Analytical Letters, 47: 996–1014, 2014

ISSN: 0003-2719 print/1532-236X online
DOI: 10.1080/00032719.2013.862624

Sensors

DETERMINATION OF BISPHENOL A USING AN ELECTROCHEMICAL SENSOR BASED ON A MOLECULARLY IMPRINTED POLYMER-MODIFIED MULTIWALLED CARBON NANOTUBE PASTE ELECTRODE

Zhidong Chen,[1] Chuangui Tang,[1,2] Yanbo Zeng,[2]
Haiqing Liu,[2] Zhengzhi Yin,[2] and Lei Li[1,2]
[1]*College of Chemistry and Chemical Engineering, Changzhou University, Changzhou, P. R. China*
[2]*College of Biological, Chemical Sciences and Engineering, Jiaxing University, Jiaxing, P. R. China*

A novel electrochemical sensor for bisphenol A was developed through the combination of a molecular imprinting technique with a multiwalled carbon nanotube paste electrode. A molecularly imprinted polymer and nonimprinted polymer were synthesized in the presence and absence of bisphenol A, and then used to prepare the electrode. The bisphenol A imprinted polymer was applied as a selective recognition element in the electrochemical sensor. Differential pulse voltammetry was used to characterize the electrochemical behavior of bisphenol A at the modified electrodes. The results showed that the imprinted sensor had highest response for bisphenol A. Parameters including the carbon paste composition, pH, and adsorption time for the imprinted sensor were optimized. Under the optimized conditions, the differential pulse voltammetry peak current was linear with the concentration of bisphenol A from 0.08 to 100.0 µM, with a detection limit of 0.022 µM. The imprinted sensor for bisphenol A exhibited good selectivity, stability, and reproducibility. This sensor was successfully used for the determination of bisphenol A in real water samples.

Keywords: Bisphenol A; Electrochemical sensor; Molecularly imprinted polymer; Multiwalled carbon nanotube paste electrode; Real water samples

INTRODUCTION

Bisphenol A (BPA) is one of the main raw materials in plastics and resins and is widely used as a plasticizer, flame retardant, antioxidant, and heat stabilizer (Vandenberg et al. 2007). However, as a kind of estrogen in the environment

Received 18 July 2013; accepted 20 October 2013.

Address correspondence to Lei Li and Yanbo Zeng, College of Biological, Chemical Sciences and Engineering, Jiaxing University, 314001, Jiaxing, P. R. China. E-mail: li@mail.zjxu.edu.cn; ybzeng@mail.zjxu.edu.cn

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lanl.

(Hengstler et al. 2011), BPA may harm human health, as it can disrupt endocrine systems. Moreover, BPA was found to be a potential carcinogen (Yi, Jeung, and Choi 2011). Owing to its nonbiodegradable property, BPA may be released into the enviroment via wastewater from industrial plants and landfill sites (Tsai 2006). Therefore, for environmental pollution control, it is desirable to develop a reliable method for its determination in environment.

In recent years, several analytical methods including liquid chromatography (LC) (Rezaee et al. 2009), gas chromatography (GC) (Cunha et al. 2012), and electrochemical methods (Y. G. Li et al. 2012) have been used to determine BPA. LC or GC provides sensitive, convenient, and effective methods for BPA, but the methods are costly and time-consuming. Electrochemical methods have the advantages of simplicity and high sensitivity with low-cost instrumentation. Electroanalysis can also be used to give appropriate results within a short time under field conditions or for on-line monitoring. A previous study on BPA showed that it is electrochemically active. The phenolic hydroxyl groups were oxidized to quinone, permitting electrochemical determination (Fan et al. 2012). Electrochemical sensors modified with suitable materials have been used to detect BPA, such as platinum/graphene-carbon nanotubes (Zheng et al. 2013), multiwalled carbon nanotube–gold nanoparticles composite (Tu et al. 2009), and mesoporous silica (F. G. Wang, Yang, and Wu 2009). These electrochemical sensors have many advantages, such as simplicity in preparation and good stability. Molecular imprinting technique has been shown to increase the selectivity of electrochemical methods (Liu et al. 2013).

Molecular imprinting is a technique for the preparation of tailor-made polymers that possess specific recognition sites for the target molecules (Y. X. Li et al. 2013; Shen et al. 2012). In the processing of these polymers, functional and cross-linking monomers are copolymerized in the presence of the analyte as the imprinted molecule. After the template is extracted from the rigid polymer network, recognition sites similar with the template molecule in shape and size may be achieved. Molecularly imprinted polymers (MIP) have unique advantages over natural biological receptors in terms of physical and chemical stability, easy preparation, low cost, and application in harsh environmental conditions (Martín-Esteban 2013). Therefore, MIPs have been successfully used in many fields, such as chromatographic separation (B. Y. Huang et al. 2011), solid-phase extraction (Baggiani et al. 2009), and electrochemical sensors based on glassy carbon electrodes (GCE) (Lian et al. 2012; Zeng et al. 2013) and carbon paste electrodes (CPE) (Alizadeh et al. 2010; Gholivand and Torkashvand 2011). MIP-based electrochemical sensors for BPA determination have been reported in recent years, such as ordered mesoporous imprinted silica (Y. Q. Wang et al. 2011), imprinted poly(o-aminothiophenol) (J. D. Huang, Zhang, Liu, et al. 2011; J. Zhang et al. 2009), and imprinted sol-gel (J. D. Huang, Zhang, Lin, et al. 2011).

Multiwalled carbon nanotubes (MWCNTs) have received great attention due to their unique physical and chemical properties such as high conductivity, large surface area, and chemical inertness (Iijima 1991; C. Gao et al. 2012). MWCNTs have been introduced as excellent materials for the construction of electrochemical sensors based on glassy carbon electrode (X. J. Zhang et al. 2012), gold electrode (Hua et al. 2011), and carbon paste electrodes (Mokhtari et al. 2012; Yang et al. 2012). Researchers have reported some papers about multiwalled carbon nanotube paste electrodes without modified MIPs (Ensafi et al. 2012; Keyvanfard et al. 2013; Taherkhani et al. 2012; K. Zhang et al. 2013). In contrast, there were fewer reports about MWCNT paste electrode modified with MIP (Rezaei et al. 2011). The combination of a multiwalled carbon nanotube paste electrode and molecularly imprinted polymers may produce sensors with good sensitivity and selectivity. Therefore, it is interesting to modify a multiwalled carbon nanotube paste electrode with a bisphenol A – molecularly imprinted polymer based on poly (4-vinyl pyridine), which exhibited high adsorption and specificity for the analyte. To the author's knowledge, the determination of BPA using this electrode combination has not been reported.

A novel MIP-based electrochemical sensor was constructed for the selective and sensitive determination of bisphenol A. BPA-molecularly imprinted polymers and non-imprinted polymers based on poly(4-vinyl pyridine) were synthesized, and then used for the preparation of multiwalled carbon nanotube paste electrodes (MWNPE). The molecularly imprinted polymer was applied as the selective recognition element for bisphenol A in the construction of electrochemical sensor. Differential pulse voltammetry (DPV) was used to investigate the electrochemical behavior of bisphenol A at the modified electrodes. Some parameters, including carbon paste composition, pH effect, and the adsorption time for the imprinted sensor, were optimized. This imprinted sensor was used for the determination of BPA in water samples.

