



Electrochemical bisphenol A sensor based on core–shell multiwalled carbon nanotubes/graphene oxide nanoribbons



Xiaodong Xin^{a,b}, Shaohua Sun^{a,b}, He Li^{a,b,c,*}, Mingquan Wang^{a,b}, Ruibao Jia^{a,b,*}

^a Urban Water Monitoring Center of Shandong Province, Jinan 250021, China

^b Jinan Water and Waste Water Monitoring Center, Jinan 250021, China

^c School of Biological Science and Technology, University of Jinan, Jinan 250022, China

ARTICLE INFO

Article history:

Received 11 August 2014

Received in revised form

25 November 2014

Accepted 27 November 2014

Available online 4 December 2014

Keywords:

Bisphenol A

Electrochemical sensor

Graphene oxide nanoribbons

Multiwalled carbon nanotubes

Chitosan

ABSTRACT

Bisphenol A (BPA) can disrupt endocrine system and cause cancer. It has been considered as an endocrine disruptor. It is important and necessary to develop a sensitive and rapid method for detection of BPA. In this study, graphene oxide nanoribbons (GONRs) were synthesized from the facile unzipping of multiwalled carbon nanotube (MWCNT) with the help of microwave energy. MWCNT/GONRs and chitosan (CS) were used to prepare electrochemical BPA sensor. Compared with graphene, MWCNT/GONRs have favorable adsorption capacity, electron transfer ability and electrocatalytic property, which could enhance the response signal toward BPA. CS also exhibits excellent film forming ability and improves the electrochemical behavior of MWCNT/GONRs modified electrode. The sensor displays a sensitive response to BPA within a wide concentration range (0.005–150 $\mu\text{g/L}$). The proposed electrochemical sensor shows low detection limit (1 ng/L), good reproducibility (RSD = 5.2%), selectivity, and acceptable stability. This proposed sensor was successfully employed to determine BPA in water samples with satisfactory results.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Bisphenol A (BPA), is one of the highest volume chemicals in the world [1,2] and extensively used in the plastic industry, dental fillings, and the lining of food cans [3,4]. Global demand for BPA grew from 3.9 million tonnes in 2006 to about 5 million tonnes in 2010. The extensive use of BPA-based polymers has led to wide spread environment contamination. BPA concentrations in the ranges 5–320 ng/L in river waters and 20–700 ng/L in sewage effluents have been reported [5–8]. BPA shows estrogenic potential [9] and acute toxicity toward aquatic organisms [10] and human cultured cells [11]. In addition, BPA is postulated to cause reproductive disorders including decrease of sperm quality in humans, birth defects due to its fetal exposure and various kinds of cancers, such as prostate, testicular, and breast cancer [12]. Therefore, it is very important to establish a sensitive and simple method for the determination of BPA.

Various analytical methods such as enzyme-linked immunosorbent assay (ELISA) [13], high-performance liquid chromatography (HPLC) [14], liquid chromatography–mass spectrometry (LC–MS) [15], gas chromatography–mass spectrometry (GC–MS) [16], have been reported for determination of BPA. By comparison, electrochemical sensor is preferred because of its reliability, fast response, cheap instrument, low cost, simple operation, short analysis time, high sensitivity, good selectivity, the potential for miniaturization and the possibility of in situ analysis. BPA is electrochemical active, but direct determination of BPA using electrochemical sensor is rare due to the poor response of BPA at traditional electrochemical sensor. To solve this problem, novel sensing material with high stability, good catalytic activity and excellent conductivity must be developed [17–19].

To increase the sensitivity and selectivity for the detection of BPA, various modified electrode such as thionine-tyrosinase and cobalt phthalocyanine modified carbon paste electrode, Mg–Al layered double hydroxide modified glassy carbon electrode, poly(thionine)-tyrosinase modified GCE, Ni(II) tetraamino metallophthalocyanine polymer modified Au electrode have been developed [20,21,3,22,23]. Carbon nanotubes (CNTs) have been widely utilized in the electrochemical detection [24–26]. Recently, platelet graphite nanofibers were found to exhibit faster electron transfer rates than CNTs because of their graphene sheet

* Corresponding authors at: Urban Water Monitoring Center of Shandong Province, Weiwu Road, Jinan 250021, Shandong, China. Tel.: +86 531 55589613; fax: +86 531 55589600.

E-mail addresses: lihedc@gmail.com (H. Li), jiauibao68@126.com, jiauibao68@163.com (R. Jia).

orientation. Graphene-based nano-materials have also attracted attention for electrochemistry applications, including energy storage and sensing [27,28]. In order to enhance the sensitivity of the sensor, graphene oxide nanoribbons (GONRs) fabricated by the microwave-assisted facile unzipping of multiwalled carbon nanotubes (MWCNTs) were introduced during the modification of electrochemical sensor owing to their unique properties involving large surface area, strong excellent conductivity, subtle electronic property catalytic ability and adsorption ability.

