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## 1. Introduction

Hormone disruptors are one of the major categories of environmental pollutants that scientists are concerned about. Bisphenol A (2,2-bis (4-hydroxyphenyl) propane, BPA) is an organic compound that widely used in the plastic industry as a monomer for producing epoxy resins and polycarbonate. In our life, BPA is ubiquitous since it can be inadvertently released into the environment to contaminate rivers and ground waters during the manufacturing process of these products. Moreover, BPA can also migrate into food and drinking water from a wide variety of food contact materials mainly derived from polycarbonates and epoxy resins, such as infant feeding bottles, tableware, storage containers and food can linings (Hu, Aizawa, & Ookubo, 2002). Thus, humans may routinely ingest trace amounts of BPA. A large number of researches have shown that BPA can mimic and interfere with hormonal activities by disrupting growth, development and reproduction (Kang, Kondo, & Katayama, 2006). Most importantly, BPA was found to possibly cause cancer (Muñoz-de-Toro et al., 2005). Therefore, the reliable, rapid and real-timely determination of trace level of BPA is extremely important for health protection and security.

At present, various methods have already been proposed to assay BPA. Chromatographic techniques, for example, liquid chromatography coupled with electrochemical, ultra-violet and fluorescence detection (Inoue, Kato, Yoshimura, Makino, & Nakazawa, 2000), liquid chromatography coupled with mass spectrometry (Pedersen & Lindholm, 1999), gas chromatography (Shin, Park, Park, & Pyo, 2001), gas chromatography coupled with mass spectrometry (Brock et al., 2001), are accurate, precise and robust. However, they often need expensive and complicated instruments, time-consuming pretreatment steps and skilled operators. Some other methods, such as fluorimetry (Wang, Zeng, Zhao, & Lin, 2006), enzyme-linked immunosorbent assay (Kuruto-Niwa, Tateoka, Usuki, & Nozawa, 2007), flow injection chemiluminescence (Wang, Wei, Du, & Zhuang, 2005) and electrochemical methods have been developed for BPA determination. Among these strategies, electrochemical methods have attracted wide attentions because of low cost of instrumentation, high sensitivity, simplicity for operators and portability. In order to enhance the electrochemical response of BPA, some chemically modified electrodes have been reported (Deng, Xu, & Feng, 2013; Gao et al., 2012; Li, Gao, Cao, & Li, 2012; Portaccio et al., 2010; Wang, Yang, & Wu, 2009; Yin, Zhou, & Ai, 2009; Yu et al., 2013). These electroanalytical methods were quite sensitive, but some of them showed poor selectivity. Furthermore, these electrochemical sensors are mostly applied to BPA's detection in environmental samples, seldom in food samples. Therefore, it is necessary

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to seek a facile, cheap, stable and highly selective method to determine BPA in food samples.

Molecular imprinting is a newly developed technology to introduce recognition properties into synthetic polymers. It has received more and more attention in recent years, and has been successfully used to recognise various molecules. In order to prepare molecularly imprinted polymers (MIPs), cross-linkers and functional monomers are polymerized with template molecules by covalent and non-covalent methods. After removal of template from the polymers, the cavity complementary in size and shape to the template is obtained in the polymer network (Alizadeh, 2010; Chen, Vittal, Nien, Liou, & Ho, 2010). In addition, MIPs possess several advantages over their biological recognition element, including stability and easiness of preparation. As a new class of materials possessing high selectivity and affinity for the target molecule, MIPs have been widely applied in sensor development (Malitesta et al., 2012).

In general, MIPs are nonconductive. To fabricate MIPs based electrochemical sensors other conductive materials should be introduced. Recently, graphene (GR) has caught a great deal of attention for its excellent electrical conductivity and extremely high specific surface area ( $2600 \text{ m}^2/\text{g}$ ) (Li, Li, Dong, Qi, & Han, 2010). It has been reported that GR and GR-based hybrid nanomaterials could effectively accelerate the electron transfer, which could lead to a more rapid and sensitive current response (Li, Chen, Zhang, Lu, & Yang, 2010; Liu et al., 2012; Su, Tang, Li, Tang, & Chen, 2011). On the other hand, acetylene black (AB), a special kind of carbon black, another carbon nano material, has also received great attention in the last few years due to their excellent properties such as excellent electric conductivity, large surface area, strong adsorptive ability, good chemical and thermal stability, and they are widely used in the fabrication of modified electrodes to increase the determining sensitivity of different species (Deng, Fei, & Feng, 2011; Deng, Xu, & Kuang, 2013; Sun & Zhang, 2006).

Herein, we want to explore applications of graphene flakes doped chitosan film as imprinted sensing nanocomposite on an acetylene black paste electrode (ABPE) for BPA detection. Our main aim is to improve qualities of the prepared imprinted sensor, such as fabrication simplicity, lower detection limit, higher sensitivity and selectivity. The function of GR, AB and the selectivity of the imprinted film towards BPA were investigated with various electrochemical measurements in detail. By clarifying the recognition mechanism and optimising some of the operating conditions, this study provided a new way for constructing sensitive and selective electrochemical sensors.

## 2. Experimental

### 2.1. Chemicals and solutions

Bisphenol A (BPA) and graphite powder was bought from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). Acetylene black (AB, purity > 99.99%) was purchased from STREM Chemicals, USA. Chitosan (CHIT, 95% deacetylation) was purchased from Shanghai Biochemical Co., Ltd., China. The stock solution of BPA (0.01 M) was prepared with ethanol and stored in a refrigerator at  $4^\circ\text{C}$ . A  $10 \text{ mg mL}^{-1}$  CHIT solution was prepared by dissolving 500 mg CHIT solid into 50 mL of 1.0% (v/v) acetic acid aqueous solution and then stirred the mixture for 2 h at room temperature until it was completely dispersed. 0.1 M phosphate buffer with pH 3.0 was used as the supporting electrolyte. All reagents were of analytical grade and used as received. All the solutions were prepared with redistilled water from quartz and all experiments were carried out at room temperature.

