*Int. J. Electrochem. Sci.*, 14 **(2019)** 3610 – 3617, doi: 10.20964/2019.04.58

**International Journal of**
**ELECTROCHEMICAL**
**SCIENCE**
www.electrochemsci.org

# Molecularly imprinted electrochemical sensor for the detection of bisphenol A

*Benzhi Liu*[1,2,*], *Jinlong Yan*[2], *Min Wang*[2], *Xiangyang Wu*[1,*]

[1] School of Environment and Safety Engineering, Jiangsu University, Zhenjiang, Jiangsu Province, China, Postcode: 212013.
[2] School of Environmental Science and Engineering, Yancheng Institute of Technology, Yancheng, Jiangsu Province, China, Postcode: 224051.
[*]E-mail: benzhiliu@163.com (B. Liu); wuxy@ujs.edu.cn (X. Wu)

*Received:* 8 January 2019 / *Accepted:* 13 February 2019 / *Published:* 10 March 2019

---

The imprinted electrochemical sensor was fabricated to determine bisphenol A by differential pulse voltammetry. Under the optimal condition, the proposed sensor exhibited a well linear relationship toward the bisphenol A concentrations in the range of 0.2 to 45 µM, with a detection limit of 0.03 µM and a correlation coefficient of 0.9965. The proposed sensor possessed high selectivity and sensitivity to bisphenol A detection, which was successfully applied to detect bisphenol A in real samples. The recoveries were in the range of 92.7–96%.

---

**Keywords:** Molecularly imprinted polymers， Electrochemical sensor， Bisphenol A

## 1. INTRODUCTION

Bisphenol A is a kind of environmental endocrine estrogen. It is an important ingredient in the production of plastic[1]. It is also used in the production of fine chemical products, such as pesticides, coatings and heat stabilizers[2–4]. It is easy to cause environmental pollution. Bisphenol A is harmful to human health, it may induce the disorder of reproductive system, children's precocious puberty, diabetes, cancer and other diseases [5–7] . Therefore, developing the detection method for bisphenol A in environment is of great significance. There are many analysis methods for bisphenol A determination, including high-performance liquid chromatography [8–10], high-performance liquid chromatography coupled with mass spectrometry [11,12], gas chromatography coupled with mass spectrometry [13], spectrophotometric method [14], enzyme-linked immunosorbent assay[15], electrochemical sensor [16–19] and so on. Among these methods, electrochemical sensor has the advantages of high sensitivity, simple instrument and easy to operate, it is often used for the determination of bisphenol A.

Molecularly imprinted polymers(MIP) have high selectivity, strong anti-interference ability and high stability, which have been widely used in the preparation of electrochemical sensors[20]. Carbon nanotubes have been used as the carrier in the preparation of MIP due to their unique properties, such as high stability, large surface area, high conductivity and facilitate the electron transfers [21, 22].