Chitosan (CS), a naturally occurred biopolymer product, is derived from chitin via deacetylation with alkali. Its superiority including excellent film forming, high permeability toward water, adhesion ability, nontoxicity together with satisfying biocompatibility, has gained growing interests in electrochemical sensor [29].

Herein, a new electrochemical sensing platform based on MWCNT/GONRs modified electrode was first constructed to develop for the determination of BPA. It was found that the response signal of BPA remarkably enhanced, suggesting that MWCNT/GONRs may be excellent sensing materials for BPA sensor. The parameters such as the concentration of MWCNT/GONRs and pH value were optimized. This sensitive and convenient electrochemical sensor was used for determination of BPA in river water samples with satisfactory results.

2. Materials and methods

2.1. Apparatus and reagents

Bisphenol A (BPA, 97%) was purchased from Acros (NJ, USA). Chitosan was acquired from Aladdin Reagent Database Inc. (Shanghai, China). All other chemicals and solvents were of analytical grade. All the chemicals were used directly without further purification. Phosphate buffered solutions (PBS) were prepared using 0.067 mol/L Na_2HPO_4 and 0.067 mol/L KH_2PO_4 stock solution. Ultrapure water was used throughout the experiments.

Transmission electron microscope (TEM) image was obtained from H-800 microscope (Hitachi, Japan). Raman spectroscopy was analyzed at a laser wave length of 633 nm by a Raman spectrometer NEXUS 670 (Thermo Nicolet, United States). Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded at room temperature in the spectral range of 4000–400 cm^{-1} using the Perkin-Elmer Spectrum One FTIR spectrometer (Perkin-Elmer, United States). All electrochemical measurements were performed on a CHI760E electrochemical workstation (Chenhua Instrument Shanghai Co., Ltd., China). A conventional three-electrode system was used for all electrochemical measurements: a glassy carbon electrode (GCE, 4 mm in diameter) as working electrode, a platinum wire electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

2.2. Synthesis of MWCNT/GONRs

According to Sun et al. [30], MWCNTs (0.05 g) were suspended in 9:1 $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ and treated with a microwave reactor with the power set 140 °C for 2 min. After the addition of KMnO_4 (0.25 g) to the solutions, the solutions were treated with the same microwave power at 65 °C for 4 min. The solutions were filtered through a Millipore membrane (0.1 μm pore size), and the solid products (MWCNT/GONRs) were washed with water several times.

2.3. Preparation of the BPA electrochemical sensor

A GCE was polished with 1.0, 0.3 and 0.05 μm alumina powder sequentially and then washed ultrasonically in ethanol and water for a few minutes, respectively. To prepare the BPA sensor, 6 μL of MWCNT/GONRs (1.0 mg/mL) was dropped onto the electrode and

dried. Then, 3 μL of chitosan (0.5%) was added onto the electrode surface. After dried and washed, the CS/(MWCNT/GONRs)/GCE modified electrode was ready to measure.

2.4. Characterization of the electrochemical sensor

The electrochemical impedance technique is employed to detect impedance change during electrode modification process. The fabrication processes were characterized by using electrochemical impedance spectroscopy (EIS). It was carried out in the presence of 2.5 mmol/L $\text{Fe}(\text{CN})_6^{4-/3-}$ as a redox probe.

The pH 7.40 PBS was used for all the electrochemical measurements. Cyclic voltammetry (CV) was recorded in PBS at 100 mV/s. For amperometric measurement of the sensor, a detection potential of 0.5 V was selected. BPA was added into the buffer and the current change was recorded. PBS (pH 7.40) as used as the determining medium for BPA. The differential CV from –0.60 to 0.60 V was recorded, and the oxidation peak current was measured for BPA.

