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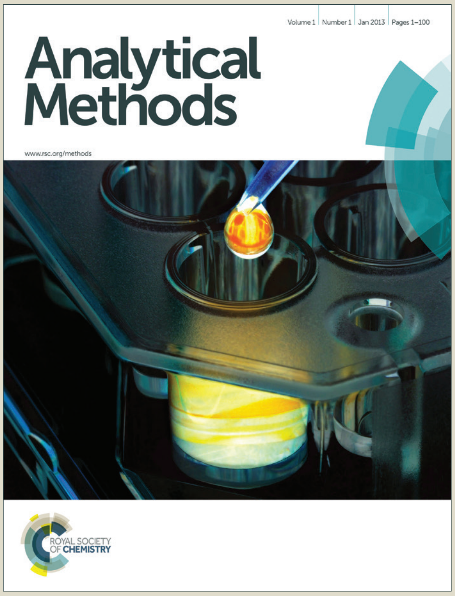

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Imprinted electrochemical sensor for bisphenol A determination based on electrodeposition of graphene and Ag nanoparticles modified carbon electrode

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Abstract

In this study, a highly sensitive and selective imprinted electrochemical sensor based on Ag nanoparticles and graphene modified carbon electrode with covalent anchoring and electrochemical reduction was prepared for the determination of bisphenol A (BPA) in aqueous solution. The imprinted film was fabricated by electrodepositing pyrrole in the presence of BPA onto graphene and Ag nanoparticles modified electrode surface. The morphologies of the electrodes were characterized with scanning electron microscopy. The electrochemical performance of the imprinted electrochemical sensor was investigated with cyclic voltammetry and differential pulse voltammetry techniques in detail. The response currents of the imprinted electrochemical sensor exhibit a linear relationship toward the negative logarithm of the concentrations of BPA ranging of $1.0 \times 10^{-11} \sim 1.0 \times 10^{-8}$ mol L^{-1}. The detection limit of the imprinted electrochemical sensor toward BPA is calculated as 3.2×10^{-12} mol L^{-1} (S/N = 3). The imprinted electrochemical sensor was successfully applied to detect BPA in real plastic samples with good recoveries ranging of 93.3% ~ 103.0%.

Keywords: Imprinted electrochemical sensor; Bisphenol A; Ag nanoparticles; Graphene; Covalent anchoring; Electrochemical reduction

1 **Introduction**

Bisphenol A (BPA) has been widely used for the production of epoxy resins, polycarbonate (PC) plastics, dental fillings, and the lining of food cans.[1,2] Unfortunately, studies showed BPA is an estrogenic contaminant, which can cause breast cancer, prostate cancer, birth defect, infertility, precocious and obesity.[3,4] Up to now, quantification of BPA has been performed by high-performance liquid chromatography (HPLC),[5,6] enzyme-linked immunosorbent assay (ELISA),[7] liquid chromatography coupled with mass spectrometry (LC–MS)[8,9] and gas chromatography coupled with mass spectrometry (GC–MS)[10]. Although these methods can offer good selectivity and detection limit, they often require expensive instrumentation and time-consuming sample pretreatment steps.

It is well known that electrochemical method has the advantages of fast response, cheap instrument, simple operation, time-saving, high sensitivity, and real-time detection in situ.[11] However, direct detection of BPA using traditional sensor is few because the selectivity of the traditional sensor response toward BPA is poor.[12] To solve this problem, an electrochemical sensor based on molecularly imprinted polymers (MIPs) can be an ideal choice due to its excellent selectivity and high stability.[13] MIPs as sensing materials can effectively overcome the interferences of other analyte species with the similar structures or functional groups.[14] Wang *et al* prepared mesoporous silica-based electrochemical sensor for sensitive determination of environmental hormone BPA.[15] Wang *et al* fabricated a BPA sensor based on ordered mesoporous silica with surface molecularly imprinting technique.[16] Although molecular imprinting technique is a highly accepted tool for the preparation of tailor-made recognition material with imprinted cavities which are able to selectively recognize target molecules,[17,18] MIPs prepared by the conventional technique have some disadvantages involving low-affinity binding, high diffusion barrier, and low-rate mass transfer. Recently, some novel nanomaterials with large surface area and high porosity 3D platform, such as graphene nanosheets and metal nanoparticles, have been developed for the preparation of MIPs to overcome these drawbacks.