### 2.2. Apparatus

Cyclic voltammetry (CV) was performed on a CHI 660D electrochemical workstation (Chenhua Instrument Co., Ltd., Shanghai, China) controlled by a microcomputer with CHI660 software. A model JP-303E polarographic analyzer (Chengdu Instrument Factory, Chengdu, China) was used to give second-order derivative linear sweep voltammograms for electroanalytical measurements. A three-electrode system was used, where an acetylene black paste electrode modified with a molecularly imprinted chitosan-graphene composite (MIP-GR/ABPE, 1 mm i.d.) was used as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials reported were versus the SCE. pH measurements were performed with a pH-3c Model pH metre (Shanghai Leichi Instrument Factory, Shanghai, China) using a combined glass electrode. Fourier transform infrared (FTIR) spectroscopic measurements were performed on IRPrestige-21 fourier transform infrared spectrometer (Shimadzu corp., Japan). High-performance liquid chromatography (HPLC) was performed on Waters model 510 system (Waters Ltd., USA) comprising a Kromasil 100-5C18 ( $250 \text{ mm} \times 4.6 \text{ mm}$ ) column equipped with a Waters 2487 dual  $\lambda$  absorbance detector using a mobile phase consisting of 20 mM PBS (pH 7)-acetonitrile (65:35, v/v) at a flow rate of  $0.8 \text{ mL min}^{-1}$ .

### 2.3. Synthesis of graphene oxide (GO)

The graphite oxide was synthesized from graphite according to our previous reports (Deng et al., 2013). To begin, 0.5 g of graphite, 0.5 g of  $\text{NaNO}_3$ , and 23 mL of  $\text{H}_2\text{SO}_4$  were stirred together in an ice bath. 3 g of  $\text{KMnO}_4$  was slowly added to the mixture. Next, the mixture was transferred to a  $35^\circ\text{C}$  water bath and stirred for about 2 h, forming a thick paste. 40 mL of water was then slowly added, the reaction solution was stirred for 30 min while the temperature was raised to  $95^\circ\text{C}$ . 100 mL of water was then added, followed by the slow addition of 3 mL of  $\text{H}_2\text{O}_2$  (30%), which turned the colour of the solution from dark brown to yellow. The resulting suspension was filtered, washed with 1 M HCl and twice with deionized water, and vacuum-dried at  $50^\circ\text{C}$  for 24 h to obtain graphite oxide. The graphite oxide was then dispersed in deionized water ( $0.25 \text{ mg mL}^{-1}$ ) and exfoliated to graphene oxide (GO) by ultrasonication for 2 h. It was then centrifuged at 6000 rpm for 30 min to remove the excess, unoxidized graphite and unexfoliated graphite oxide.

### 2.4. Fabrication of the imprinted and non-imprinted sensor

The acetylene black paste electrode (ABPE) was prepared by thoroughly mixing 1.20 g AB powder with 0.30 g solid paraffin in a mortar, and then the mixture was heated until the solid paraffin melted. The resultant paste was tightly pressed into the end cavity (1 mm in diameter) of the electrode body immediately, and the surface was polished with a piece of smooth paper until it had a shiny appearance. Then the electrode was subjected to cyclic potential sweeps between 0.2 and 1.2 V in 1.0 M  $\text{H}_2\text{SO}_4$  until a stable cyclic voltammogram was obtained. For the preparation of the imprinted sensor, 1.0 mL BPA (10 mM) was mixed with 1 mL CHIT ( $10 \text{ mg mL}^{-1}$ ) and 1 mL GO suspension ( $0.25 \text{ mg mL}^{-1}$ ). The mixture was stirred for 1 h and then subjected to ultrasonic agitation for 2 h. After that, 2  $\mu\text{L}$  of BPA-CHIT-GO mixture was transferred on the surface of the pretreated ABPE and the solvent was evaporated in air. Subsequently, the modified electrode was immersed into 0.5 M sulfuric acid at room temperature for 1 h, thoroughly washed with distilled water and air-dried. The electrode was tagged as BPA-CHIT-GO/ABPE. Removal of the template molecules was achieved by cyclic potential sweeping the modified electrode in 0.1 M HCl between 0.2 and 1.2 V repeatedly till there was no

signal of BPA. Afterwards, the electrode was immersed in a 0.1 M phosphate buffer (pH 6.5) and the potential was hold at  $-1.2$  V for 120 s. Thus GO was reduced to GR and the obtained electrode was denoted as MIP-GR/ABPE. A control electrode (non-imprinted electrode, NIP-GR/ABPE) was prepared under the same experimental conditions but without adding the template molecule. In order to show the unique properties of GR and AB, the imprinted chitosan film modified electrode (MIP/ABPE) and conventional carbon paste electrode made with graphite powder (CPE) were also prepared. These electrodes were stored at room temperature before use.

## 2.5. Sample preparation

Samples of plastic bottled drinking water of different brands and canned beverages (soft drinks, energy drinks and beer) commercially available in the local supermarket were used in this work. Beverages were transferred into a beaker and degassed in an ultrasonic bath. An aliquot (200 mL) of the samples was shaken vigorously for 5 min with 20 mL of methylene dichloride. The methylene dichloride layer was transferred to a flask, and the extractant was evaporated to dryness under reduced pressure at  $40^\circ\text{C}$ . The residue was dissolved in 1 mL of ethanol and collected in a 10-mL electrochemical cell, filled up to the mark with 0.1 M phosphate buffer (pH 3.0).