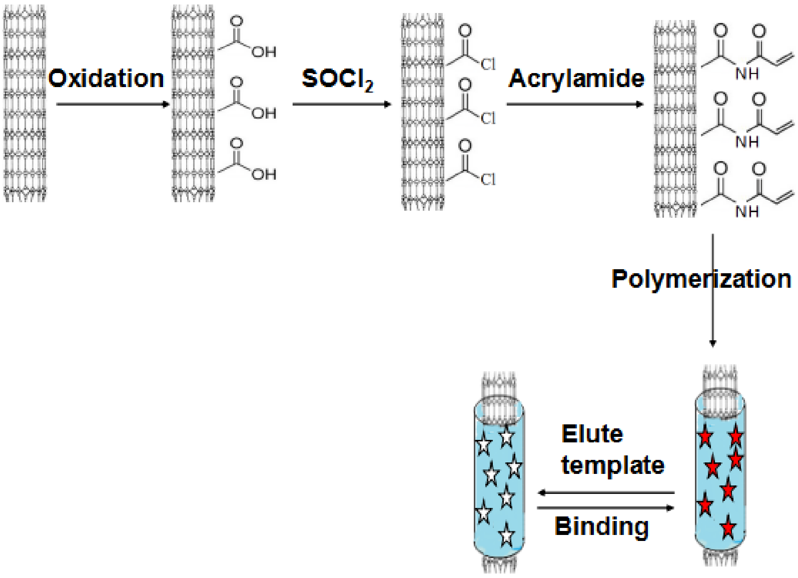

**Figure 1.** Preparation of molecularly imprinted polymers on carbon nanotubes.

In this work, the multi-walled carbon nanotubes were first acrylamide-functionalized and as a carrier to synthesize molecularly imprinted polymers.The acrylamide on the surface of carbon nanotubes can induce the polymerization to selectively occur on the surface of carbon nanotubes, which could increase the number and density of the imprinting cavities. The preparation of molecularly imprinted polymers on carbon nanotubes was illustrated in Fig. 1.The prepared molecularly imprinted electrochemical sensor has wide linear range, low detection limit, high selectivity and sensitivity. It was used for the determination of bisphenol A in water samples.

## 2. EXPERIMENTAL

### *2.1 Reagents and instrumentation*

Multi-walled carbon nanotubes (MWCNT) were obtained from Shenzhen Nanotech Port Co., Ltd (Shenzhen, China) with a diameter about 20 nm. The purity was more than 97%. Bisphenol A, methacrylic acid (MAA), N, N- dimethformamide (DMF) were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. Acrylamide ( AA), ethyleneglycol dimethacrylate (EGDMA), azodiisobutyronitrile (AIBN) were purchased from Aladdin reagent (Shanghai) Co., Ltd. All other chemical reagents were purchased from Nanjing Chemical Reagent Co. (Nanjing China). All solutions were prepared with double-distilled water.

Electrochemical experiments were performed on a CS350 Electrochemical Workstation (Wuhan Corrtest Instruments CO., LTD, Wuhan, China). Three-electrode system was used for the electrochemical measurements. MIP or NIP modified glassy carbon electrode was used as the working electrode. The saturated calomel electrode and platinum wire electrode were employed as the reference and the counter electrode, respectively.

### *2.2 Modification of MWCNT*

The MWCNT was modified to MWCNT-COOH and MWCNT-AA according to our previous report[23].

### *2.3 Preparation of imprinted polymers*

The preparation of molecularly imprinted polymers was according to our previous report[23] with minor modification. 0.15 g MWCNT-AA, 0.22 g bisphenol A and 0.35 g MAA were added to 30 mL acetonitrile, after ultrasonication for 10 min and stirring for 2h, 3.6 g EGDMA and 20 mg AIBN were added to the stirring mixture, then bubbled with $N_2$ to removed $O_2$. The mixture was stirred for 24 h at 60℃, then the product was cooled to room temperature and collected after centrifugation. Then, acetic acid/ethanol solution (V (acetic): V (ethanol) = 1: 10) was used to elute the template molecules and unreacted functional monomers and crosslinker. Distilled water was used to wash the acetic acid and ethanol. The product was collected and dried at 60℃, thus, the imprinted polymer (MWCNT-MIP) was obtained. The preparation of non-imprinted polymer (MWCNT-NIP) was similar to the preparation of imprinted polymers except bisphenol A was added.

### *2.4 Fabrication of the modified electrode*

Prior to use, the glassy carbon electrode(GCE) was carefully polished with a leather containing 0.05 µm $Al_2O_3$ slurry, then cleaned in ethanol and distilled water. MWCNT-MIP or MWCNT-NIP was dispersed in acetone with the aid of ultrasonication to prepare 3 mg $ml^{-1}$ suspension. Then 10 µl of the suspension was dropped onto the GCE surface and dried in air to prepare MWCNT-MIP /GCE or MWCNT-NIP /GCE .

### *2.5 Experimental measurements*

The cyclic voltammograms(CV) were performed in a 2.0 mM $K_3[Fe(CN)_6]$ solution containing 0.1 M KCl, the scanning potential range was -0.3 V to +0.6 V and the scan rate was 100 mV $s^{-1}$. The differential pulse measurements were performed from -0.1 to +0.7 V ( step increment of 5 mV, amplitude of 50 mV, pulse period of 0.1 s).