Graphene has attracted considerable attentions in recent years because of its two-dimensional structure and extraordinary properties, which holds great promise for potential applications in nanomaterial and nanotechnology. [19] Lian *et al* prepared an imprinted electrochemical sensor based on chitosan-silver nanoparticles/graphene -multiwalled carbon nanotubes using surface coating for the determination of neomycin.[20] Xu *et al* prepared a graphene membrane modified electrode using surface coating for the detection of 2,4-dichlorophenol.[21] However, these commonly surface coating modification methods for the preparation of graphene modified electrode are facing some drawbacks. The thickness of the graphene film is hard to control and the graphene film may flak off easily from the sensor surface, which could affect the reproducibility and stability of the modified electrode.

The aim of this study is to develop a novel imprinted electrochemical sensor based on graphene modified carbon electrode with the method of covalent anchoring and electrochemical reduction graphene for the detection of BPA in aqueous solution. Firstly, graphene was modified steadily on carbon electrode via covalently modified with diazonium salt reaction and electrochemically reduction graphene oxide (GO) to graphene. Then, Ag nanoparticles were electrochemical deposited onto the graphene modified electrode surface. The combination of covalently modification and electrochemical reduction nanoparticle technique with MIPs technique offered an attractive route to enhance the sensitivity, stability and selectivity of the imprinted sensor. The MIPs electrochemical sensor was employed to detect BPA in water samples successfully.

2 Experiments

2.1 Reagents and Apparatus

Graphite powder, $KMnO_4$, H_2SO_4, H_3BO_3, HCl, KNO_3, $AgNO_3$, N-hydroxy succinimide, N, N'-dicyclohexylcarbodiimide, ethylenediamine, H_2O_2, and potassium ferricyanide were all analytical grade and obtained from Beijing Chemical Reagents Company. BPA, 3, 3’, 5, 5’-tetrabromobisphenol A (TBBPA), and tetrabromo bisphenol S (TBBPS) were obtained from Alfa Aesar Company (Tianjin, China). Sodium nitrite ($NaNO_2$) was obtained from Dalian Xindie Chitin Company (Dalian, China).

All electrochemical experiments were carried out on a CHI660B electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd, China). Scanning electron microscope (SEM) images were obtained with a field-emission scanning electron microscope (JEOL JSM-6700F). Infrared spectra were measured with a Fourier transform infrared spectrometer (FT-IR, Nicolet iS10, Thermo 137 scientific, USA) in the range of 400 cm^{-1}- 4000 cm^{-1}.

2.2 Preparation of graphene oxide

Graphene oxide (GO) was prepared from graphite powder using Hummers method with minor modification.[22] Briefly, 1 g of graphite, 1 g of $NaNO_3$ and 46 mL of H_2SO_4 were stirred together in an ice bath. Next, 6 g of $KMnO_4$ was slowly added. Once mixed, the solution was transferred into a water bath (35 ± 5 °C) and stirred for 1 h to form a thick paste. Then, 80 mL of water was added and the solution was stirred for 30 min at 90 ± 5 °C. Finally, 200 mL of water was added and then followed by the slow addition of 6 mL of H_2O_2 (30%). When the color of the solution turns from dark brown to yellow, the warm solution was filtered and washed in succession with 200 mL of water, HCl (5%) and distilled water for 3 times. Finally, the product was dried in a vacuum overnight at room temperature.

2.3 Preparation of amido functionalized graphene oxide (GO-NH_2)

The synthesis of GO-NH_2 was performed by a two-step process. Firstly, 300 mg of GO was dispersed into 200 mL of distilled water uniformly under sonicated for 30 min. After that, 1.24 g of H_3BO_3, 2.3 g of N-hydroxy succinimide and 4.12 g of N, N'-dicyclohexylcarbodiimide were added into the dispersion. The mixture was stirred for 1 h at 50 °C. Then, 35 mL of ethylenediamine was added dropwise to the mixture and stirred for 4 h. In this process, GO-NH_2 would be prepared by the chemical reaction between the –COOH of the graphene oxide and the –NH_2 of the ethylenediamine to form –CO–NH_2. The reaction product was washed with water and ethanol in succession. Finally, the resulting GO-NH_2 was dried overnight under vacuum at 50 °C.