3. Results and discussion

3.1. Characterization of MWCNT/GONRs

Transmission electron microscopy (TEM) images of MWCNTs and MWCNT/GONRs are shown by Fig. 1(a) and 1(b), respectively. Graphene sheet structures were found on both sides of the nanotubes in Fig. 1(b), and the central cores of nanotubes remained slightly dark and tubelike. This type of core-shell heterostructure is termed a MWCNT/GONRs nanomaterial. Raman spectroscopy is often taken as a useful tool to study carbon materials. Herein Raman spectroscopy was used to further analyze the structure of MWCNT/GONRs. It is obvious that D band (1300 cm^{-1}) and G band (1580 cm^{-1}) were identified for MWCNTs and MWCNT/GONRs from Fig. 1(c), which was in accordance with [31]. The average size of the sp^2 carbon domain is proportional to the intensity ratio of the D and G lines (I_D/I_G ratio). Comparing with MWCNTs, MWCNT/GONRs showed higher I_D/I_G ratio which indicated MWCNT/GONRs suffered a decrease in the size of the sp^2 -hybridized carbon domain by the unzipping procedure [32]. Samples were also characterized by Fourier transform infrared spectroscopy (FTIR). In Fig. 1(d), the increase of the COO–H/O–H stretching region (3600–2800 cm^{-1}) implies an increase in the number of carboxyl and hydroxyl functional groups because of the oxidation procedure.

3.2. Characterization of the BPA sensor

The responses of different modified electrodes in same concentration of BPA (25 $\mu\text{g/L}$) were shown in Fig. 2(A). The oxidation current of BPA on MWCNT/GONRs modified GCE (curve c) was higher than that on bare GCE (curve a), indicating that MWCNT/GONRs had obviously catalytic activity toward BPA oxidation. The oxidation current of BPA on CS modified GCE (curve b) was higher than that on bare GCE (curve a). When CS was immobilized on the surface of MWCNT/GONRs modified GCE, a higher current response for the oxidation of BPA was observed (curve d) compared with CS modified GCE (curve b) and MWCNT/GONRs modified GCE (curve c). The results may be attributed to two factors: first, MWCNT/GONRs can be fixed by CS, which can maintain the electrochemical activity of MWCNT/GONRs; second, CS can adsorb BPA due to its excellent biocompatibility and film-forming, increasing the signal response.

In the nyquist diagram, the semicircle diameter of electrochemical impedance spectroscopy (EIS) is equal to R_{et} . EIS was used

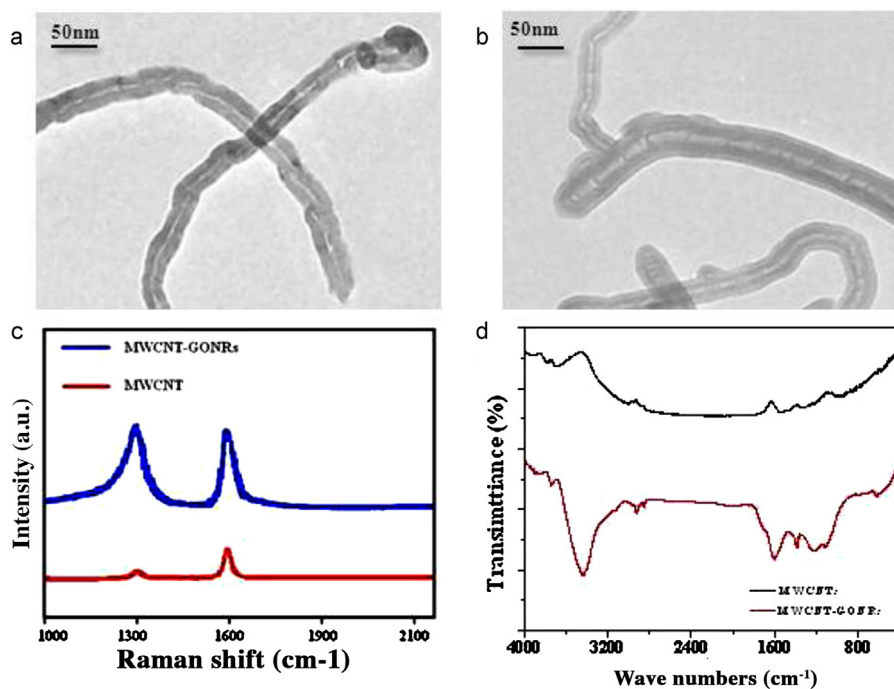


Fig. 1. Characterization of MWCNT/GONRs. (a) TEM of MWCNTs; (b) TEM of MWCNT/GONRs; (c) Raman spectra of MWCNTs and MWCNT/GONRs; (d) FTIR of MWCNTs and MWCNT/GONRs.

to characterize the stepwise construction process of the surface-modified electrodes. Fig. 2(B) showed the nyquist diagrams of electrochemical impedance spectra. Almost a straight line could be observed for bare GCE (curve b), which implied the characteristic of a diffuse limiting step of the electrochemical process. After being coated with MWCNT/GONRs, the EIS of the modified electrode (curve a) was similar to that of the bare GCE electrode. It may be that the MWCNT/GONRs immobilized on the electrode similar to a conducting wire, which makes it easier for the electron transfer. When CS was assembled on the electrode, a very small semicircle at high frequencies and linear part at low frequencies was observed (curve c). This may be ascribed to the weak conductivity of CS. The above results could clearly suggest the success of the assembly of the electrode.