## 3. RESULTS AND DISCUSSION

### *3.1 Cyclic voltammograms of the modified electrodes*

Cyclic voltammetry is also used to study the electron transfer performance for a modified electrode [24]. Fig. 2 shows the cyclic voltammograms(CV) of different modified electrodes in 2.0 mM $K_3[Fe(CN)_6]$ solution containing 0.1 M KCl. As can be seen from curve a, a pair of well-fined redox peaks were observed which related to the redox of $K_3[Fe(CN)_6]$. It suggested that the cavities in the MIP after template removal acted as channels for electron transport. Curve b shows the CV of MWCNT-MIP /GCE after incubation with 0.1 mM bisphenol A. The peak current of this redox peaks were lower than those observed in curve a, which indicated that the binding of bisphenol A in MIP film resulted in blockage of the cavities, and hence hindered the diffusion of $K_3[Fe(CN)_6]$. However, for the CV of MWCNT-NIP /GCE(curve c), the peaks became very poor and peak current very low, it was because that the polymer film had lower electron transfer rate and electrical conductivity and limited the diffusion of $K_3[Fe(CN)_6]$.

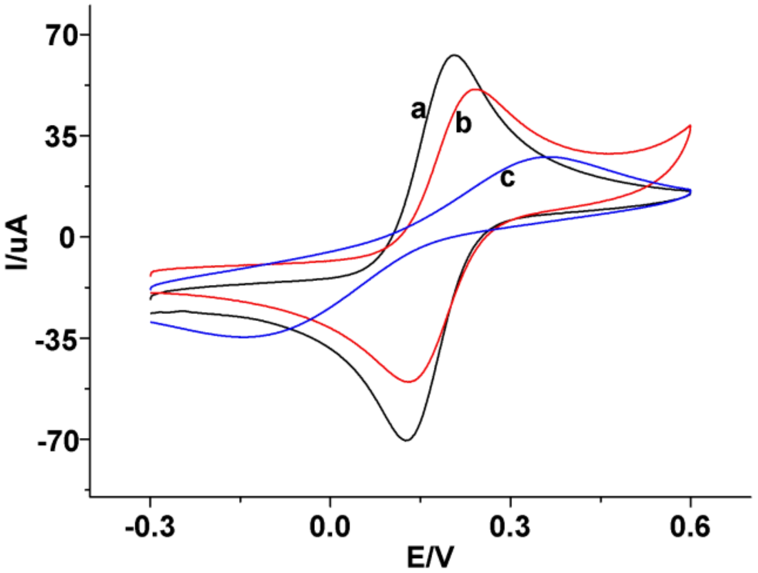

**Figure 2.** Cyclic voltammograms of 2.0 mM $K_3[Fe(CN)_6]$ at MWCNT-MIP/GCE(a), MWCNT-MIP/GCE after incubation with bisphenol A (b), and MWCNT-NIP/GCE (c).

### *3.2 Optimization of experimental conditions*

The MIP amount modified on the surface of glassy carbon electrode could affect the sensitivity of the MWCNT-MIP /GCE. As can be seen from Fig. 3A, the peak current difference(ΔIp) increases with increasing the MIP amount, then the ΔIp almost keep constant when the MIP amount exceed 10 μL . Therefore, the MIP amount of 10 μL could be suitable to offer the high sensitivity.