2.4 Preparation of MIPs electrochemical sensor

The detailed preparation procedures of the imprinted sensor were illustrated in Fig. 1. Piror to modification, the bare carbon electrode (CE, home-made, the size of 7 mm × 3.5 mm) was polished to a mirror-like with 0.3 and 0.05 μm alumina slurry in succession. Then, the CE was washed successively with deionized water and ethanol in an ultrasonic bath and dried in air before use. For preparation of GO modified electrode, the bare CE was immersed into 1 mL of 1.0 mg mL^{-1} GO-NH_2 dispersion containing 0.5 mol L^{-1} HCl and 10 mg mL^{-1} $NaNO_2$ overnight. Then graphene oxide modified on electrode was reduced electrochemically to graphene by cyclic voltammetry scanning for 6 cycles under the potential of -0.4 V ~ -1.4 V at 50 mV s^{-1} in 0.1 mol L^{-1} NaCl solution.

Ag nanoparticles were modified on the electrode according to previously reported method.[23] Briefly, the graphene modified electrode was scanned with cyclic voltammetry (CV) at 50 mV $s^{-1}$for 5 cycles under the potential range of 0.1 ~ 1.0 V in 0.1 mol L^{-1} KNO_3 solution containing 5.0×10^{-3} mol L^{-1} $AgNO_3$.

Molecularly imprinted electrode was prepared by coelectrodeposition of polypyrrole and the template molecule BPA on the surface of Ag nanoparticles and graphene modified electrode (denoted as graphene-Ag/CE) using CV scanning at the potential range of 0 ~ 0.8 V. Prior to electrodeposition, the graphene-Ag/CE was washed with deionized water. Nine cycles of CV at 50 mV s^{-1} in 20 mL of 0.2 mol L^{-1} pyrrol phosphate buffer solution (PBS, pH = 7.5) containing 5.0 mg mL^{-1} BPA were performed. After coelectrodeposition, the MIPs electrode was immersed in elution mixture solvent of methanol/acetic acid (4:1, v/v) to remove the template from the imprinted film until BPA could no longer be detected with ultraviolet spectrograph at 270 nm in the elution.

For comparison, the non-imprinted polymers (NIPs) modified electrode based on graphene-Ag (NIPs-graphene-Ag/CE) was prepared by the same procedures, but without addition of the template BPA in the electrodeposition process.

(Fig. 1 is inserted here)

2.5 Preparation of sample solution

All the plastic products were purchased from a local supermarket. These samples were cut into pieces by scissors and washed twice with deionized water. Then, the plastic products were treated as the following process to obtain sample solutions. About 1.0 g of plastic product pieces and 30 mL of ethanol were added into a beaker. Heated at 50 ^{o} C for 4 h, the beaker was sealed for 5 days. The soil was obtained from the school yard of Jishou University, and immersed in the distilled water in a beaker for 48 h. Finally, the solutions (both plastic solution and soil solution) were collected by filtrating and stored in a flask. The spiked sample solutions were prepared with the same method only addition BPA standard solution with different concentrations.

2.6 Electrochemical determination

Electrochemical measurements were performed with a three-electrode system into a 20 mL glass cell. Unless otherwise mention, the electrochemical experiments were performed using a three-electrode system which was comprised of a working electrode (the modified carbon electrode), a platinum wire (the auxiliary electrode) and a saturated calomel electrode (SCE). The electrochemical performances of the modified electrodes were characterized by using different techniques including CV and differential pulse voltammetry (DPV). CV was carried out from −0.3 to +0.8 V with a scanning rate of 50 mV s^{-1} in 5.0 mmol L^{-1} $Fe(CN)_6^{3-/4-}$ PBS (pH 7.5). DPV was conducted from −0.3 to +0.8 V in PBS (pH 7.5) containing different concentrations of BPA.