## 2.6. Electrochemical measurements

Certain concentration of BPA and 0.1 M phosphate buffer (pH 3.0) were transferred to a 10 mL cell, and the electrode-system was installed on it. The accumulation time of the imprinted sensor in BPA test solution was 180 s. Second-order derivative linear sweep voltammograms were recorded. The potential scan ranges were 0.2–1.2 V with a scan rate of  $0.2\text{ V s}^{-1}$ . After every measurement, the template-entrapped electrode was submitted to potential scanning in 0.1 M HCl with the purpose of removing BPA molecules for reuse. Complete regeneration was verified by the disappearance of the oxidation peak of BPA. The same procedure was carried out in the sample analysis and all electrochemical experiments were performed at room temperature.

# 3. Results and discussion

## 3.1. Template removal by CV

Before the rebinding adsorption of MIP-GR/ABPE, template should be removed from imprinted matrix. In this work, CV was performed to extract BPA molecules from the imprinted matrix. As shown in Fig. S1 (presented in Electronic Supplementary Material, ESM), the template-entrapped electrode was subjected to cyclic potential sweeps repeatedly between 0.2 and 1.2 V in 0.1 M HCl solution at the scan rate of  $0.1\text{ V s}^{-1}$ . A very sharp and well-defined oxidation peak at 0.902 V was clearly recorded. After cyclic potential sweeping repeatedly for 30 cycles, there was almost no electrochemical response observed. The disappearance of CV signal confirmed that BPA had almost been removed. To corroborate the fact that the template was completely extracted from the imprinted matrix, The UV-visible spectral analysis was also conducted before and after the elution step. The sensor was immersed in ethanol for 5 h, the UV-visible spectrum showed a distinctive peak of the phenolic hydroxyl groups of BPA at 275 nm. After removing BPA via electrochemical induced elution, there was no absorption peak observed in the ethanol solution.

## 3.2. Characterization of the sensor

### 3.2.1. FTIR spectra

The interaction force between template molecule and functional monomer is very important to the recognition property of the sensor. BPA has  $-\text{OH}$ , and CHIT has  $-\text{OH}$  and  $-\text{NH}_2$ . Therefore, BPA could combine with CHIT by hydrogen bond. In order to illustrate that interactions have been existed between BPA and CHIT, the Fourier transform infrared (FTIR) spectroscopic measurements were performed. Fig. S2 (ESM) presents the FTIR spectra of pure CHIT film, BPA and BPA-CHIT composite film. The spectrum of pure CHIT film shows the absorption peaks at about  $3447\text{ cm}^{-1}$  for the  $-\text{OH}$  groups,  $3363\text{ cm}^{-1}$  for the  $-\text{NH}_2$  groups, at about  $2884\text{ cm}^{-1}$  for the aliphatic  $\text{C-H}$  stretching vibration,  $1657\text{ cm}^{-1}$  for the absorption peaks of the rest  $-\text{CONH}_2$  groups, and  $1152\text{ cm}^{-1}$  for the  $\text{C-O-C}$  groups (curve a). The spectrum of BPA exhibits the characteristic bands of  $-\text{OH}$  stretching vibration at about  $3353\text{ cm}^{-1}$ ,  $\text{C-H}$  stretching vibration at about  $2965\text{ cm}^{-1}$ , benzene ring skeleton  $\text{C=C}$  stretching vibration at  $1450\text{--}1600\text{ cm}^{-1}$ ,  $\text{C-O}$  stretching vibration at  $1020\text{--}1275\text{ cm}^{-1}$ ,  $\text{C-C}$  stretching vibration at  $750\text{--}1200\text{ cm}^{-1}$  (curve b). In the curve c, the absorption band at about  $3300\text{ cm}^{-1}$  is broaden and the absorption band corresponding to  $\text{NH}_2$  deformation vibration in CHIT moves from  $1591$  to  $1565\text{ cm}^{-1}$  compared with curve a. It indicates that CHIT and BPA must interact with each other through forming hydrogen bond etc.

### 3.2.2. CV characterization of different electrodes

CV of ferricyanide is an effective and convenient tool to monitor the surface status and the barrier of the modified electrode during each assembly step. Fig. 1 shows the CV responses of  $1.0\text{ mM K}_3[\text{Fe}(\text{CN})_6]$  solution in 0.1 M KCl at the CPE, ABPE, GO/ABPE, NIP-GR/ABPE and MIP-GR/ABPE, respectively. As is shown, the electrochemical response for  $\text{Fe}(\text{CN})_6^{3-/4-}$  is a quasi-reversible process with the peak-to-peak separation of 158 mV at  $0.1\text{ V s}^{-1}$  on the CPE (curve a). While on the ABPE, a significant increase in redox peak current is observed, and the peak-to-peak separation is 125 mV (curve b). It is undoubtedly attributed to the unique characteristics of AB such as excellent electric conductivity and large surface area. After ABPE was coated with GO, the redox peak current of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  declined greatly due to the weak conductivity of GO and negative charge repulsion force between the ionised groups such as  $\text{COO}^-$  in GO and  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  (curve c). Compared with GO/ABPE, the electrochemical behaviour of the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  was