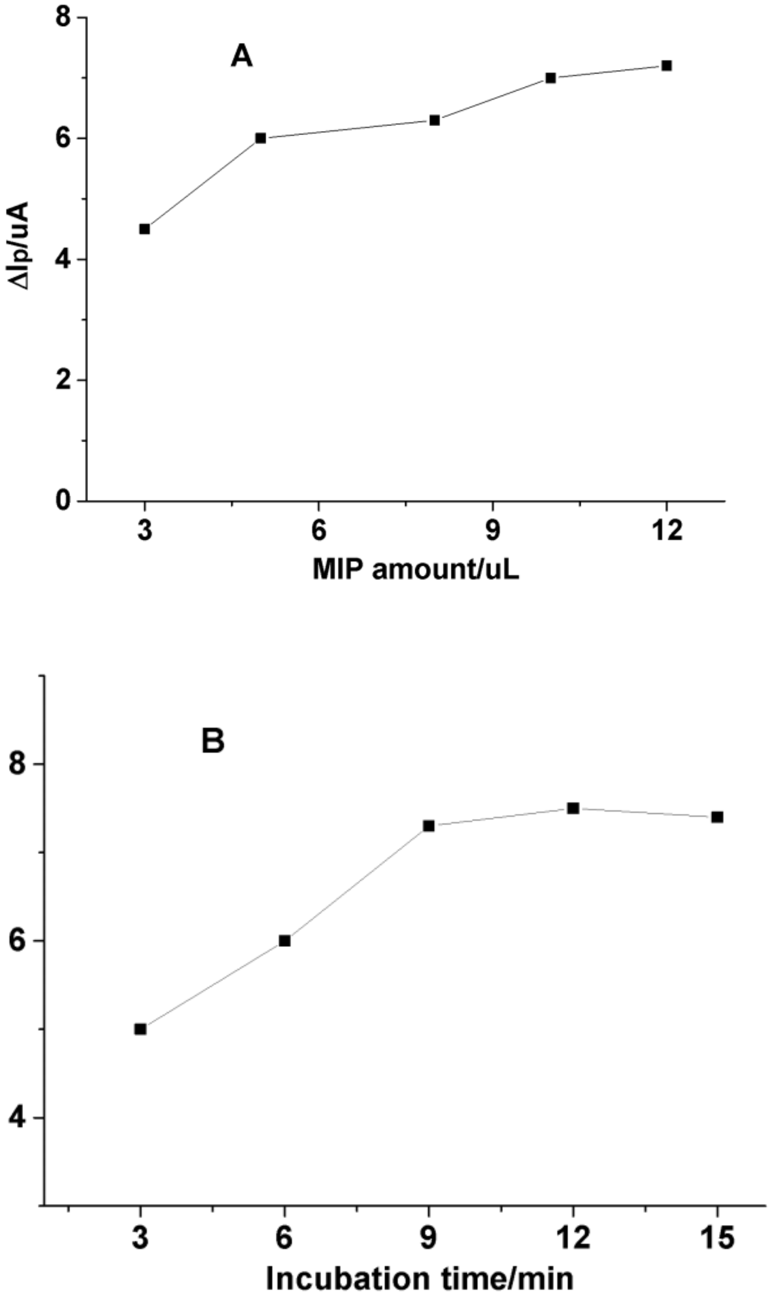

**Figure 3.** The effect of MIP amount(A) and the incubation time(B) on the ΔIp of MWCNT-MIP/GCE.

Incubation time is an important factor in the molecularly imprinted electrochemical sensors. The effect of incubation time was studied in the range of 3- 15 min. As can be seen from Fig. 3B, the ΔIp increases with increasing incubation time and achieved balance at about 9 min, indicating that the adsorption equilibrium was achieved. The results are similar to the previous reports [25, 26]. Therefore, the incubation time of 9 min was applied in the following measurements.

### *3.3 Determination of bisphenol A*

Differential pulse voltammetry (DPV) has high sensitivity in elctrochemical experiments, it was used for the determination of bisphenol A in this work. Fig. 4 shows the DPVs of the MWCNT-MIP /GCE at different concentrations of bisphenol A.

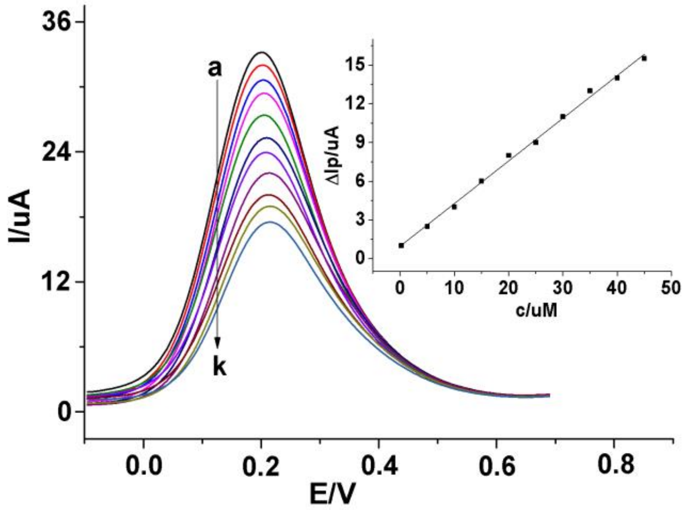

**Figure 4.** DPVs of the MWCNT-MIP/GCE with different concentrations of bisphenol A. From a-k: 0; 0.2; 5; 10; 15; 20; 25; 30; 35; 40; 45μM. Inset: Plot of the *Δ*Ip *vs* concentration of bisphenol A.