3. Results and discussion

3.1 Preparation and characterization of BPA imprinted electrochemical sensor

Prior to the GO-NH_2 modification on the electrode surface, the GO and GO-NH_2 were characterized with FT-IR and the results were showed in Fig. 1S. The FT-IR spectrum of GO shows a broad absorption band at 3382 cm^{-1}, which is characterization of the –OH groups, and absorption bands at 1620 cm^{-1} and 1732 cm^{-1}, which are typical of –COOH group. After amination, obvious changes were observed in FT-IR spectra of GO-NH_2. Compared with the FT-IR of the GO, the peak at 1730 cm^{-1} disappears, and a new broad band emerges at 1650 cm^{-1} corresponding to the C=O characteristic stretching band. The band at 1580 cm^{-1} corresponds to the –NH– bending vibration, the peak at 1249 cm^{-1} corresponds to C–N stretching vibration and the peak at 640 cm^{-1} corresponds to the bending vibration of the –CO–NH–. The bands at 892 cm^{-1} and 1535 cm^{-1} correspond to in plane bending vibration and out-of-plane bending vibration band of the –NH_2 group. The bands at 1435 cm^{-1}, 2927 cm^{-1} and 2948 cm^{-1}

contribute to the bending vibration, the asymmetric and symmetric stretch vibration modes of –C−H_2 groups, respectively. The band at 1314 cm^{-1} corresponds to in plane binding stretching of –OH. These results indicated that the amino groups were covalently bonded to the GO successfully.[24, 25]

The GO-NH_2 modified carbon electrode was prepared according to the method of electrochemical reduction graphene oxide to graphene.[26] When the bare electrode was immersed in GO-NH_2 dispersion containing HCl and $NaNO_2$ overnight in an ice bath, the GO-NH_2 was modified onto the electrode surface through the diazotization reaction. Then graphene oxide modified on the electrode was electrochemically reduced to graphene by cyclic voltammetry scanning for 6 cycles under the potential of -0.4 V~ -1.4 V at 50 mV s^{-1} in 0.1 mol L^{-1} NaCl solution. As shown in Fig. 2A, a sharp irreversible peak at -0.95 V was observed during the first cycle, followed by greatly diminished currents in subsequent cycles. And after 5 cycles, the current become stable, which suggested the GO are reduced to graphene successfully.

(Fig. 2 is inserted here)

Figure 2B shows the cyclic voltammograms of the graphene modified electrode in the mixture solution of 0.1 mol L^{-1} KNO_3 and 5.0×10^{-3} mol L^{-1} $AgNO_3$. Each cyclic voltammogram exhibits a cathodic peak at 0.30 V and an anodic peak at 0.50 V. The cathodic peak was ascribed to the reduction of Ag^+ to form Ag nanoparticles on the electrode surface, and the anodic peak corresponds to the oxidation of the silver electrodeposition.[23,27] After CV scanning for 5 cycles, the electrodeposition of silver ions and dissolving of Ag nanoparticles were equilibrating, which suggested the Ag nanoparticles were electrodeposited on the graphene modified electrode successfully.

MIPs film was modified on the graphene-Ag/CE using cyclic voltammetry scanning for nine cycles in 0.2 mol L^{-1} pyrrole PBS (pH 7.5) containing 5 mg mL^{-1} BPA under potential range of 0 ~ 0.8V with a scan rate of 50 mV s^{-1}. As shown in Fig. 2C, the currents decreased with the increment of CV cycles. When the CV scanning over 8 cycles, the currents is similar, which indicated the imprinted film was deposited on the electrode surface successfully.

Figure 3 shows the SEM images of various modified CE surfaces. The bare CE shows a smooth and homogeneous surface (shown in Fig. 3a). However, after modification of graphene, some slices coating on the electrode surface were observed in Fig. 3b. When Ag nanoparticles were electrodeposited on the grapheme modified electrode surface (shown in Fig. 3c), the homogenous distribution of Ag nanoparticles with the average size of 50~80 nm were observed onto the electrode surface. After electrodeposition of pyrrole and BPA on the modified graphene-Ag/CE, uneven imprinted layers were observed on the surface of graphene-Ag/CE obviously (shown in Fig. 3d), which indicated the MIPs/graphene-Ag/CE was fabricated successfully.