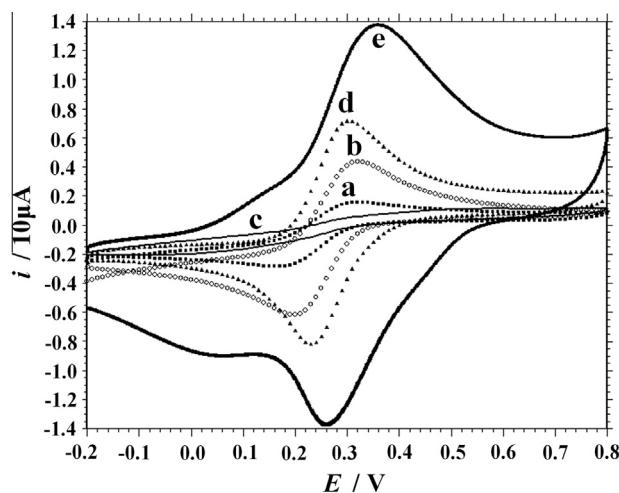
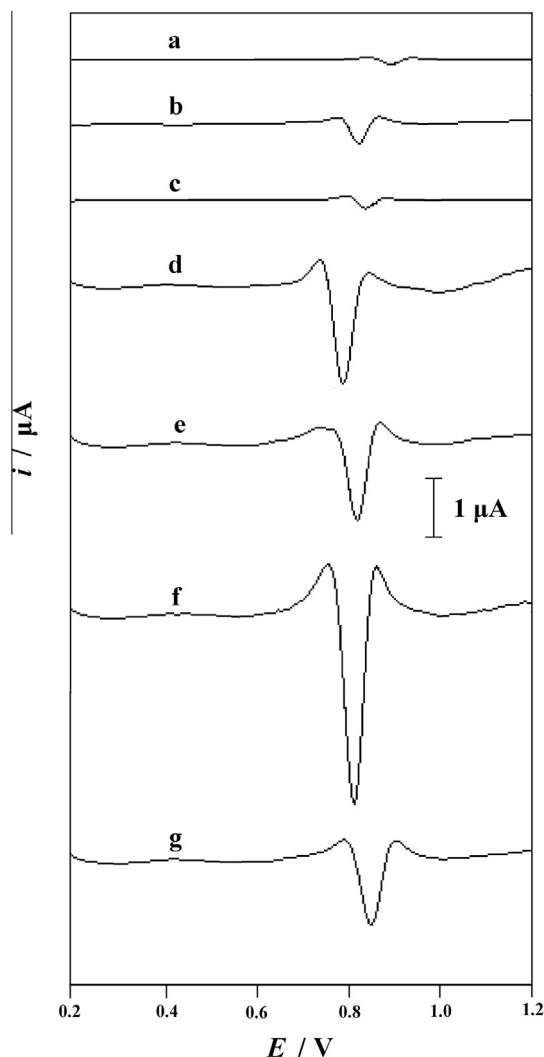


Fig. 1. Cyclic voltammograms for different electrodes in the presence of  $1\text{ mM K}_3[\text{Fe}(\text{CN})_6]$  and  $0.1\text{ M KCl}$ : (a) CPE, (b) ABPE, (c) GO/ABPE, (d) NIP-GR/ABPE and (e) MIP-GR/ABPE. Scan rate:  $0.1\text{ V s}^{-1}$ .

dramatically improved at the NIP-GR/ABPE, with the  $\Delta E_p$  value decreased to 75 mV, which could be attributed to the excellent electrical conductivity of GR present on the electrode surface (curve d). Once the template BPA was extracted from the imprinted matrix, the redox current of  $\text{Fe}(\text{CN})_6^{3-/4-}$  further increased, as shown in curve e. This could be explained that after removal of the template, the  $\text{K}_3[\text{Fe}(\text{CN})_6]$  molecules could pass through the vacant recognition sites or binding cavity and reached the surface of the electrode more easily.

### 3.3. Voltammetric behaviour of BPA

Second-order derivative linear sweep voltammetry is a widely used analytical technique for the enhancement of sensitivity and specificity in quantitative analysis, which has a higher current, better signal-to-background characteristics and better resolution of overlapping than cyclic voltammetry (Deng, Xu, Feng, & Li, 2012; Li, Zhao, & Huang, 2007). The second-order derivative linear sweep voltammograms of 5  $\mu\text{M}$  BPA in 0.1 M phosphate buffer with pH 3.0 at different electrodes were recorded after 180 s accumulation time. As shown in Fig. 2, on the surface of the CPE, a small



**Fig. 2.** Second-order derivative linear sweep voltammograms of 5.0  $\mu\text{M}$  BPA recorded at different electrodes: (a) CPE, (b) ABPE, (c) GO/ABPE, (d) GR/ABPE, (e) MIP/ABPE, (f) MIP-GR/ABPE and (g) NIP-GR/ABPE in 0.1 M phosphate buffer (pH 3.0). Accumulation time: 180 s, scan rate: 0.2 V  $\text{s}^{-1}$ .