**Table 1.** The bisphenol A determination performance comparison with other modified electrodes.

| Modified electrode | Linear range (μM) | LOD(μM) | References |
|---|---|---|---|
| MIP-NP/CTAB/CPE | 0.6-100 | 0.1 | [27] |
| β -CD/IL/CPE | 0.1-11 | 0.08 | [28] |
| Pt NP/Gr－CNT/GCE | 0.06-10 | 0.04 | [29] |
| MIPPy/GQD/GCE | 0.1-50 | 0.04 | [30] |
| MWCNT-MIP /GCE | 0.2 - 45 | 0.03 | this work |

Note: MIP-NP: molecularly imprinted nanoparticles; CTAB: cetyltrimethyl; CPE: carbon paste electrode; IL: ionic liquid; *β* -CD: *β* -cyclodextrin; Pt NP: Pt nanoparticles; Gr–CNT: graphene–carbon nanotubes; MWCNT: multiwalled carbon nanotubes; GCE: glass carbon electrode; MIPPy: molecularly imprinted polypyrrole; GQD: graphene quantum dots.

As can be seen from the curves in the figure, the peak currents decreased with increasing the concentration of bisphenol A. As shown in Fig. 4 inset, the *Δ*Ip are linearly to the concentrations of bisphenol A in the range of 0.2 to 45 μM, with a detection limit of 0.03 μM.

The linear regression equation can be expressed as ΔIp (μA) = 0.959 + 0.33c (μM), with a correlation coefficient $r$ = 0.9965. Table 1 shows a comparison for bisphenol A determination performance of the MWCNT-MIP /GCE and other modified electrodes reported previously. It was found that the proposed sensor had high sensitivity, wide linear range, and low detection limit.

### *3.4 Selectivity of the MWCNT-MIP /GCE*

The selectivity of the MWCNT-MIP /GCE was evaluated. For the determination of 15 μM bisphenol A, the concentration of 20-fold of estradiol, phenol, nonylphenol, catechol and 200-fold of $Ca^{2+}$, $Mg^{2+}$, $Al^{3+}$, $Cu^{2+}$, $SO_4^{2-}$ and $NO_3^-$ did not interfere with the determination of bisphenol A. The above results indicated that the selectivity of the MWCNT-MIP /GCE toward the target molecule bisphenol A was high.

### *3.5 Real sample analysis*

The recovery experiments with adding standard solution was performed in order to evaluate the performance of the MWCNT-MIP /GCE in practical analytical applications. The imprinted sensor was used to detect the concentration of bisphenol A in tap water. The tape water samples were collected from our laboratory. A standard addition method was applied. After spiking 5 and 15 μM bisphenol A into the water samples, the found concentrations of bisphenol A were 4.8 and 13.9 μM, respectively. The recovery was in the range of 92.7% to 96%. The RSD for the measurements was less than 4.5%. The results showed that the MWCNT-MIP /GCE has the potential for the detection of bisphenol A in the environment.

## 4. CONCLUSION

In this work, we presented a molecularly imprinted electrochemical sensor. The sensor was used for the detection of bisphenol A, the detection range was 0.2 to 45 μM with a detection limit of 0.03 μM. The proposed sensor was applied for the detection of bisphenol A in real samples with good recovery.

ACKNOWLEDGEMENTS
This work was sponsored by the University Natural Science Research Project of Jiangsu Province of China (16KJB550007) and Postdoctoral Foundation of Jiangsu Province (1701105B).