3.3. Optimization of electrochemical signaling

To achieve an optimal electrochemical signaling, the concentration of MWCNT/GONRs and the effect of the pH value of substrate

solution on the response of the BPA sensor were investigated. As shown in Fig. 3(A), the current response increased with increasing amount of MWCNT/GONRs immobilized on the electrode and reached the maximum at 1.0 mg/mL, then decreased significantly when the amount of MWCNT/GONRs increased from 1.0 mg/mL to 3.0 mg/mL. It could be attributed to the increase of film thickness, which led to an increase of interface electron transfer resistance, making the electron transfer more difficult. Therefore, 1.0 mg/mL MWCNT/GONRs immobilized on the electrode was chosen for subsequent experiments.

The effect of pH value on the current response of the electrochemical sensor toward 25 $\mu\text{g/L}$ BPA was investigated with the pH range from 4.7 to 8.5 and the results were shown in Fig. 3(B), curve a). The oxidation peak current increased with the increasing pH value from 4.7 to 7.4. Then the current decreased when the solution pH exceeded 7.4. The maximum response to pH was lower than the pKa of BPA (pKa=9.73 [33]), which suggested that the non-dissociated BPA could be adsorbed better than the dissociated BPA on the CS/(MWCNT/GONRs)/GCE surface [34]. Therefore,

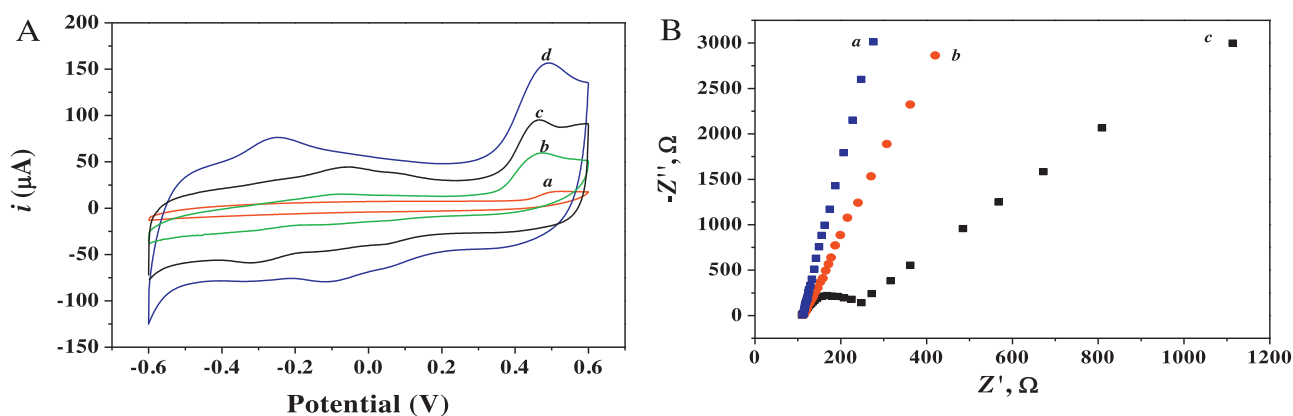


Fig. 2. (A) CV on the response to 25 $\mu\text{g/L}$ BPA in PBS. (a) A bare GCE, (b) CS modified GCE, (c) MWCNT/GONRs modified GCE, (d) (MWCNT/GONRs)/CS modified GCE; and (B) EIS in $\text{Fe}(\text{CN})_6^{4-/-3-}$ solution. (a) (MWCNT/GONRs) modified GCE, (b) a bare GCE, (c) (MWCNT/GONRs)/CS modified GCE.