oxidation peak (0.892 V, 0.07875  $\mu\text{A}$ ) for the electro-oxidation of BPA is observed (curve a), revealing that the electrode process is very sluggish. In the case of the ABPE, the response is considerably improved, a well-defined oxidation peak with a peak potential of 0.824 V and a peak current of 0.4257  $\mu\text{A}$  is obtained for BPA (curve b), suggesting that the oxidation of BPA is more favourable at the ABPE, which is undoubtedly attributed to the unique characteristics of AB. After GO was modified onto the ABPE surface, the peak current decreased (0.836 V, 0.2025  $\mu\text{A}$ , curve c), suggesting the retarded electron transfer due to the poor conductivity of GO. When GO is reduced, the anodic peak at GR/ABPE shifted negatively to 0.796 V, the peak current increased greatly to 1.941  $\mu\text{A}$  and the peak shape was well-defined (curve d). The remarkable enhancement of the peak current and the lowered reduction overpotential are clear evidences of the enhancement effects of GR. As can be seen, at the MIP-GR/ABPE, BPA exhibited a much higher current response ( $I_p = 3.930 \mu\text{A}$ , curve f) compared to the GR/ABPE. Meanwhile, the electrochemical response of the NIP-GR/ABPE to BPA was also examined. Under the same conditions, it could be seen that the oxidation peak current of BPA at the MIP-GR/ABPE was also higher than that obtained at the NIP-GR/ABPE ( $I_p = 1.389 \mu\text{A}$ , curve g), indicating that the template BPA imprinted procedure was successful. The MIP can provide many specific sites for BPA, which plays an important role in sensing BPA. On the other hand, without GR the obtained MIP/ABPE presented weaker response to BPA ( $I_p = 1.584 \mu\text{A}$ , curve e) than that at the MIP-GR/ABPE. Therefore, the MIP-GR/ABPE virtually combines the effect of MIP, GR and AB, and gives excellent electrochemical response to BPA.

### 3.4. Fabrication of imprinted sensor

The concentration of BPA in the BPA-CHIT-GO mixture determines the imprinted film structure and influences the amount of recognition sites available for selective rebinding of templates, which was found to play a key role in the sensor performance. Effect of the BPA concentration on the rebinding of BPA was investigated. As shown in Fig. S3A (ESM), 1 mL different concentrations of BPA were used to prepared the imprinted sensor. The rebinding amount of BPA increased with increasing BPA concentration from 0 to 10 mM, which indicated that the imprinted sites were successfully produced. The rebinding of BPA was found saturated if further increasing BPA concentration from 10 to 20 mM. Therefore, the optimum concentration of BPA is 10 mM for the sensor preparation.

GO concentration is also a crucial factor on the sensor performance. Too high concentration of GO would weaken the combination stability between BPA and CHIT, while too low concentration would lead to slow electron transfer rate. As shown in Fig. S3B (ESM), different concentrations of GO were examined, and the maximum peak height of BPA was obtained for 0.25  $\text{mg mL}^{-1}$  GO.

In general, the thickness of imprinted film affects the amount of recognition sites and elution effect, which could easily be adjusted by controlling the dosage of BPA-CHIT-GO mixture loaded on the electrode surface. Fig. S3C (ESM) demonstrates that the oxidation peak current of BPA gradually increases with improving the volume of BPA-CHIT-GO mixture from 0 to 2  $\mu\text{L}$ . Then it decreases slowly. Therefore, the volume of BPA-CHIT-GO mixture loaded on the ABPE surface was kept at 2  $\mu\text{L}$ .

It is well known that chitosan is a hydrophilic membrane showing a big swelling degree and lower selective property in the water. Treatment of chitosan with crosslinking agents is a common strategy for decreasing swelling and maintaining a better shape of the "memory" cavity structure. In the present study, glutaraldehyde, epichlorohydrin and sulfuric acid were used as cross-linking agent, respectively. The results showed that the peak current of BPA is largest in the case of sulfuric acid. The structure and properties of sulfuric acid-crosslinked chitosan film were studied by infrared



spectroscopy, elemental analysis, and X-ray diffraction in previous reports (Cui et al., 2008; Ma, Chen, Zheng, Youn, & Chen, 2011), and the strong interactions between chitosan  $\text{NH}_3^+$  groups and  $\text{SO}_4^{2-}$  anions improved the performance of imprinted film.

### 3.5. Optimisation of the experimental conditions

#### 3.5.1. Supporting electrolytes

As a key factor affecting the electrochemical responses of BPA at the MIP-GR/ABPE, different supporting electrolytes were tested by second-order derivative linear sweep voltammetry, including Britton–Robinson buffer, phosphate buffer, acetate buffer,  $(\text{CH}_2)_6\text{N}_4$ -HCl buffer,  $\text{KHC}_8\text{H}_4\text{O}_4$ -HCl buffer (each 0.1 M). It was found that the oxidation peak current was highest and the peak shape was best defined in phosphate buffer. Consequently, 0.1 M phosphate buffer was chosen as supporting electrolyte for quantitative analysis of BPA.

#### 3.5.2. Solution pH

The effect of the pH value of the phosphate buffer on the current response of MIP-GR/ABPE to 5  $\mu\text{M}$  BPA was investigated in the pH range from 2.94 to 5.89. The second-order derivative linear sweep voltammograms were shown in Fig. S4A (ESM) and the relationships between the peak current and the peak potential with pH were also plotted (Fig. S4B and C). It was found that the current response decreases gradually with pH values increasing. Therefore, considering the sensitivity of the determination of BPA, a pH value of 3.0 was chosen for the subsequent analytical experiments. At the same time, the peak potential ( $E_p$ ) changes with pH, and a linear shift of  $E_p$  towards negative potential with an increasing pH indicated that protons are directly involved in the oxidation of BPA. It obeys the following equation:  $E_p$  (mV) =  $-58.96 \text{ pH} + 1008.4$  ( $R = 0.9922$ ). A slope of  $58.96 \text{ mV pH}^{-1}$  suggests that the number of electron transfer is equal with that of hydrogen ions taking part in the electrode reaction (Yin et al., 2009).