EXPERIMENTAL

Instrumentation and Reagents

Electrochemical analysis was performed with a three-electrode system using a Chi 660D electrochemical workstation (Chenhua Instruments Co., Shanghai, China). Surface morphological images were taken by a Hitachi S-4800 scanning electronic microscopy (Hitachi Co. Ltd., Japan). A multiwalled carbon nanotube paste electrode modified with molecularly imprinted or non-imprinted polymers was used as the working electrode. A platinum wire and a silver/silver chloride electrode were used as the counter and reference electrodes, respectively. Bisphenol F was purchased from Alfa Aesar China Co., Ltd. Ethylene glycol dimethacrylate (EGDMA), 2,2′-azobisisobutyronitrile (AIBN), 4-vinyl pyridine, toluene, phenol, para-tertiary butyl phenol, bisphenol AF, nitrophenol, bisphenol A, nitrobenzene, and graphite powder were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Multiwalled carbon nanotubes were obtained from Shenzhen Nanotech. Port Co., Ltd. (Shenzhen, China). Benzene, toluene, and paraffin oil were purchased from Hangzhou Chemical Reagent Co., Ltd. (Hangzhou, China). Other chemicals were analytical grade and were purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). 2,2′-Azobisisobutyronitrile was recrystallized from methanol and then dried at room temperature in a vacuum. The 4-Vinyl pyridine was purified via reduced pressure distillation to remove the polymerization inhibitor.

Synthesis of Bisphenol A – Molecularly Imprinted Polymer

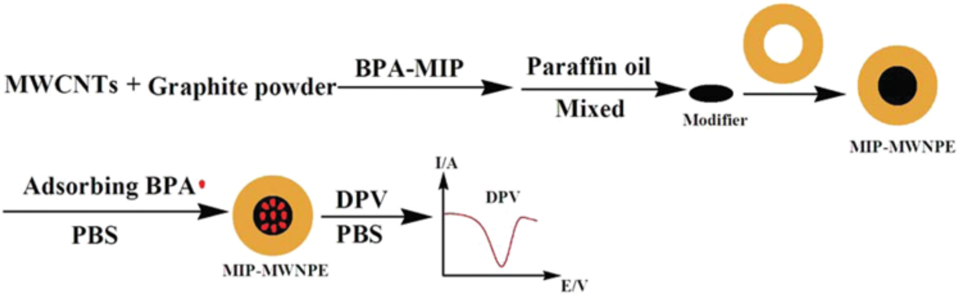
Bisphenol A molecularly imprinted polymers were synthesized based on bisphenol F as the template as described in a previous report (Lin et al. 2012).

The 30.0 mL of toluene were stirred in a 150-mL round-bottomed flask, and 86.4 mg bisphenol F (as the template), 185.0 µL 4-vinyl pyridine (as the functional monomer), 320.0 µL ethylene glycol dimethacrylate (as the cross-linker), and 40.0 mg 2,2′-azobisisobutyronitrile (as the initiator) were added. The solution was mixed thoroughly and then degassed by nitrogen gas for 15 min. The temperature was increased to 60°C, and the reaction was allowed to proceed for 24 h. The resulting product was collected and extracted using a Soxhlet apparatus with methanol-acetic acid (9:1, *v*/*v*) for 24 h to remove the template. The bisphenol A nonimprinted polymer was prepared by the same procedure, only without using the template molecule in the polymerization process.

Sensor Preparation

The preparation for molecularly imprinted polymer multiwalled carbon nanotube paste electrodes (MIP-MWNPE) and its application for the determination of BPA are illustrated in Scheme 1. For construction of the sensors (MIP-MWNPE or nonimprinted polymer-MWNPE), 80.0 mg of graphite powder, 20.0 mg of BPA-MIP (or BPA-NIP), and 5.0 mg of MWCNT were mixed in a mortar. 20.0 µL paraffin oil were added and homogenized with a pestle for 30 min. The homogenous paste (the modifier) was tightly pressed into the end hole of the sensor body (2.00 mm diameter, 3 mm depth), and the surface was polished. The carbon paste electrode (CPE) was prepared by the same procedure, only without using molecularly imprinted polymers (or non-imprinted polymers) and multiwalled carbon nanotubes. Moreover, the multiwalled carbon nanotube paste electrode was prepared by the same procedure, only without using MIP (or NIP).

Phosphate buffer solution (PBS, 0.1 M, pH 8.0) was used as the supporting electrolyte. The modified electrodes were dipped into the desired concentration of BPA for 2 min. Then differential pulse voltammograms of the modified electrodes were recorded between 0.2 and 0.8 V. The pulse amplitude, pulse period, and pulse width of DPV were 50 mV, 0.2 s, and 50 ms, respectively. Cyclic voltammetry was performed from 0.1 to 0.9 V under similar conditions.



Scheme 1. The preparation for molecularly imprinted polymer multiwalled carbon nanotube paste electrode and the process of electrochemical detecting method for bisphenol A.

RESULTS AND DISCUSSION

Morphology of the Molecularly Imprinted Polymer and Nonimprinted Polymer

The morphology of MIP and NIP was investigated by scanning electronic microscopy (SEM). As shown in Figure 1, MIP and NIP display microspheric particles of diameters of about 0.5 and 1.2 μm, respectively. The diameter of NIP particles was larger than MIP, which was similar to microspheres prepared by classical precipitation polymerization (Jin et al. 2012).

Electrochemical Behavior of Bisphenol A

Figure 2A shows cyclic voltammograms from a molecularly imprinted polymer multiwalled carbon nanotube paste electrode in the presence and absence of 100.0 μM BPA. No redox peak was observed without BPA. However, a well-defined

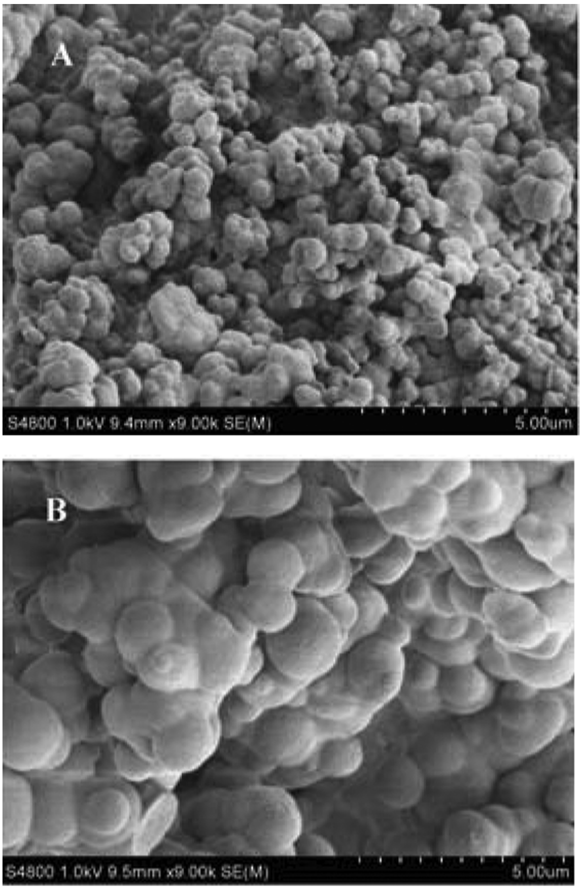


Figure 1. Scanning electron micrographs of (A) molecularly imprinted polymer and (B) non-imprinted polymer.