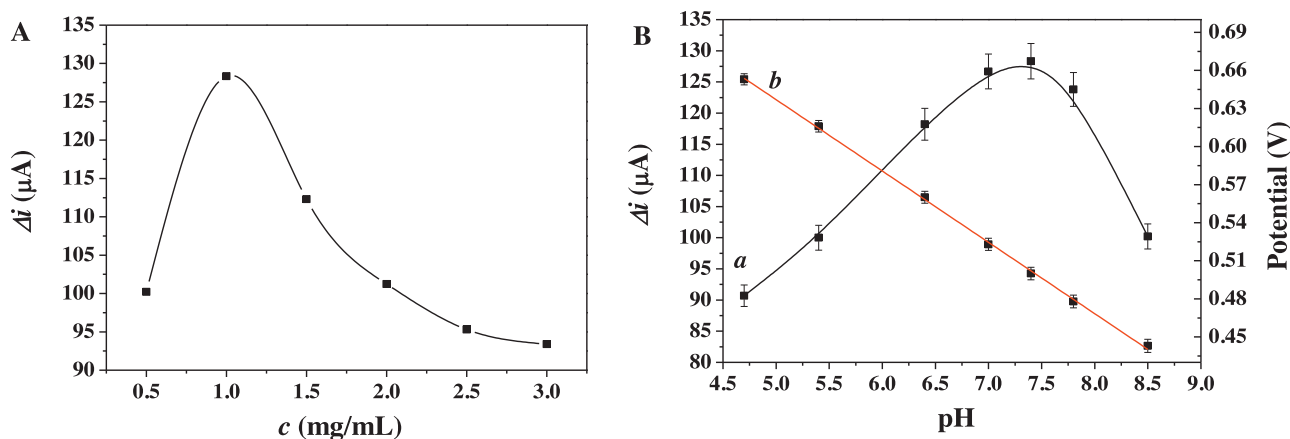


Fig. 3. Effects of the concentration of MWCNT/GONRs (A) and pH (B) on the oxidation current (a), oxidation potential (b) on the response to 25 $\mu\text{g/L}$ BPA.

considering the sensitivity of the determination of BPA, a pH value of 7.4 was chosen for the subsequent analytical experiments. The relationship between the oxidation peak potential (E_{pa}) and pH was also shown in Fig. 3(B), curve b). A linear shift of E_{pa} toward negative potential with an increasing pH indicated that protons were directly involved in the oxidation of BPA and it obeyed the following equation:

$$E_{pa} (\text{V}) = -0.0562 \text{ pH} + 0.9179 \quad (R^2 = 0.999)$$

A slope of 0.0562 V/pH is approximately close to the theoretical value of 0.0576 V/pH, indicating that the electron transfer is accompanied by an equal number of protons in electrode reaction [21,35].

3.4. Amperometric response

Under the optimal experimental conditions, the cyclic voltammetry responses at different concentrations were shown in Fig. 4. It was found that the BPA peak current increased with the increasing concentration of BPA. The response was proportional to BPA concentration in the range from 0.005 to 25 $\mu\text{g/L}$ with a correlation coefficient of 0.997 (inset of Fig. 4) and in the range from 25 to 150 $\mu\text{g/L}$ with a correlation coefficient of 0.999. Additionally, the limit of detection (LOD) was 1 ng/L at a signal-to-noise ratio of 3, which was lower than previous reported methods [3,36–41] (Table S1), indicating that this proposed method could potentially

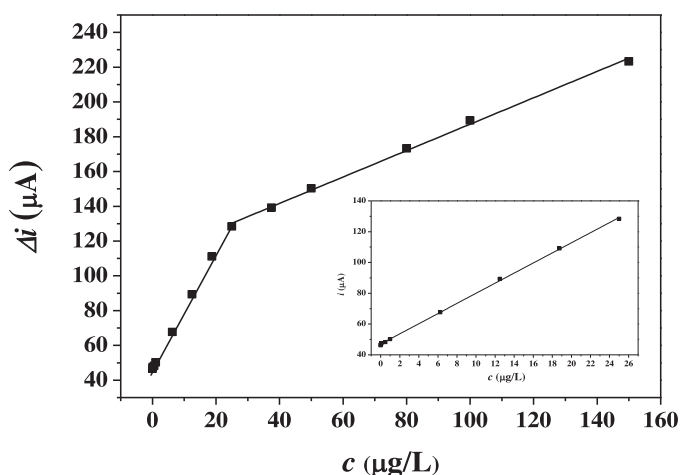


Fig. 4. Calibration curve for the detection of BPA at different concentrations.

be used for monitoring of BPA concentration sensitively. The low detection limit could be attributed to the good adsorption capacity and large specific surface area of MWCNT/GONRs, the enhanced electron transfer of BPA with MWCNT/GONRs and excellent film forming of CS.

To evaluate the repeatability of the developed sensor, 25 $\mu\text{g/L}$ BPA was examined 5 times using CS/(MWCNT/GONRs)/GCE. The relative standard deviation was less than 5% (Fig. S1), which manifested that this method had an acceptable reproducibility. The oxidation peak currents of 25 $\mu\text{g/L}$ BPA in the absence and presence of different concentrations of interferences were measured by the sensor. It was found that 50-fold concentration of 2,5-dinitrophenol, 2,4-dinitrophenol, nitrophenol had little influence on the signals of BPA with deviations below 15% (Fig. S2). Some ions such as 100-fold concentration of K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Zn^{2+} , Cu^{2+} had no influence on BPA determination (Fig. S2). It indicated the selectivity of the sensor was acceptable. The stability of the sensor was also examined by checking periodically their current responses in PBS (pH 7.4). When the sensor was not in use, it was stored in air. After three weeks, the catalytic current of the sensor decreased to about 92% of its initial value with the concentration of 25 $\mu\text{g/L}$ BPA. The slow decrease in the current response showed the well stability of the sensor.