(Fig. 3 is inserted here)

Cyclic voltammetry (CV) was used to investigate the electrochemical properties of different modified electrodes including bare electrode, graphene modified electrode, graphene-Ag/CE, MIPs-graphene-Ag/CE before and after extraction the template with $Fe(CN)_6^{3-/4-}$ as probe. As shown in Fig. 4, after modification with graphene, an increment of the response current (shown in Fig. 4b) was observed than that of the bare electrode (shown in Fig. 4a). While the peak current of the graphene and Ag nanoparticles modified electrode (shown in Fig. 4c) was higher than that of the graphene modified electrode (shown in Fig. 4b). The reason was contributed to the higher effective surface area and excellent conductive effect of Ag nanoparticles, which can increase the transfer rate of $Fe(CN)_6^{3-/4-}$. Figure 4d shows the cyclic voltammogram of the MIPs electrochemical sensor before removing BPA in 5.0 mmol L^{-1} $Fe(CN)_6^{3-/4-}$ PBS (pH 7.5), in which the peak current was lower than that of the MIPs electrochemical sensor after removing of BPA (shown in Fig. 4e). The reason can attribute to the fact that when BPA was extracted from the MIPs film, lots of imprinted cavities were generated. The porosity enhanced the diffusion of $Fe(CN)_6^{3-/4-}$ through the imprinted film. There was just little electrochemical response with the NIPs film modified graphene-Ag/CE (Fig. 4f) because the film was too dense without imprinted cavities.

(Fig. 4 is inserted here)

3.2 Optimization of experimental conditions

In order to improve the sensitivity and stability of the imprinted electrochemical sensor, the optimum number of CV scanning cycles during the electropolymerization process was investigated. As shown in Fig. 5A, the current response of the imprinted electrochemical sensor with CV scanning 9 cycles toward BPA (5mg mL^{-1}) reached the maximum. The current response decreased when the scan cycles was less than nine cycles was because that the imprinted polymers membranes became very thin and easy to break when removing the template molecule. When the scan cycles were over nine cycles, although greater deposition of BPA contributes to a higher number of imprinted sites and better membrane stability, it becomes difficult to remove the template from excessively thick membranes. This reduces the number of accessible imprinted sites, leading to low binding capacity and slow kinetics.[28]

The buffers with different pH values ranging from 6.0 to 9.0 were investigated to investigate the influence of pH on the electrochemical performance of the MIPs-graphene-Ag/CE. As shown in Fig. 5B, the response currents of the imprinted electrochemical sensor increased when the pH values increased from 6.0 to 7.5. However, the peak currents decreased rapidly when the pH values increased from 7.5 to 9.0. This phenomenon could be attributed to the imprinted cavities of the MIPs electrochemical sensor combining more the template molecules at pH 7.5. Thus the imprinted electrochemical sensor exhibited the maximum response current. Therefore, pH 7.5 PBS was used as the medium for the determination of BPA.

The MIPs-graphene-Ag/CE was washed with methanol/acetic acid (4:1, v/v) solution repeatedly for 5 min, 10 min, 15 min, 20 min, 30 min, and 50 min to remove BPA to optimize the best elution time. As shown in Fig. 5C, the biggest response current of the MIPs-graphene-Ag/CE toward 1.0×10^{-8} mol L^{-1} BPA was obtained when the elution time was 20 min. It was because when the elution time was less than 20 min, the template molecule BPA was eluted off incompletely. And the response currents remained constant subsequently. Thus, 20 min elution time was selected in our subsequent test.

3.3 Calibration curve

Since differential pulse voltammetry (DPV) is much higher sensitive than that of cyclic voltammetry, it was used to investigate the detection performance of the MIPs-graphene-Ag/CE toward BPA in 5.0 mmol L^{-1} $Fe(CN)_6^{3-/4-}$ PBS (pH=7.5). Figure 6 shows the DPV curves of the MIPs-graphene-Ag/CE toward BPA solution with different concentrations range of $1.0 \times 10^{-11} \sim 1.0 \times 10^{-8}$ mol L^{-1}. The results showed that the response peak currents (I, mA) of the MIPs-graphene-Ag/CE are proportional to the negative logarithm of the concentrations of BPA (-logC) in a wider concentration range of $1.0 \times 10^{-11} \sim 1.0 \times 10^{-8}$ mol L^{-1}. The linear equation is as follows.

$$I\ (mA) = -0.13\ \log C + 1.896 \qquad (R = 0.992)$$

The detection limit was calculated as 3.2×10^{-12} mol L^{-1} (S/N = 3). The low detection limit could be attributed to the sensitizing effect of the Ag nanoparticles and graphene modified on the MIPs electrochemical sensor.