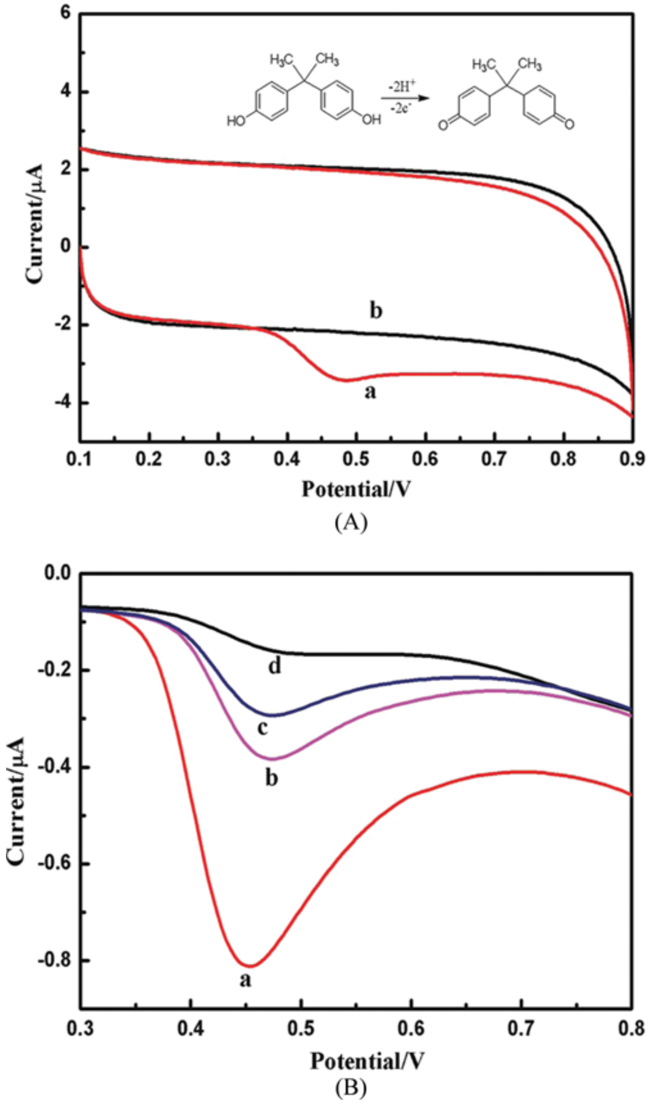


Figure 2. (A) Cyclic voltammograms of multiwalled carbon nanotube paste electrode in (a) the presence and (b) absence of 100.0 μM bisphenol A; (B) differential pulse voltammetry peak current of 50.0 μM bisphenol A at (a) molecularly imprinted polymer multiwalled carbon nanotube paste electrode, (b) non-imprinted polymer multiwalled carbon nanotube paste electrode, (c) multiwalled carbon nanotube paste electrode, and (d) carbon paste electrode. Conditions: 0.1 M phosphate buffer solution (pH 8.0), adsorption time, 2 min. The inset: the mechanism for the electrochemical reaction of bisphenol A at the molecularly imprinted polymer multiwalled carbon nanotube paste electrode.

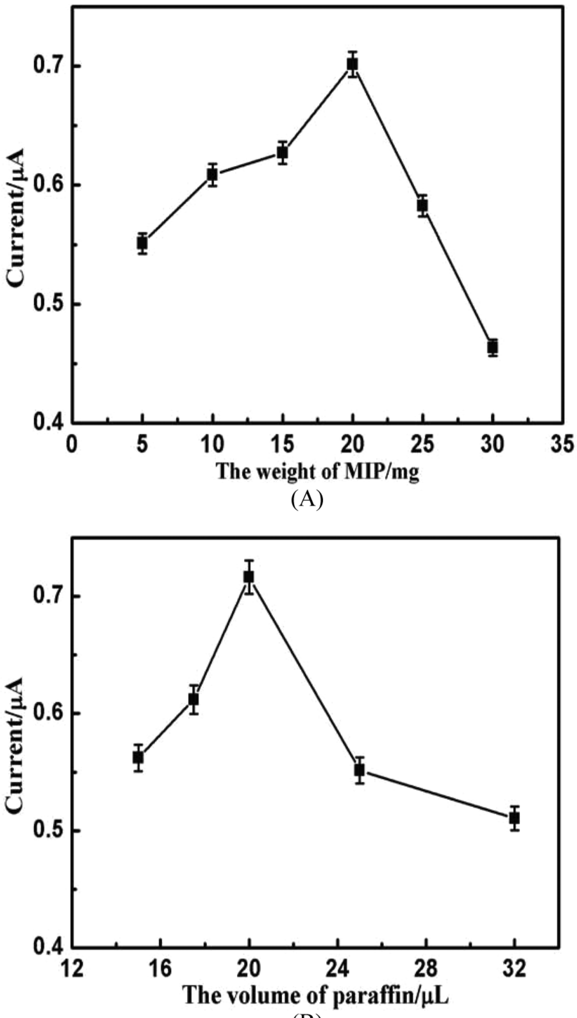
oxidation peak was observed during the sweep from 0.10 to 0.90 V at MIP-MWNPE in the presence of 100.0 μM BPA, while no corresponding reduction peak was observed. Bisphenol A at the molecularly imprinted polymer-multiwalled carbon nanotube paste electrode exhibited a well-defined oxidation peak resulting from the oxidation of BPA to BPA-quinone (Y. Gao et al. 2012), which can be ascribed to a two-electron and two-proton process (the inset of Figure 2A). The results showed that the oxidation reaction was irreversible, which is in agreement with previous reports (Zheng et al. 2013). As shown in Figure 2B, the peak current response of 50.0 μM BPA at different electrodes was investigated by differential pulse voltammetry (DPV). There were obvious oxidation peaks (about 0.45 V) at these electrodes. Among these electrodes, the carbon paste electrode had the lowest response for BPA (curve d). The multiwalled carbon nanotube paste electrode (curve c) had higher response for BPA than the carbon paste electrode, which can be attributed to the good electrochemical activity of the multiwall carbon nanotubes. After modifying the molecularly imprinted polymer with the multiwalled carbon nanotube paste electrode, the oxidation peak value of BPA at the MIP-MWNPE was obviously higher than at the MWNPE, indicating that molecularly imprinted polymer exhibited high adsorption for BPA. In addition, the oxidation peak value of BPA at the MIP-MWNPE (curve a) was nearly 2.5 times that of the NIP-MWNPE (curve b). This phenomenon may be explained by the presence of lower cavities for BPA in the non-imprinted polymer. The NIP-MWNPE had higher peak current response to BPA compared with the MWNPE. It may be ascribed to the lower specificity of the NIP for the template molecule compared with the MIP, but it is porous and has some adsorption for the template molecule (Baggiani et al. 2012). Therefore, although the introduction of NIP to the MWNPE may affect the conductivity, some adsorption for BPA at NIP-MWNPE may contribute to a higher response compared with MWNPE. In this case, adsorption may play a more important role. To achieve the highest sensitivity for BPA, the MIP-MWNPE was used for the determination of BPA.

Optimization of Parameters for Determination of Bisphenol A

The MIP-MWNPE sensor was prepared with different ingredients, including graphite powder, multiwalled carbon nanotubes, the molecularly imprinted polymer, and paraffin oil. In order to find the best composition for MIP-MWNPE, the amounts of the MIP and paraffin oil were optimized. When the bisphenol A – molecular imprinted polymer amount was lower than 20 mg (Figure 3A), the DPV peak current increased with the amount of MIP. This increase current may be attributed to more recognition sites provided by larger amounts of MIP on the electrode surface. In contrast, when the MIP amount was higher than 20 mg, a decrease in current was observed. This phenomenon was due to lower conductivity with high amounts of molecularly imprinted polymer. Hence, the optimum amount of MIP was 20 mg.