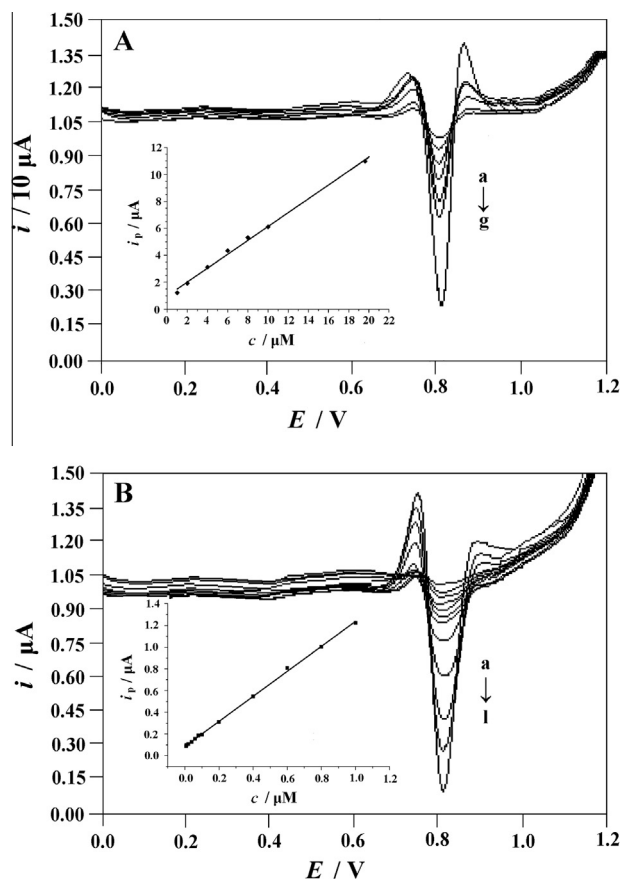
#### 3.5.3. Accumulation time

The accumulation step is usually a simple and effective way to enhance the sensitivity of the MIP-based sensor. After template molecules were removed from the imprinted matrix, the MIP-GR/ABPE was incubated in a stirring 0.1 M phosphate buffer (pH 3.0) containing 10  $\mu\text{M}$  BPA for different accumulation time. As shown in Fig. S5 (ESM), the peak current increased rapidly with the increase in the accumulation time at the initial stage, and a stable response was obtained after 180 s, meaning that the saturated rebinding of BPA onto the MIP-GR/ABPE is achieved. Thus, the optimum accumulation time should be 180 s for the electrochemical determination. The speedy response might result from the GR which could enhance electron transfer on the electrode interface and promote the oxidation of BPA.

### 3.6. Analytical performance

#### 3.6.1. Calibration curve

In this work, second-order derivative linear sweep voltammograms were recorded to obtain the linear range and detection limit. As shown in Fig. 3, under the optimised experimental conditions, the peak current increases with BPA concentration increasing. The inset of Fig. 3 shows the corresponding calibration curves, demonstrating that in the range from 8.0 nM to 1.0  $\mu\text{M}$  and 1.0 to 20  $\mu\text{M}$ , the anodic peak current has a good linear relationship with BPA concentration, with the linear regression equation  $I_p$  ( $\mu\text{A}$ ) =  $1.1521 c$  ( $\mu\text{M}$ ) +  $0.0853$  ( $r = 0.9996$ ) and  $I_p$  ( $\mu\text{A}$ ) =  $0.5146 c$  ( $\mu\text{M}$ ) +  $0.989$  ( $r = 0.9954$ ). The detection limit ( $S/N = 3$ ) is estimated



**Fig. 3.** Second-order derivative linear scan voltammograms obtained at MIP-GR/ABPE in 0.1 M phosphate buffer (pH 3.0) containing different concentrations of BPA. (A) From a–g: 1, 2, 4, 6, 8, 10, and 20  $\mu\text{M}$ . Insets: plot of the peak current as a function of concentration of BPA in the range of 1–20  $\mu\text{M}$ ; (B) from a–l: 0.008, 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0  $\mu\text{M}$ . Insets: plot of the peak current as a function of concentration of BPA in the range of 8 nM–1  $\mu\text{M}$ . Accumulation time: 180 s, scan rate:  $0.2 \text{ V s}^{-1}$ .

to be 6.0 nM for 180 s accumulation. The determination performances of MIP-GR/ABPE were compared with other modified electrodes and the results were listed in Table 1. It can be seen that MIP-GR/ABPE offered a wider linear range and a lower detection limit than most of previous reports. Meanwhile, the imprinted sensor displayed excellent selectivity towards the target molecule BPA. To further confirm the advantages of MIP-GR/ABPE for selective BPA determination, this method was also compared with other imprinted electrochemical sensors for BPA (Deng, Xu, Li, & Kuang, 2013; Huang et al., 2011a, 2011b; Wang, Yang, Xu, & Zhang, 2011; Zhang, Xu, Wang, & Lu, 2009; Zhu, Cao, & Cao, 2014). The results were also listed in Table 1. It is noteworthy that the quick and easy-to-made renewal of the electrode, short incubation time as well as the characteristics of low detection limit, wide linear range, good repeatability and reproducibility, simple fabrication and low-cost, are the predominant advantages of proposed sensor over other existing imprinted sensor. In previous work, we reported the determination of BPA by using salicylaldehyde-modified chitosan modified electrode (Deng et al., 2013) and molecularly imprinted chitosan film modified electrode (Deng et al., 2013). In the present study, the sensitivity of the sensor could be enhanced by an increase in the electrochemical conductivity and in the surface area provided by the use of graphene. Therefore, based on the combination of graphene and molecularly imprinting technology, the developed sensor not only improves the selectivity but also the sensitivity to BPA.

**Table 1**

Comparison of the efficiency of some modified electrodes in the electrochemical determination of bisphenol A.