3.5. Analysis of BPA in river water samples

In order to confirm the sensitivity and applicability of the proposed method, the fabricated sensor was used to determine BPA in river water. The determination of BPA was checked via a recovery study according to the described analytical procedure, under the optimized conditions. The recoveries were in the range from 94.3% to 106.7% ($n=5$), indicating that the proposed procedure was sensitive and accurate enough for practical application.

To further investigate the availability of this sensor for BPA detection, a comparison of the results obtained by the proposed sensor and HPLC method was made. Abscissa represents the measured concentrations by HPLC, and ordinate represents the measured concentrations by the sensor. BPA content determined by the two methods agreed well and the plot of BPA contents obtained by the two methods gave a straight line ($y=0.954x+0.225$) with a correlation coefficient of 0.9993 (Fig. S3). The intercept confidence interval (0.225 ± 0.243) and the slope confidence interval (0.954 ± 0.384) at 95% of confidence ($n=3$) were calculated. The value 1 is included in the slope confidence interval and the value 0 is included in the intercept confidence interval, which indicated the well accuracy of the method.

4. Conclusions

This work develops a sensitive and reliable electrochemical sensor utilizing MWCNT/GONRs and CS as electrode modification materials for BPA detection. The oxidation peak current of BPA was significantly enhanced after electrode modification. The reasons can be attributed to the catalytic activity and conductivity of MWCNT/GONRs, and the high adsorption capacity of CS. The sensor displays a linear response within a wide BPA concentration range (0.005 to 150 $\mu\text{g/L}$). The proposed sensor shows low detection limit (1 ng/L), good reproducibility (RSD = 5.2%), selectivity and acceptable stability. This new method possesses some obvious advantages, such as high determination sensitivity, simple preparation process, rapid response and low cost. The practical application in determining water samples was satisfactory with recovery from 94.3% to 106.7%.

Acknowledgements

This study was supported by National Science and Technology Major Project (no. 2012ZX07404-003) and Postdoctoral Science Foundation of China (no. 2012M521295).

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.snb.2014.11.128>.