The optimum amount of paraffin oil as a binder in the MIP-MWNPE was investigated. When the paraffin oil amount was lower than 20 μL (Figure 3B), an increasing DPV peak current was observed with the amount of paraffin oil. In addition, when the paraffin oil amount was higher than 20 μL, the current decreased with the increasing amount of paraffin oil, which is due to the lower conductivity by high amounts of paraffin oil. Therefore, 20 μL was selected as the optimum amount of paraffin oil.

As shown in Figure 4A, the DPV peak current of the molecularly imprinted polymer multiwalled carbon nanotube paste electrode for 50.0 μM BPA was



(A)

(B)

Figure 3. (A) Differential pulsed voltammetry peak current of the molecularly imprinted polymer multiwalled carbon nanotube paste electrode for 50.0 μM bisphenol A with different amounts of molecularly imprinted polymer and (B) differential pulsed voltammetry peak current of the molecularly imprinted polymer multiwalled carbon nanotube paste electrode for 50.0 μM bisphenol A with different amounts of paraffin oil.

investigated with pH values ranging from 5.0 to 10.0. It is observed that the oxidation current increased with pH values from 5.0 to 8.0. However, when pH value was higher than 8.0, the current decreased. Therefore, a pH value of 8.0 was chosen for subsequent analytical experiments. As shown in Figure 4B, the DPV peak current of MIP-MWNPE for 50.0 μM BPA with different adsorption times was investigated. The peak current increased within 1 min, and leveled off at 2 min. Consequently, 2 min was selected as the optimum adsorption time.

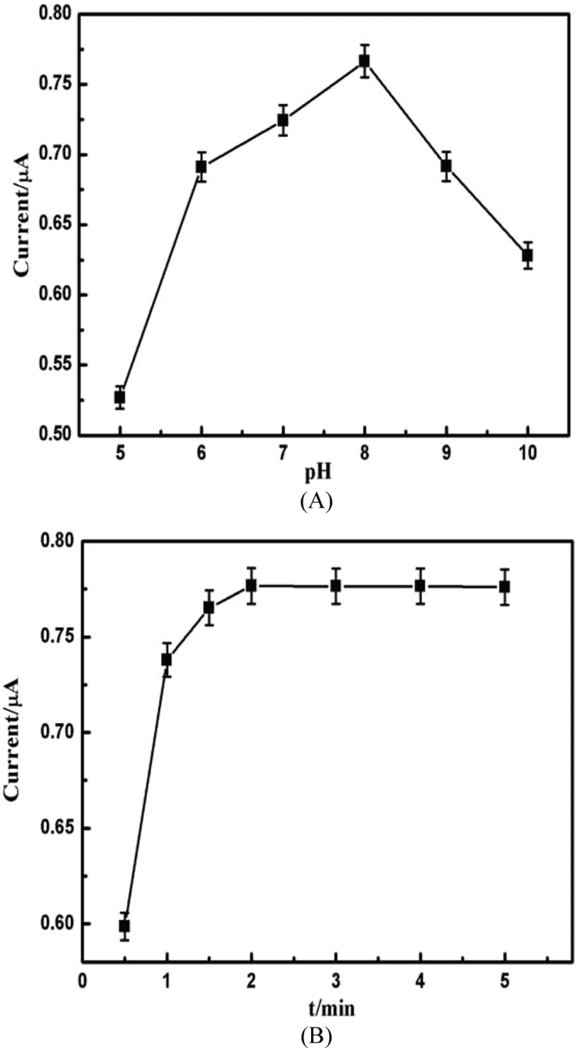


Figure 4. Influence of the (A) pH and (B) adsorption time on the differential pulsed voltammetry peak current of the molecularly imprinted polymer multiwalled carbon nanotube paste electrode for 50.0 μM bisphenol A.

Electrode Characterization

Electrochemical behavior of the modified electrodes was investigated using $[Fe(CN)_6]^{3-/4-}$ as a redox probe by cyclic voltammetery (Figure 5). A pair of redox peaks was observed at the carbon paste electrode (curve d). However, the redox peaks were obviously increased after the modification of multiwalled carbon nanotubes (curve c), which can be attributed to their large surface area and good electrocatalytic activity (Zhu et al. 2013). The redox peaks at the nonimprinted polymer multiwalled carbon nanotube paste electrode was higher than at the multiwalled carbon nanotube paste electrode. It could be ascribed to the fact that

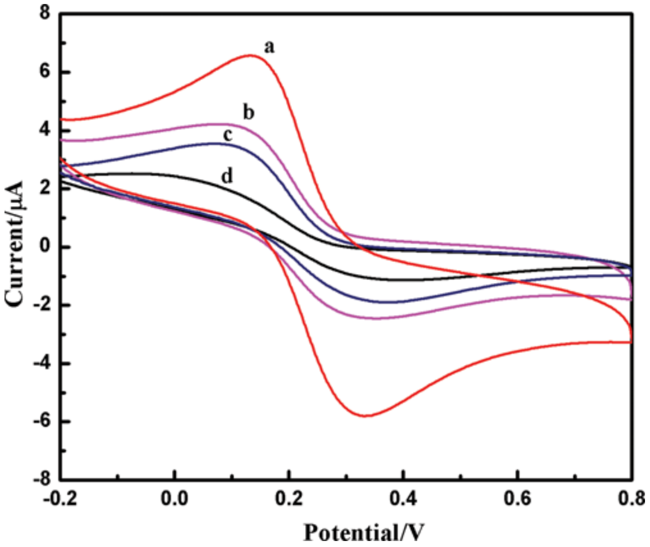


Figure 5. Cyclic voltammograms of (a) molecularly imprinted polymer multiwalled carbon nanotube paste electrode, (b) nonimprinted polymer multiwalled carbon nanotube paste electrode, (c) multiwalled carbon nanotube paste electrode, and (d) carbon paste electrode in 1 mM $[Fe(CN)_6]^{3-/4-}$(1:1) solution containing 0.2 M KCl. Conditions: scan rate, 50 mV s^{-1}; amplitude, 25 mV.

the NIP is porous (Baggiani et al. 2012), and may adsorb the $[Fe(CN)_6]^{3-}$ or $[Fe(CN)_6]^{4-}$. Although the introduction of the NIP may affect the conductivity, higher adsorption for $[Fe(CN)_6]^{3-}$ or $[Fe(CN)_6]^{4-}$ for the NIP-MWNPE may contribute to the higher current response compared with the MWNPE. The results were consistent with the behavior of the non-imprinted polymer multiwalled carbon nanotube paste electrode for BPA. The redox peaks at the MIP-MWNPE (curve a) were higher than those of NIP-MWNPE (curve b). The results suggested that cavities produced in the MIP after the removal of template BPA molecules may enhance the diffusion of $[Fe(CN)_6]^{3-/4-}$ and promote the redox reaction of $[Fe(CN)_6]^{3-/4-}$ on the electrode surface.