Technique	Electrode	Linear range (M)	Detection limit (M)	References
Amperometry	Single-walled carbon nanotubes/ $\beta$ -cyclodextrin conjugate modified GCE	$1.08 \times 10^{-8}$ – $1.85 \times 10^{-5}$	$1.0 \times 10^{-9}$	Gao et al. (2012)
Amperometry	Multi-walled carbon nanotubes/melamine complex modified GCE	$1.0 \times 10^{-8}$ – $4.08 \times 10^{-5}$	$5.0 \times 10^{-9}$	Li et al. (2012)
Amperometry	Thionine modified CPE	$1.5 \times 10^{-7}$ – $4.5 \times 10^{-5}$	$1.5 \times 10^{-7}$	Portaccio et al. (2010)
DPV	Cobalt phthalocyanine modified CPE	$8.75 \times 10^{-8}$ – $1.25 \times 10^{-5}$	$1.0 \times 10^{-8}$	Yin et al. (2009)
DPV	Mesoporous silica MCM-41 modified CPE	$2.20 \times 10^{-7}$ – $8.8 \times 10^{-6}$	$3.8 \times 10^{-8}$	Wang et al. (2009)
DPV	$\beta$ -Cyclodextrin modified ionic liquid-based CPE	$1.0 \times 10^{-7}$ – $1.1 \times 10^{-5}$	$8.3 \times 10^{-8}$	Yu et al. (2013)
Derivative voltammetry	Salicylaldehyde-modified chitosan modified ABPE	$4.0 \times 10^{-8}$ – $1.0 \times 10^{-5}$	$2.0 \times 10^{-8}$	Deng et al. (2013)
Derivative voltammetry	Molecularly imprinted chitosan film modified ABPE	$8.0 \times 10^{-8}$ – $1.0 \times 10^{-5}$	$6.0 \times 10^{-8}$	Deng et al. (2013)
Amperometry	Molecularly imprinted poly (2-aminothiophenol)-gold nanoparticles modified GCE	$8.0 \times 10^{-6}$ – $6.0 \times 10^{-2}$	$1.38 \times 10^{-7}$	Huang et al. (2011)
CV	Surface molecularly imprinted ordered mesoporous silica modified CPE	$1.0 \times 10^{-7}$ – $5.0 \times 10^{-4}$	$3.222 \times 10^{-8}$	Wang et al. (2011)
Amperometry	Molecularly imprinted sol-gel/gold nanoparticles-multi-walled carbon nanotubes modified gold electrode	$1.13 \times 10^{-7}$ – $8.21 \times 10^{-3}$	$3.6 \times 10^{-9}$	Huang et al. (2011)
CV	Molecularly imprinted poly (2-aminothiophenol) modified GCE	$6.0 \times 10^{-7}$ – $5.5 \times 10^{-5}$	$2.0 \times 10^{-7}$	Zhang et al. (2009)
CV	Magnetic molecularly imprinted nanoparticles-surfactant modified CPE	$6.0 \times 10^{-7}$ – $1.0 \times 10^{-4}$	$1.0 \times 10^{-7}$	Zhu et al. (2014)
Derivative voltammetry	Molecularly imprinted chitosan-graphene composite film modified ABPE	$8.0 \times 10^{-9}$ – $1.0 \times 10^{-6}$ ; $1.0 \times 10^{-6}$ – $2.0 \times 10^{-5}$	$6.0 \times 10^{-9}$	Present work

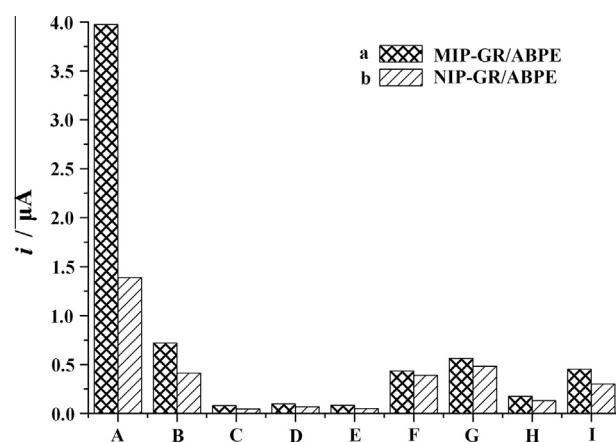
DPV: differential pulse voltammetry; CV: cyclic voltammetry; GCE: glassy carbon electrode; CPE: carbon paste electrode; ABPE: acetylene black paste electrode.

### 3.6.2. Repeatability, reproducibility and stability

To investigate the repeatability of the imprinted sensor, repetitive measurements were carried out in solutions containing 5.0  $\mu$ M BPA at the same MIP-GR/ABPE. After every measurement, the MIP-GR/ABPE was subjected to cyclic potential sweeps repeatedly between 0.2 and 1.2 V in 0.1 M HCl to remove BPA molecules for reuse. Complete regeneration was verified by the disappearance of the oxidation peak of BPA. The results of ten measurements showed a relative standard deviation (RSD) of 2.5%. It revealed that the imprinted sensor had good reversibility with subsequent washing and incubation procedures. Additionally, the reproducibility of the imprinted sensor was estimated with determining the response of 5.0  $\mu$ M BPA using six imprinted sensors prepared independently under the same conditions. The relative standard deviation (RSD) was 4.2%. Stability of the proposed electrode was also tested. When the electrode was kept in 0.5 M  $\text{H}_2\text{SO}_4$  at room temperature for 10 days, the sensor retained 91.7% of its initial current response.