References

- [1] E. Burrige, Bisphenol A: product profile, *Eur. Chem. News* 17 (2003) 14–20.
- [2] C.A. Staples, K. Woodburn, N. Caspers, T. Hall, G.M. Kleck, A weight of evidence approach to the aquatic hazard assessment of bisphenol A, *Hum. Ecol. Risk Assess.* 8 (2002) 1083–1105.
- [3] H.S. Yin, L. Cui, S.Y. Ai, H. Fan, L.S. Zhu, Electrochemical determination of bisphenol A at Mg–Al–CO₃ layered double hydroxide modified glassy carbon electrode, *Electrochim. Acta* 55 (2010) 603–610.
- [4] Y. Hideyuki, H. Hajime, N. Hitoshi, Y. Masatoshi, Liquid chromatographic determination of bisphenols based on intramolecular excimer-forming fluorescence derivatization, *Anal. Chim. Acta* 488 (2003) 211–221.
- [5] H. Fromme, T. Kuchler, T. Otto, K. Pilz, J. Müller, A. Wenzel, Occurrence of phthalates and bisphenol A and F in the environment, *Water Res.* 36 (2002) 1429–1438.
- [6] F.J. Ruiz, S. Rubio, D. Pérez-Bendito, Vesicular coacervative extraction of bisphenols and their diglycidyl ethers from sewage and river water, *J. Chromatogr. A* 1163 (2007) 269–276.
- [7] A. Ballesteros-Gómez, F.J. Ruiz, S. Rubio, D. Pérez-Bendito, Determination of bisphenols A and F and their diglycidyl ethers in wastewater and river water by coacervative extraction and liquid chromatography–fluorimetry, *Anal. Chim. Acta* 603 (2007) 51–59.
- [8] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: a national reconnaissance, *Environ. Sci. Technol.* 36 (2002) 1202–1211.
- [9] H. Segner, J.M. Navas, C. Schäfers, A. Wenzel, Effects of estrogenic and antiandrogenic compounds on the testis structure of the adult guppy (*Poecilia reticulata*), *Ecotoxicol. Environ. Saf.* 54 (2003) 16–24.
- [10] C.A. Staples, J.W. Davis, An examination of the physical properties, fate, ecotoxicity and potential environmental risks for a series of propylene glycol ethers, *Chemosphere* 49 (2002) 61–73.
- [11] Y. Nakagawa, T. Suzuki, S. Tayama, Metabolism and toxicity of benzophenone in isolated rat hepatocytes and estrogenic activity of its metabolites in MCF-7 cells, *Toxicology* 156 (2000) 27–36.
- [12] R. Steinmetz, N.A. Mitchner, A. Grant, D.L. Allen, R.M. Bigsby, N. Ben-Jonathan, The xenoestrogen bisphenol A induces growth, differentiation, and c-fos gene expression in the female reproductive tract, *Endocrinology* 139 (1998) 2741–2747.
- [13] M.C. Estevez, R. Galve, F. Sanchez-Baeza, M.P. Marco, Direct competitive enzyme-linked immunosorbent assay for the determination of the highly polar short-chain sulfophenyl carboxylates, *Anal. Chem.* 77 (2005) 5283–5293.
- [14] K. Inoue, K. Kato, Y. Yoshimura, T. Makino, H. Nakazawa, Determination of bisphenol A in human serum by high-performance liquid chromatography with multi-electrode electrochemical detection, *J. Chromatogr. B: Analyt. Technol. Biomed. Life Sci.* 749 (2000) 17–23.
- [15] M. Liu, Y. Hashi, F. Pan, J. Yao, G. Song, J. Lin, Automated on-line liquid chromatography–photodiode array–mass spectrometry method with dilution line for the determination of bisphenol A and 4-octylphenol in serum, *J. Chromatogr. A* 1133 (2006) 142–148.
- [16] R.J.W. Meesters, H.F. Schroder, Simultaneous determination of 4-nonylphenol and bisphenol A in sewage sludge, *Anal. Chem.* 74 (2002) 3566–3574.
- [17] H.S. Yin, Y.L. Zhou, J. Xu, S.Y. Ai, L. Cui, L.S. Zhu, Amperometric biosensor based on tyrosinase immobilized onto multiwalled carbon nanotubes–cobalt phthalocyanine–silk fibroin film and its application to determine bisphenol A, *Anal. Chim. Acta* 659 (2010) 144–150.
- [18] H.S. Yin, Y.L. Zhou, S.Y. Ai, Q.P. Chen, X.B. Zhu, X.G. Liu, L.S. Zhu, Sensitivity and selectivity determination of BPA in real water samples using PAMAM dendrimer and CoTe quantum dots modified glassy carbon electrode, *J. Hazard. Mater.* 174 (2010) 236–243.
- [19] M. Aída, H.F. Javier, V. Luis, M.T. Martínez, E. Alberto, Controlled chemistry of tailored graphene nanoribbons for electrochemistry: a rational approach to optimizing molecule detection, *RSC Adv.* 4 (2014) 132–139.
- [20] M. Portaccio, D.D. Tuoro, F. Arduini, M. Lepore, D.G. Mita, N. Diano, L. Mita, D. Moscone, A thionine-modified carbon paste amperometric biosensor for catechol and bisphenol A determination, *Biosens. Bioelectron.* 25 (2010) 2003–2008.
- [21] H.S. Yin, Y.L. Zhou, S.Y. Ai, Preparation and characteristic of cobalt phthalocyanine modified carbon paste electrode for bisphenol A detection, *J. Electroanal. Chem.* 626 (2009) 80–88.
- [22] E. Dempsey, D. Diamond, A. Collier, Development of a biosensor for endocrine disrupting compounds based on tyrosinase entrapped within a poly(thionine) film, *Biosens. Bioelectron.* 20 (2004) 367–377.
- [23] V. Chauke, F. Matemadombo, T. Nyokong, Remarkable sensitivity for detection of bisphenol A on a gold electrode modified with nickel tetraamino phthalocyanine containing Ni–O–Ni bridges, *J. Hazard. Mater.* 178 (2010) 180–186.