Electrochemical Surface Area

The electrochemical surface area for the molecularly imprinted polymer multiwalled carbon nanotube paste electrode and carbon paste electrode can be calculated by the slope of a plot of Q vs. $t^{1/2}$, which was obtained by chronocoulometry using 0.1 mM $K_3[Fe(CN)_6]$ as model complex based on Eq. (1) given by Anson (1964):

$$Q(t) = \frac{2nFACD^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads} \tag{1}$$

where A is the surface area of the working electrode, c is the concentration of substrate, D is the diffusion coefficient (D of $K_3[Fe(CN)_6]$ is $7.6 \times 10^{-6}\, cm^2\, s^{-1}$ (Zeng

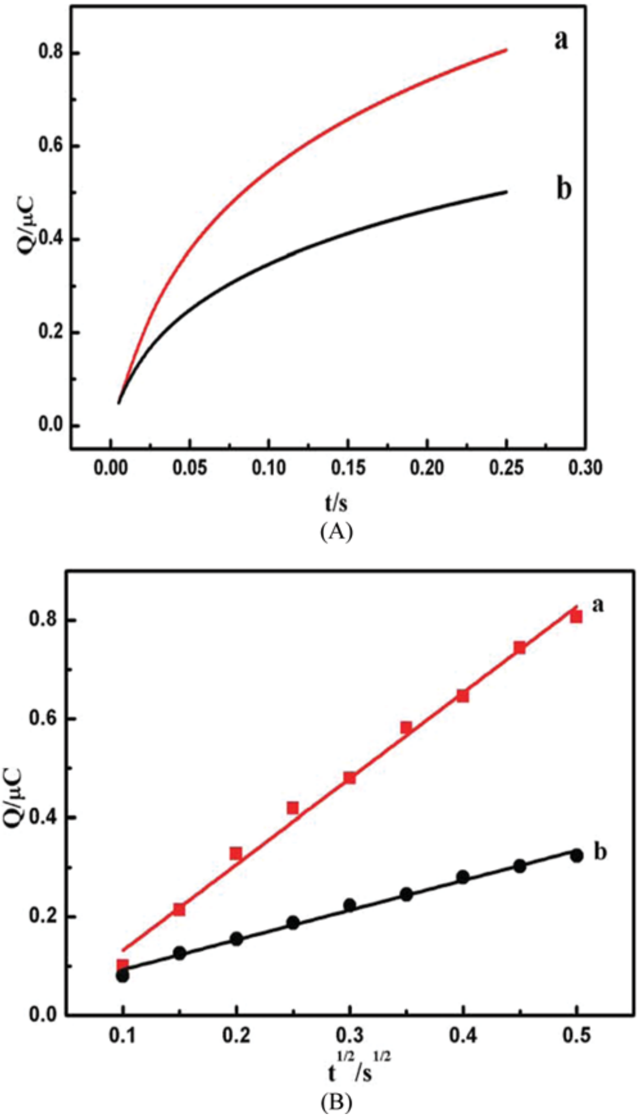


Figure 6. (A) Plot of Q-t curves for (a) molecularly imprinted polymer multiwalled carbon nanotube paste electrode and (b) carbon paste electrode in 0.1 mM $K_3[Fe(CN)_6]$; (B) plot of Q-$t^{1/2}$ curves for (a) molecularly imprinted polymer multiwalled carbon nanotube paste electrode and (b) carbon paste electrode in 0.1 mM $K_3[Fe(CN)_6]$; The pulse width, sample interval, and quiet time of chronocoulometry were 0.25 s, 0.25 ms, and 2 s, respectively.

et al. 2012)), Q_{dl} is double layer charge that is eliminated by background subtraction, and Q_{ads} is the Faradic charge due to the oxidation of absorbed BPA. Figure 6 shows that the slope between Q and $t^{1/2}$ for the MIP-MWNPE and CPE can be calculated to be 1.7837×10^{-6} and 0.60278×10^{-6}, respectively. Thus, the surface area (A) was 0.029 cm^{-2} and 0.01 cm^{-2} for the bare molecularly imprinted polymer multiwalled carbon nanotube paste electrode and the carbon paste electrode. The results indicate that the electrochemical effective surface area increased after modification of the carbon paste with multiwalled carbon nanotubes and molecularly imprinted polymers, which enhanced the adsorption of bisphenol A, leading to an increase in current and a decrease in detection limit (Yin, Cui, et al. 2010).

Selectivity of the Sensor

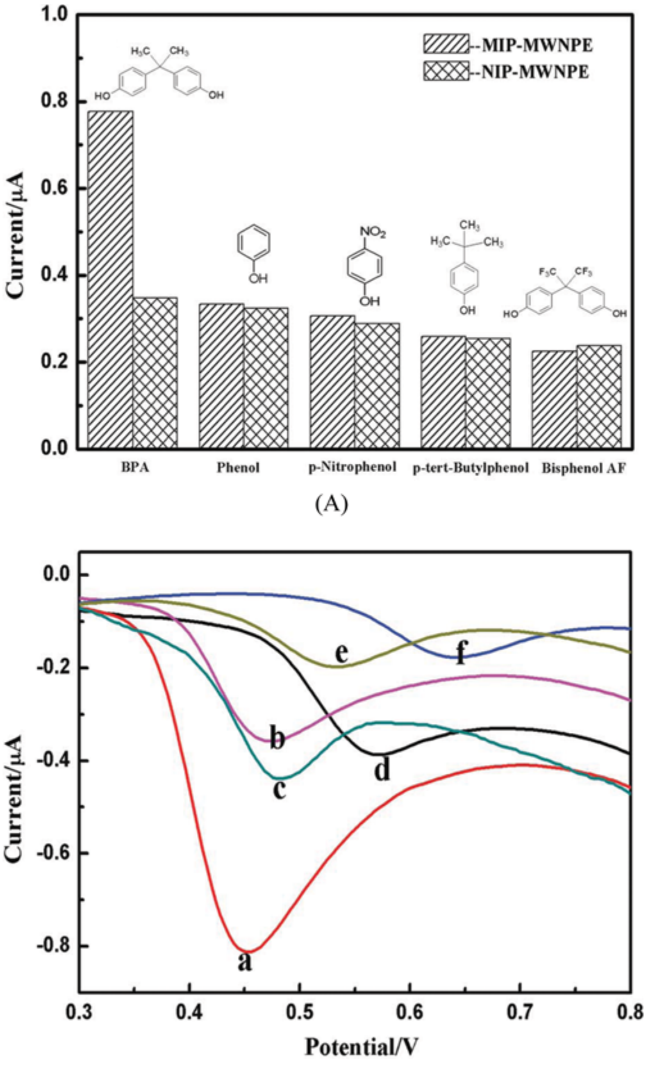
To evaluate the selectivity of the fabricated electrodes, the differential pulse voltammetry peak current responses for BPA and analogs, including phenol, p-nitrophenol, p-tert-butyl phenol, and bisphenol AF were investigated. As shown in Figure 7A, the peak current response of the molecularly imprinted polymer multiwalled carbon nanotube paste electrode for 50.0 μM analogs mentioned above was lower than that of BPA. It can be explained that the analogs have the similar structure as BPA, but their molecular sizes are not identical. Therefore, the cavities formed in BPA-MIP did not bind its analogs tightly, leading to lower response. Figure 7B shows differential pulse voltammograms of the non-imprinted polymer multiwalled carbon nanotube paste electrode for 50.0 μM BPA and its analogs. The response amount of NIP-MWNPE for BPA and analogs were similar, which may be attributed to fewer cavities in the non-imprinted polymer.