(Fig. 6 is inserted here)

3.4 Reproducibility and selectivity

Reproducibility and selectivity are key elements of an imprinted electrochemical sensor. The reproducibility for ten MIPs-graphene-Ag/CE prepared with same procedure was investigated by comparing the response currents of these MIPs electrochemical sensors toward 1.0×10^{-9} mol L^{-1} BPA in 5.0 mmol L^{-1} $Fe(CN)_6^{3-/4-}$ PBS (pH=7.5). The relative standard deviation (RSD) is calculated as 4.5%, which revealed that the imprinted electrochemical sensor had good reproducibility.

The selectivity of the imprinted electrochemical sensor was also investigated by comparing its response current toward the analytes with similar molecular structures involving 3, 3’, 5, 5’-tetrabromobisphenol A (TBBPA), tetrabromo bisphenol S (TBBPS) and bisphenol A (BPA). Figure 7 shows the DPV results of the determination of 1.0×10^{-9} mol L^{-1} BPA with the coexistence interference of 5.0×10^{-8} mol L^{-1} TBBPS or TBBPA. As shown in Fig. 7, the DPV response current of the MIPs-graphene-Ag/CE with the coexistence of 5.0×10^{-8} TBBPS or TBBPA is almost equal to that in 1.0×10^{-9} mol L^{-1} BPA solution. Likewise, some inorganic ions such as 100-fold concentrations of Mg^{2+}, Ca^{2+}, Cu^{2+}, Fe^{3+}, Al^{3+}, SO_4^{2-}, PO_4^{3-} and NO_3^- have little influence on the determination of BPA. These results indicated that the MIPs-graphene-Ag/CE possesses a high selectivity toward BPA.

3.5 Applications

The proposed imprinted electrochemical sensor was used to detect BPA in different plastic samples and soil samples under optimized condition to evaluate the performance of the MIPs-graphene-Ag/CE in practical analytical applications. A known-amount of sample standard solution was added into PBS (pH=7.5), and then analyzed according to the section 2.5. Each sample solution undergoes five parallel determinations. The data given in Table 1 indicated that our approach could provide satisfactory results for the determination of BPA, and the recoveries was ranging from 93.3% to 103.0%.

(Table 1 is inserted here)

A comparison of the graphene-Ag/CE with other reported modified electrodes for BPA detection was listed in Table 2. It was found that the proposed imprinted electrochemical sensor had a fairly sensitivity, a large linear range and low detection limit.

(Table 2 is inserted here)

4. Conclusions

In this work, an imprinted electrochemical sensor with high sensitivity and selectivity was proposed by using with covalent anchoring and electrochemical reduction graphene oxide to graphene for the determination of BPA in water samples. The results showed Ag nanoparticles and graphene nanocomposite could remarkably enhance the response current due to their higher effective surface area and excellent conductive effect. This new imprinted electrochemical sensor possessed high determination sensitivity, simple preparation process, rapid response and low cost for the determination of BPA. The results showed that a wide linear range ($1.0 \times 10^{-11} \sim 1.0 \times 10^{-8}$ mol L^{-1}) for the detection of BPA with a low detection limit of 3.2×10^{-12} mol L^{-1} for S/N = 3 was obtained. The practical application in determining water samples was satisfactory with recoveries from 93.3% to 103.0%

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Figure captions

Figure 1 Preparation procedure of BPA molecularly imprinted electrochemical sensor

Figure 2 Cyclic voltammograms of electrochemical reduction GO in 0.1 mol L^{-1} NaCl solution. Scan rate is 50 mV s^{-1}; (B) Cyclic voltammograms for the GO modified electrode in mixture solution of 0.1 mol L^{-1} KNO_3 and 5.0×10^{-3} mol L^{-1} $AgNO_3$; (C) Cyclic voltammograms for electrochemical polymerization of pyrrole (0.2 mol L^{-1}) in the presence of BPA (5 mg mL^{-1}) in phosphate buffer solution (pH 7.5). All CVs were set up in the same scan rate at 50mV s^{-1}.

Figure 3 SEM images of bare electrode (a), graphene modified electrode (b), graphene-Ag/CE (c), and MIPs-graphene-Ag/CE (d).