- [24] J. Wang, M. Musameh, Carbon nanotube/teflon composite electrochemical sensors and biosensors, *Anal. Chem.* 75 (2003) 2075–2079.
- [25] S.N. Kim, J.F. Rusling, F. Papadimitrakopoulos, Carbon nanotubes for electronic and electrochemical detection of biomolecules, *Adv. Mater.* 19 (2007) 3214–3228.
- [26] I. Dumitrescu, P.R. Unwin, J.V. Macpherson, Electrochemistry at carbon nanotubes: perspective and issues, *Chem. Commun.* 45 (2009) 6865–7052.
- [27] L. Tang, Y. Wang, Y. Li, H. Feng, J. Lu, J. Li, Preparation, structure, and electrochemical properties of reduced graphene sheet films, *Adv. Funct. Mater.* 19 (2009) 2782–2789.
- [28] M. Pumera, Graphene-based nanomaterials and their electrochemistry, *Chem. Soc. Rev.* 39 (2010) 4146–4157.
- [29] L. Tan, Y.Q. Chen, H. Yang, Y. Shi, J.F. Si, G.M. Yang, Z.S. Wu, P. Wang, X.X. Lu, H.P. Bai, Y.H. Yang, Alpha-1-fetoprotein antibody functionalized Au nanoparticles: catalytic labels for the electrochemical detection of α -1-fetoprotein based on TiO₂ nanoparticles synthesized with ionic liquid, *Sens. Actuators, B: Chem.* 142 (2009) 316–320.
- [30] C.L. Sun, C.T. Chang, H.H. Lee, J. Zhou, J. Wang, T.K. Sham, W.F. Pong, Microwave-assisted synthesis of a core-shell MWCNT/GONR heterostructure for the electrochemical detection of ascorbic acid, dopamine, and uric acid, *ACS Nano* 5 (2011) 7788–7795.
- [31] A. Martín, A. Escarpa, Graphene: the cutting-edge interaction between chemistry and electrochemistry, *TrAC-Trends Anal. Chem.* 56 (2014) 13–26.
- [32] M. Cheng, R. Yang, L. Zhang, Z. Shi, W. Yang, D. Wang, G. Xie, D. Shi, G. Zhang, Restoration of graphene from graphene oxide by defect repair, *Carbon* 50 (2012) 2581–2587.
- [33] H. Sambe, K. Hoshina, K. Hosoya, J. Haginaka, Simultaneous determination of bisphenol A and its halogenated derivatives in river water by combination of isotope imprinting and liquid chromatography–mass spectrometry, *J. Chromatogr. A* 1134 (2006) 16–23.
- [34] L. Fernández, C. Borrás, H. Carrero, Electrochemical behavior of phenol in alkaline media at hydrotalcite-like clay/anionic surfactants/glassy carbon modified electrode, *Electrochim. Acta* 52 (2006) 872–884.
- [35] T. Luczak, Preparation and characterization of the dopamine film electrochemically deposited on a gold template and its applications for dopamine sensing, *Electrochim. Acta* 53 (2008) 5725–5731.
- [36] Y. Zhang, L. Wang, D. Lu, X. Shi, C. Wang, X. Duan, Sensitive determination of bisphenol A base on arginine functionalized nanocomposite graphene film, *Electrochim. Acta* 80 (2012) 77–83.
- [37] F.R. Wang, J.Q. Yang, K.B. Wu, Mesoporous silica-based electrochemical sensor for sensitive determination of environmental hormone bisphenol A, *Anal. Chim. Acta* 638 (2009) 23–28.
- [38] C.M. Yu, L.L. Gou, X.H. Zhou, N. Bao, H.Y. Gu, Chitosan–Fe₃O₄ nanocomposite based electrochemical sensors for the determination of bisphenol A, *Electrochim. Acta* 56 (2011) 9056–9063.
- [39] H. Fan, Y. Li, D. Wu, H. Ma, K. Mao, D. Fan, B. Du, H. Li, Q. Wei, Electrochemical bisphenol A sensor based on N-doped graphene sheets, *Anal. Chim. Acta* 711 (2012) 24–28.
- [40] Y. Li, Y. Gao, Y. Cao, H. Li, Electrochemical sensor for bisphenol A determination based on MWCNT/melamine complex modified GCE, *Sens. Actuators, B: Chem.* 171–172 (2012) 726–733.
- [41] G.F. Pereira, L.S. Andrade, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, Electrochemical determination of bisphenol A using a boron-doped diamond electrode, *Electrochim. Acta* 82 (2012) 3–8.

Biographies

Xiaodong Xin received her Master's degree in Environmental Engineering from the University of Jinan in 2011. She specialized in electrochemistry. After graduation, she works in Urban Water Monitoring Center of Shandong Province and continues to engage in this aspect research. By now, she has published more than 10 articles in famous journals, such as *Biosensors and Bioelectronics*, *Analytica Chimica Acta*, *Chemical Engineering Journal*, *Journal of Colloid and Interface Science*.

He Li is a professor at School of Biological Science and Technology in University of Jinan. He received his Ph.D. degree from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences in 2004. After graduation, Dr. Li joined University of Jinan in China. His research interests are mainly focused on developing various functional nanomaterials for biosensing and nanomedicine.

Ruibao Jia received his Doctor's degree in Municipal Engineering from Tsinghua University. He works in Urban Water Monitoring Center of Shandong Province. He specialized in analytic chemistry and water treatment technology. He has published more than 50 articles in famous journal.