Linearity, Stability, and Reproducibility of the Sensor

Under optimized conditions, DPV was used to investigate the linearity and detection limit of the MIP-MWNPE sensor for BPA. As shown in Figure 8A, the peak current increased with successive addition of different BPA concentrations. Figure 8B illustrates a corresponding plot showing a linear relationship between peak current and BPA concentration in the range of 0.08 to 100.0 μM ($R = 0.9993$). The detection limit was 0.022 μM ($S/N = 3$, defined as the concentration of BPA corresponding to the three times the standard deviation for 11 replicate detections of the blank solution). The results of MIP-MWNPE for detecting BPA are compared in Table 1 with those of other published electrochemical methods (Q. A. Li et al. 2010; Yin, Zhou, et al. 2010). The results demonstrated a wide linear range and low detection limit of the prepared sensor, indicating the advantages of this method. The excellent analytical figures of merit may be attributed to the high adsorption and specificity for BPA. The reproducibility and stability of the sensor based on MIP-MWNPE were investigated by the determination of 50.0 μM BPA. Good reproducibility was observed with a relative standard deviation (RSD) of 4.27% for 7 measurements. A response of 93.0% of the initial current was retained for the MIP-MWNPE after it was stored in refrigerator for two weeks.

Interference Studies

In order to apply the sensor for environmental samples, the effect of inorganic ions and organic compounds were investigated. The DPV determination of 5.0 μM BPA was tested in the presence of spiked known amounts of interfering ions and organic compounds. The tolerance limit was defined as the amount of the interfering

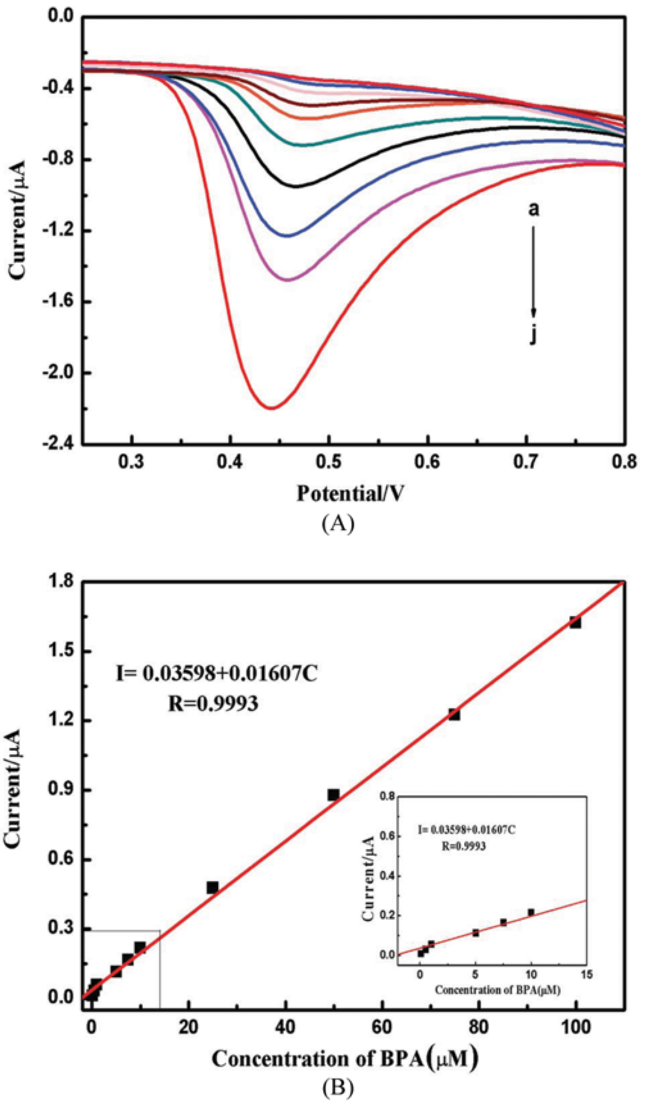


(A)

(B)

Figure 7. (A) Differential pulse voltammetry peak current responses for bisphenol A and analogs at the molecularly imprinted polymer multiwalled carbon nanotube paste electrode and the non-imprinted polymer multiwalled carbon nanotube paste electrode. (B) Differential pulse voltammograms of the molecularly imprinted polymer multiwalled carbon nanotube paste electrode response for (a) bisphenol A, (b) nonimprinted polymer multiwalled carbon nanotube paste electrode response for bisphenol A and its analogs: (c) p-nitrophenol, (d) phenol, (e) p-tert-butylphenol, (f) bisphenol AF. Conditions: 50.0 μM bisphenol A or analogs, 0.1 M phosphate buffer solution, pH = 8.0, and an adsorption time of 2 min.

substance that caused a change in ±5% in the peak current intensity reading. The tolerable limits of interfering substances are given in Table 2. The results indicate that the MIP-MWNPE exhibited a high adsorption and strong affinity toward BPA compared with metal ions and organic compounds.



(A)

(B)

Figure 8. (A) Differential pulsed voltammetry current response curve at molecularly imprinted polymer multiwalled carbon nanotube paste electrode with addition of increasing concentration of bisphenol A; (B) calibration curve for bisphenol A. The inset is the expansion of selected range. Concentration of bisphenol A (µM): (a) 0.08, (b) 0.5, (c) 1.0, (d) 5.0, (e) 7.5, (f) 10.0, (g) 25.0, (h) 50.0, (i) 75.0, and (j) 100.0.

Analytical Application

To demonstrate the feasibility of the molecularly imprinted polymer multiwalled carbon nanotube paste electrode for practical analysis, the proposed procedure was applied to the determination of bisphenol A in water samples. The river water samples were collected from Nanhu River of Jiaxing City. Tap water samples were obtained from our lab and the pure water samples were provided by

Table 1. Comparison with other electrochemical methods for the determination of bisphenol A

Electrochemical method	Linear range (μM)	Detection limit (μM)	Reference
Pt nanoparticles-Gr-CNTs[a]/GCE	0.06–80.0	0.042	(Zheng et al. 2013)
Mesoporous silica/CPE	0.088–0.22	0.038	(F. G. Wang, Yang, and Wu 2009)
ITO[b] electrode mediated by $[Ru(bpy)_3]^{2+}$	5–120	0.290	(Li et al. 2010)
Tyrosinase-MWNTs-CoPc-SF[c]/GCE	0.05–3.0	0.030	(Yin, Zhou, et al. 2010)
Imprinted OMS[d]/CPE	0.1–500.0	0.032	(Y. Q. Wang et al. 2011)
Imprinted poly(o-aminothiophenol)-AuNPs/GCE	8.0–6000	0.138	(J. D. Huang, Zhang, Liu, et al. 2011)
Imprinted poly(o-aminothiophenol)/GCE	0.6–55.0	0.200	(J. Zhang et al. 2009)
MIP-MWNPE	0.08–100.0	0.022	This work

[a] Gr-CNTs: graphene-carbon nanotubes.
[b] ITO: indium tin oxide.
[c] CoPc-SF: cobalt phthalocyanine-silk fibroin.
[d] OMS: ordered mesoporous silica.