## References

1. A.M. Calafat, Z. Kuklenyik, J.A. Reidy, S.P. Caudill, J. Ekong and L.L. Needham, *Environ. Health Perspect.,* 113 (2005) 391.
2. Y. Mutou, Y. Ibuki, Y. Terao, S. Kojima and R. Goto, *Environ. Toxicol. Pharmacol.,* 21 (2006) 283.
3. J. Maia, J.M. Cruz, R. Sendón, J. Bustos, J.J. Sanchez and P. Paseiro, *Food Res. Int.,* 42 (2009)1410.
4. C. Wu, Q. Cheng, L. Li, J. Chen and K. Wu, *Electrochim. Acta,* 115 (2014) 434.
5. I.A. Lang, T.S. Galloway, A. Scarlett, W.E. Henley, M. Depledge and R.B. Wallace, *J. Am. Med. Assoc.,* 300(2008)1303.
6. H. Mielke and U. Gundert-Remy, *Toxicol. Lett.,* 190 (2009) 32.

7. S.H. Safe, *Environ. Health Perspect.,* 108 (2000) 487.
8. X. Jiang, W. Tian, C. Zhao, H. Zhang and M. Liu, *Talanta,* 72 (2007) 119.
9. Y. Zhuang, M. Zhou, J. Gu and X. Li, *Spectrochim. Acta A*, 122 (2014) 153.
10. J. Ou, L. Hu, L. Hu, X. Li and H. Zou, *Talanta,* 69 (2006) 1001.
11. H. Sambe, K. Hoshina, K. Hosoya and J. Haginaka, *J. Chromatogr. A,*1134 (2006) 16.
12. M. Kawaguchi, Y. Hayatsu, H. Nakata, Y. Ishii, R. Ito, K. Saito and H. Nakazawa, *Anal. Chim. Acta,* 539 (2005) 83.
13. D.H. Li, J.R. Oh and J. Park, *J. Chromatogr.* A, 1012 (2003)207.
14. K. Takeda andT. Kobayashi, *J. Membr. Sci.,* 275 (2006) 61.
15. M.P. Zhao, Y.Z. Li, Z.Q. Guo, X.X. Zhang and W.B. Chang, *Talanta,* 57 (2002) 1205.
16. A. Ozcan, *Electroanalysis,* 26 (2014) 1631.
17. Y. Zhu, C.Q. Zhou, X.P. Yan, Y. Yan and Q. Wang, *Anal. Chim. Acta,* 883 (2015) 81.
18. Y. Jiao, K. Sung-Eun, C. Misuk, Y. Ik-Keun, C. Woo-Seok and L. Youngkwan, *Biosens. Bioelectron.,* 61 (2014) 38.
19. W.Y. Chen, L.P. Mei, J.J. Feng, T. Yuan, A.J. Wang and H.Y. Yu, Microchim. Acta, 182 (2015) 703.
20. L. Zhu, Y. Cao and G. Cao, *Biosens. Bioelectron.,* 54 (2014) 258.
21. C.L. Sun, C.T. Chang, H.H. Lee, J.G. Zhou, J. Wang, T.K. Sham and W.F. Pong, *ACS Nano,* 5 (2011) 7788.
22. X.D. Xin, S.H. Sun, H. Li, M.Q. Wang and R.B. Jia, *Sens. Actuators B,* 209 (2015) 275.
23. B. Liu, J. Yan, M. Wang and X. Wu, *Int. J. Electrochem. Sci.,* 13 (2018)11953.
24. J. Zhang, Y. Wang, R. Lv and L. Xu, *Electrochim. Acta,* 55 (2010) 4039.
25. Y. Yun , M. Pan, G. Fang, Y. Yang, T. Guo, J. Deng, B. Liu and S. Wang, *Sens. Actuators B,* 238 (2017) 32.
26. H. Wang, S. Yao, Y. Liu, S. Wei, J. Su and G. Hu, *Biosens. Bioelectron.,* 87 (2017) 417.
27. L. Zhu, Y. Cao and G. Cao, *Biosens. Bioelectron.,* 54 (2014) 258.
28. X. Yu, Y. Chen, L. Chang, L. Zhou, F. Tang and X. Wu, *Sens. Actuators B,* 186 (2013) 648.
29. Z. Zheng, Y. Du, Z. Wang, Q. Feng and C. Wang, *Analyst,* 138 (2013) 693.
30. F. Tan, L. Cong, X. Li, Q. Zhao, H. Zhao, X. Quan and J. Chen, *Sens. Actuators B,* 233(2016) 599.