### 3.6.3. Selectivity

Selectivity is one of potential merits for an imprinted sensor. In order to investigate the selectivity of the imprinted sensor, the MIP-GR/ABPE and NIP-GR/ABPE was incubated separately in BPA, 4-tert-butylphenol, phenol, p-nitrophenol, o-nitrophenol, hydroquinone, catechol, p-aminophenol and o-aminophenol solution (each 5  $\mu$ M) for 180 s and the response currents were recorded. As shown in Fig. 4, the sensitivity of the MIP-GR/ABPE towards BPA was approximately 3 times larger than NIP-GR/ABPE, indicating the proposed sensor had excellent specificity. Noticeably, the peak current magnitude of BPA at the MIP-GR/ABPE was higher than other compounds, although they possess the identical electroactive groups. The results revealed that the proposed sensor exhibited good selectivity towards BPA. Furthermore, the influence of other substances was also tested by the MIP-GR/ABPE as potential sources of interference. It was found that 1000-fold of



**Fig. 4.** Current responses of (A) bisphenol A, (B) 4-tert-butylphenol, (C) phenol, (D) p-nitrophenol, (E) o-nitrophenol, (F) hydroquinone, (G) catechol, (H) p-aminophenol and (I) o-aminophenol (each 5.0  $\mu$ M) at the (a) MIP-GR/ABPE and (b) NIP-GR/ABPE. Supporting electrolyte: 0.1 M phosphate buffer with pH 3.0; accumulation time: 180 s, scan rate: 0.2 V  $\text{s}^{-1}$ .

$\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{V}^{5+}$ ,  $\text{Ni}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  had no obvious effect on the determination of 5  $\mu$ M BPA. Therefore, satisfactory selectivity of MIP-GR/ABPE for BPA was obtained.

### 3.6.4. Real sample analysis

To evaluate the applicability of the developed method, different brands of mineral water samples in plastic bottles and canned beverages were analysed. The sample solutions were prepared as described in Section 2.5 and BPA was determined following above developed procedure using the standard addition method. All the samples investigated were analysed with one imprinted sensor and three measurements were performed at each concentration. Every time after analysing one sample and removing the template,

**Table 2**Determination of BPA in plastic bottled drinking water and canned beverages ( $n = 3$ ).

Sample <sup>a</sup>	Found by this method <sup>b</sup> / $\mu\text{g L}^{-1}$	Added/ $\mu\text{g L}^{-1}$	Total found by this method <sup>b</sup> / $\mu\text{g L}^{-1}$	Recovery/%	Content determined by this method <sup>b</sup> / $\mu\text{g L}^{-1}$	Content determined by HPLC <sup>b</sup> / $\mu\text{g L}^{-1}$
Mineral water (brand A)	11.40 $\pm$ 0.68	22.80	32.83 $\pm$ 2.51	94	0.57 $\pm$ 0.04	0.51 $\pm$ 0.06
Mineral water (brand B)	5.70 $\pm$ 0.46	22.80	26.68 $\pm$ 1.82	92	0.28 $\pm$ 0.02	0.32 $\pm$ 0.04
Mineral water (brand C)	7.30 $\pm$ 0.68	22.80	29.18 $\pm$ 1.82	96	0.36 $\pm$ 0.03	0.44 $\pm$ 0.05
Lemon flavoured soft drink	16.87 $\pm$ 1.37	22.80	38.08 $\pm$ 3.19	93	0.84 $\pm$ 0.07	0.78 $\pm$ 0.09
Grape flavoured soft drink	8.21 $\pm$ 0.46	22.80	30.10 $\pm$ 2.74	96	0.41 $\pm$ 0.03	0.52 $\pm$ 0.05
Orange soft drink	15.05 $\pm$ 1.14	22.80	36.02 $\pm$ 2.51	92	0.75 $\pm$ 0.05	0.78 $\pm$ 0.08
Colo	6.38 $\pm$ 0.46	22.80	28.27 $\pm$ 2.28	96	0.32 $\pm$ 0.02	0.36 $\pm$ 0.04
Red Bull energy drink	5.47 $\pm$ 0.46	22.80	29.18 $\pm$ 2.28	104	0.27 $\pm$ 0.02	0.32 $\pm$ 0.03
Tea	18.24 $\pm$ 1.82	22.80	42.41 $\pm$ 2.74	106	0.91 $\pm$ 0.09	0.98 $\pm$ 0.10
Beer	10.72 $\pm$ 0.68	22.80	32.38 $\pm$ 2.51	95	0.54 $\pm$ 0.04	0.50 $\pm$ 0.05

<sup>a</sup> All samples were collected from local supermarkets.<sup>b</sup> Average  $\pm$  confidence interval, the confidence level is 95%.

current responses were measured in 5.0  $\mu\text{M}$  BPA standard solution and the RSD was calculated to be 3.5%. It indicated that binding of BPA to the “cavity” was reversible. The results were shown in Table 2. From Table 2, we can see that the concentration of BPA in drinking water and beverages were much lower than European standard. These samples were spiked with certain levels of BPA and analysed. The recoveries of BPA achieved were in the range of 92–106%. High-performance liquid chromatography (HPLC) was also used to detect the content of BPA to testify the accuracy of this method. The results of both the methods were listed and compared in Table 2, and have been found to be in good agreement with each other, which showed that the developed method was of good accuracy and reliability in practical applications.

#### 4. Conclusion

In summary, a simple molecular imprinting procedure was developed to prepare a BPA-imprinted electrochemical sensor based on an acetylene black paste electrode modified with molecularly imprinted chitosan-graphene composite film. The sensor provided a better site accessible imprinting surface with high sensitivity and good selectivity for fast BPA recognition. The sensor preparation conditions, suitable operating conditions, calibration curve, detection limit, and selectivity in BPA detection were presented and discussed. The study provided a practical method in BPA analysis and a promising approach in sensor preparation.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.foodchem.2014.02.074>.

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