Table 2. Tolerance limit of interfering substances on the determination of 5.0 μM bisphenol A using the molecularly imprinted polymer multiwalled carbon nanotube paste electrode

Interfering substance	Tolerance limit (μM)
Na^+, K^+, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, Br^-, CO_3^{2-}	1000.0
Cu^{2+}	375.0
Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}	250.0
Fe^{3+}	125.0
Nitrobenzene,N,N′-dimethyl formamide	100.0
Benzene, toluene, dimethylbenzene	25.0

Caikang Pure Water Company of Jiaxing City. The water samples were treated with a 0.45-μm filter to eliminate particulates. The concentration values of BPA in the water samples were detected by the molecularly imprinted polymer multiwalled carbon nanotube paste electrode. No voltammetric response corresponding to bisphenol A was observed when the real water samples were analyzed; thus, different

Table 3. Determination of bisphenol A in river, tap, and pure water samples ($n = 5$)

Sample	Added BPA (μM)	Found BPA (μM)	Recovery (%)	RSD (%)
River water	2.5	2.61	104.4	3.4
River water	5.0	4.90	98.0	2.1
River water	10.0	9.75	97.5	4.0
Tap water	2.5	2.32	92.8	4.6
Tap water	5.0	5.09	101.8	3.7
Tap water	10.0	10.50	105.0	3.2
Pure water	2.5	2.42	96.8	4.2
Pure water	5.0	4.96	99.2	3.9
Pure water	10.0	10.20	102.0	2.9

quantities of BPA were added to the samples. The results are summarized in Table 3, and the recoveries were between 92.8% and 105.0%. The results revealed that MIP-MWNPE can be used to detect BPA in water samples.

CONCLUSIONS

A novel electrochemical sensor based on the molecularly imprinted polymer multiwalled carbon nanotube paste electrode was fabricated for the determination of bisphenol A. A bisphenol A molecularly imprinted polymer was applied as the selective recognition element in the construction of electrochemical sensor. The molecularly imprinted polymer multiwalled carbon nanotube paste electrode had higher response for bisphenol A than the non-imprinted polymer multiwalled carbon nanotube paste electrode, multiwalled carbon nanotube paste electrode, and carbon paste electrode. The experiment results demonstrated wide linear range and low detection limit of the imprinted sensor. In addition, the imprinted sensor for bisphenol A exhibited good selectivity, stability, and reproducibility. The molecularly imprinted polymer multiwalled carbon nanotube paste electrode was successfully used for the determination of bisphenol A in real water samples.

FUNDING

This work was supported by the National Natural Science Foundation of China (No. 21177049, No. 51103063), the Zhejiang Provincial Natural Science Foundation (No. Y4110545, No. LQ12B05005), the Program for Science and Technology of Jiaxing (No. 2013AY11017) and the Students Research Training Program of Jiaxing University (No. 851713012).

REFERENCES

Alizadeh, T., M. Zare, M. R. Ganjali, P. Norouzi, and B. Tavana. 2010. A new molecularly imprinted polymer (MIP)-based electrochemical sensor for monitoring 2,4,6-trinitrotoluene (TNT) in natural waters and soil samples. *Biosens. Bioelectron.* 25: 1166–1172.

Anson, F. 1964. Application of potentiostatic current integration to the study of the adsorption of cobalt (III)–(ethylenedinitrilo (tetraacetate)) on mercury electrodes. *Anal. Chem.* 36: 932–934.

Baggiani, C., L. Anfossi, P. Baravalle, C. Giovannoli, G. Giraudi, C. Barolo, and G. Viscardi. 2009. Determination of banned Sudan dyes in food samples by molecularly imprinted solid phase extraction-high performance liquid chromatography. *J. Sep. Sci.* 32: 3292–3300.

Baggiani C., C. Giovannoli, L. Anfossi, C. Passini, P. Baravalle, and G. Giraudi. 2012. A connection between the binding properties of imprinted and nonimprinted polymers: a change of perspective in molecular imprinting. *J. Am. Chem. Soc.* 134: 1513–1518.

Cunha, S. C., C. Cunha, A. R. Ferreira, and J. O. Fernandes. 2012. Determination of bisphenol A and bisphenol B in canned seafood combining QuEChERS extraction with dispersive liquid-liquid microextraction followed by gas chromatography-mass spectrometry. *Anal. Bioanal. Chem.* 404: 2453–2463.

Ensafi, A. A., H. Bahrami, H. Karimi-Maleh, and S. Mallakpour. 2012. Carbon paste electrode prepared from chemically modified multiwall carbon nanotubes for the voltammetric determination of isoprenaline in pharmaceutical and urine samples. *Chinese J. Catal.* 33: 1919–1926.

Fan, H. X., Y. Li, D. Wu, H. M. Ma, K. X. Mao, D. W. Fan, B. Du, H. Li, and Q. Wei. 2012. Electrochemical bisphenol A sensor based on N-doped graphene sheets. *Anal. Chim. Acta.* 711: 24–28.

Gao, C., Z. Guo, J. H. Liu, and X. J. Huang. 2012. The new age of carbon nanotubes: An updated review of functionalized carbon nanotubes in electrochemical sensors. *Nanoscale.* 4: 1948–1963.

Gao, Y., Y. Cao, D. Yang, X. Luo, Y. Tang, and H. Li. 2012. Sensitivity and selectivity determination of bisphenol A using SWCNT-CD conjugate modified glassy carbon electrode. *J. Hazard. Mater.* 199–200: 111–118.

Gholivand, M. B., and M. Torkashvand. 2011. A novel high selective and sensitive metronidazole voltammetric sensor based on a molecularly imprinted polymer-carbon paste electrode. *Talanta.* 84: 905–912.

Hengstler, J. G., H. Foth, T. Gebel, P. J. Kramer, W. Lilienblum, H. Schweinfurth, W. Volkel, K. M. Wollin, and U. Gundert-Remy. 2011. Critical evaluation of key evidence on the human health hazards of exposure to bisphenol A. *Crit. Rev. Toxicol.* 41: 263–291.

Hua, M. Y., Y. C. Lin, R. Y. Tsai, H. C. Chen, and Y. C. Liu. 2011. A hydrogen peroxide sensor based on a horseradish peroxidase/polyaniline/carboxy-functionalized multiwalled carbon nanotube modified gold electrode. *Electrochim. Acta.* 56: 9488–9495.

Huang, B. Y., Y. C. Chen, G. R. Wang, and C. Y. Liu. 2011. Preparation and evaluation of a monolithic molecularly imprinted polymer for the chiral separation of neurotransmitters and their analogues by capillary electrochromatography. *J. Chromatogr. A* 1218: 849–855.

Huang, J. D., X. M. Zhang, Q. Lin, X. R. He, X. R. Xing, H. X. Huai, W. J. Lian, and H. Zhu. 2011. Electrochemical sensor based on imprinted sol–gel and nanomaterials for sensitive determination of bisphenol A. *Food Control.* 22: 786–791.

Huang, J. D., X. M. Zhang, S. Liu, Q. Lin, X. R. He, X. R. Xing, and W. J. Lian. 2011. Electrochemical sensor for bisphenol A detection based on molecularly imprinted polymers and gold nanoparticles. *J. Appl. Electrochem.* 41: 1323–1328.

Iijima, S. 1991. Helical microtubules of graphitic carbon. *Nature.* 354: 56–58.

Jin, Y., M. Jiang, Y. Shi, Y. Lin, Y. Peng, K. Dai, and B. Lu. 2008. Narrowly dispersed molecularly imprinted microspheres prepared by a modified precipitation polymerization method. *Anal. Chim. Acta.* 612: 105–113.

Keyvanfard, M., R. Shakeri, H. Karimi-Maleh, and K. Alizad. 2013. Highly selective and sensitive voltammetric sensor based on modified multiwall carbon nanotube paste electrode for simultaneous determination of ascorbic acid, acetaminophen and tryptophan. *Mater. Sci. Eng. C* 33: 811–816.

Li, Q. A., H. Li, G. F. Du, and Z. H. Xu. 2010. Electrochemical detection of bisphenol A mediated by $[Ru(bpy)_3]^{2+}$ on an ITO electrode. *J. Hazard. Mater.* 180: 703–709.

Li, Y. G., Y. Gao, Y. Cao, and H. M. Li. 2012. Electrochemical sensor for bisphenol A determination based on MWCNT/melamine complex modified GCE. *Sens. Actuators, B.* 171: 726–733.

Li, Y. X., M. Hong, Miaomiao, Q. Bin, Z. Y. Lin, Z. W. Cai, and G. N. Chen. 2013. Novel composites of multifunctional Fe_3O_4@Au nanofibers for highly efficient glycoprotein imprinting. *J. Mater. Chem. B* 1: 1044–1051.

Lian, H. T., Z. H. Sun, X. Y. Sun, and B. Liu. 2012. Graphene doped molecularly imprinted electrochemical sensor for uric acid. *Anal. Lett.* 45: 2717–2727.

Lin, Z. K., W. J. Cheng, Y. Y. Li, Z. R. Liu, X. P. Chen, and C. J. Huang. 2012. A novel superparamagnetic surface molecularly imprinted nanoparticle adopting dummy template: An efficient solid-phase extraction adsorbent for bisphenol A. *Anal. Chim. Acta.* 720: 71–76.

Liu, B. Q., D. P. Tang, B. Zhang, X. H. Que, H. H. Yang, and G. N. Chen. 2013. Au(III)-promoted magnetic molecularly imprinted polymer nanospheres for electrochemical determination of streptomycin residues in food. *Biosens. Bioelectron.* 41: 551–556.

Martín-Esteban, A., 2013. Molecularly-imprinted polymers as a versatile, highly selective tool in sample preparation. *TrAC-Trends Anal. Chem.* 45: 169–181.

Mokhtari, A., H. Karimi-Maleh, A. A. Ensafi, and H. Beitollahi. 2012. Application of modified multiwall carbon nanotubes paste electrode for simultaneous voltammetric determination of morphine and diclofenac in biological and pharmaceutical samples. *Sens. Actuators, B* 169: 96–105.

Rezaei, Behzad, Najmeh Majidi, Ali A. Ensafi, and Hassan Karimi-Maleh 2011. Molecularly imprinted-multiwall carbon nanotube paste electrode as a biosensor for voltammetric detection of rutin. *Anal. Methods.* 3: 2510–2516.

Rezaee, M., Y. Yamini, S. Shariati, A. Esrafili, and M. Shamsipur. 2009. Dispersive liquid-liquid microextraction combined with high-performance liquid chromatography-UV detection as a very simple, rapid and sensitive method for the determination of bisphenol A in water samples. *J. Chromatogr. A* 1216: 1511–1514.

Shen, X. T., L. H. Zhu, N. Wang, L. Ye, and H. Q. Tang. 2012. Molecular imprinting for removing highly toxic organic pollutants. *Chem. Commun.* 48: 788–798.

Taherkhani, A., H. Karimi-Maleh, A. A. Ensafi, H. Beitollahi, A. Hosseini, M. A. Khalilzadeh, and H. Bagheri. 2012. Simultaneous determination of cysteamine and folic acid in pharmaceutical and biological samples using modified multiwall carbon nanotube paste electrode. *Chin. Chem. Lett.* 23: 237–240.

Tsai, W. T. 2006. Human health risk on environmental exposure to bisphenol-A: A review. *J. Environ. Sci. Heal. C* 24: 225–255.

Tu, X. M., L. S. Yan, X. B. Luo, S. L. Luo, and Q. J. Xie. 2009. Electroanalysis of bisphenol A at a multiwalled carbon nanotubes-gold nanoparticles modified glassy carbon electrode. *Electroanal.* 21: 2491–2494.

Vandenberg, L. N., R. Hauser, M. Marcus, N. Olea, and W. V. Welshons. 2007. Human exposure to bisphenol A (BPA). *Reprod. Toxicol.* 24: 139–177.

Wang, F. G., J. Q. Yang, and K. B. Wu. 2009. Mesoporous silica-based electrochemical sensor for sensitive determination of environmental hormone bisphenol A. *Anal. Chim. Acta.* 638: 23–28.

Wang, Y. Q., Y. Y. Yang, L. Xu, and J. Zhang. 2011. Bisphenol A sensing based on surface molecularly imprinted, ordered mesoporous silica. *Electrochim. Acta.* 56: 2105–2109.

Yang, C., Y. Chai, R. Yuan, J. Guo, and F. Jia. 2012. Ligand-modified multi-walled carbon nanotubes for potentiometric detection of silver. *Anal. Sci.* 28: 275–282.

Yi, B. R., E. B. Jeung, and K. C. Choi. 2011. Altered gene expression following exposure to bisphenol a in human ovarian cancer cells expressing estrogen receptors by microarray. *Reprod. Fert. Develop.* 23: 201–201.

Yin, H. S., L. Cui, S. Y. Ai, H. Fan, and L. S. Zhu. 2010. Electrochemical determination of bisphenol A at Mg-Al-CO_3 layered double hydroxide modified glassy carbon electrode. *Electrochim. Acta.* 55: 603–610.

Yin, H. S., Y. L. Zhou, J. Xu, S. Y. Ai, L. Cui, and L. S. Zhu. 2010. 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: 144–150.

Zeng, Y. B., Y. Zhou, L. Kong, T. S. Zhou, and G. Y. Shi. 2013. A novel composite of SiO_2-coated graphene oxide and molecularly imprinted polymers for electrochemical sensing dopamine. *Biosens. Bioelectron.* 45: 25–33.

Zeng, Y. B., D. J. Yu, Y. Y. Yu, T. S. Zhou, and G. Y. Shi. 2012. Differential pulse voltammetric determination of methyl parathion based on multiwalled carbon nanotubes-poly(acrylamide) nanocomposite film modified electrode. *J. Hazard. Mater.* 217–218: 315–322.

Zhang, J., L. Xu, Y. Q. Wang, and R. H. Lu. 2009. Electrochemical sensor for bisphenol a based on molecular imprinting technique and electropolymerization membrane. *Chinese J. Anal. Chem.* 37: 1041–1044.

Zhang, K., J. Zhou, J. Liu, K. J. Li, Y. F. Li, L. X. Yang, and B. X. Ye. 2013. Sensitive determination of colchicine at carbon paste electrode doped with multiwall carbon nanotubes. *Anal. Methods.* 5: 1830–1836.

Zhang, X. J., Y. Huang, A. X. Gu, G. F. Wang, B. Fang, and H. Q. Wu. 2012. Hydrogen peroxide sensor based on carbon nanotubes/β-Ni(OH)$_2$ nanocomposites. *Chinese J. Chem.* 30: 501–506.

Zheng, Z. X., Y. L. Du, Z. H. Wang, Q. L. Feng, and C. M. Wang. 2013. Pt/graphene-CNTs nanocomposite based electrochemical sensors for the determination of endocrine disruptor bisphenol A in thermal printing papers. *Analyst.* 138: 693–701.

Zhu, A. H., G. L. Xu, L. Li, L. L. Yang, H. Zhou, and X. W. Kan. 2013. Sol-gel imprinted polymers based electrochemical sensor for paracetamol recognition and detection. *Anal. Lett.* 46: 1132–1144.