Figure 4 Cyclic voltammograms of bare electrode (a), graphene modified electrode (b), graphene-Ag/CE (c), MIPs-graphene-Ag/CE before (d) and after (e) extraction with methanol/acetic acid (4:1, v/v), NIPs-graphene-Ag/CE (d) in 5.0mmol/L $Fe(CN)_6^{3-/4-}$ PBS (pH 7.5). Scan rate is 50 mV s^{-1}.

Figure 5 (A) Effect of the different cycles (2 cycles, 5 cycles, 7 cycles,9 cycles, 11 cycles, 15 cycles, 20 cycles) of the electropolymerization of MIPs; (B) The influence of different pHs on the response of the MIPs-graphene-Ag/CE. The concentration of BPA was 1.0 × 10^{-9} mol L^{-1}; (C) Effect of elution time (5 min, 10 min, 15 min, 20 min, 30 min, 50 min) on the current response of the sensor to BPA.

Figure 6 (A) Differential pulse voltammograms of the MIPs-graphene-Ag/CE towards different concentrations of BPA (1 ~ 7 correspond to TBBPS concentration of 1.0 × 10^{-8}, 5.0 × 10^{-9}, 1.0 × 10^{-9}, 5.0 × 10^{-10}, 1.0 × 10^{-10}, 5.0 × 10^{-11}and 1.0 × 10^{-11} mol L^{-1}, respectively); (B) Calibration curves of MIPs-graphene-Ag/CE in different concentrations of BPA solution.

Figure 7 Differential pulse voltammograms results of the imprinted sensor toward 1.0 × 10^{-9} mol L^{-1} BPA and the coexistence interference of 5.0 × 10^{-8} mol L^{-1} TBBPS or TBBPA

Table captions

Table 1 Determination of BPA in plastic samples

Table 2 Comparison of different modified electrodes for BPA determination

Figure 1

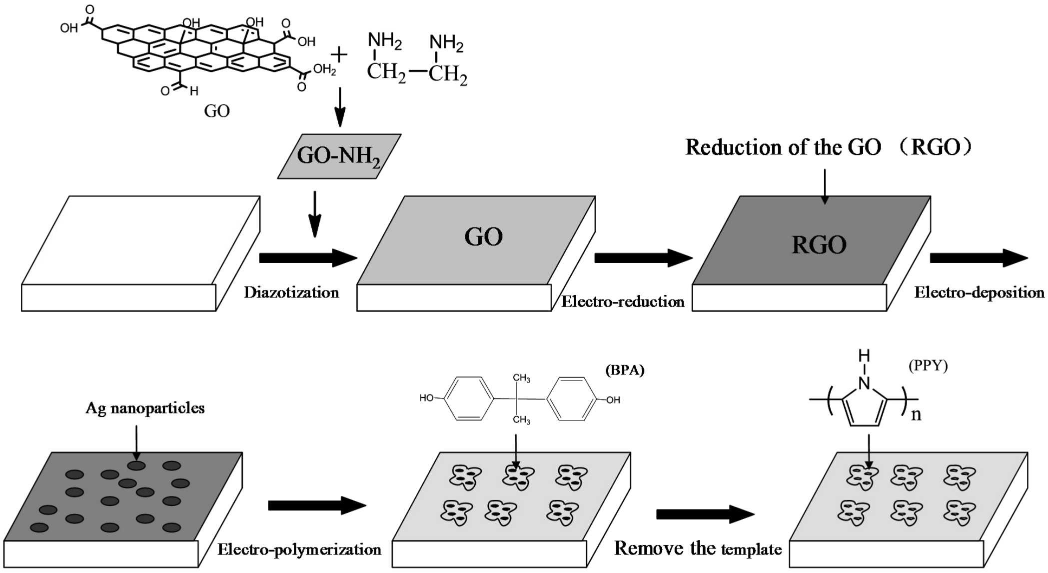

OH
O
OH
OH
O
OH
OH2
O
O
H
GO
+
NH2 NH2
CH2—CH2
GO-NH2
Reduction of the GO （RGO）
GO
RGO
Diazotization
Electro-reduction
Electro-deposition
Ag nanoparticles
(BPA)
HO
CH3
CH3
OH
H
N
(PPY)
n
Electro-polymerization
Remove the template

Figure 2

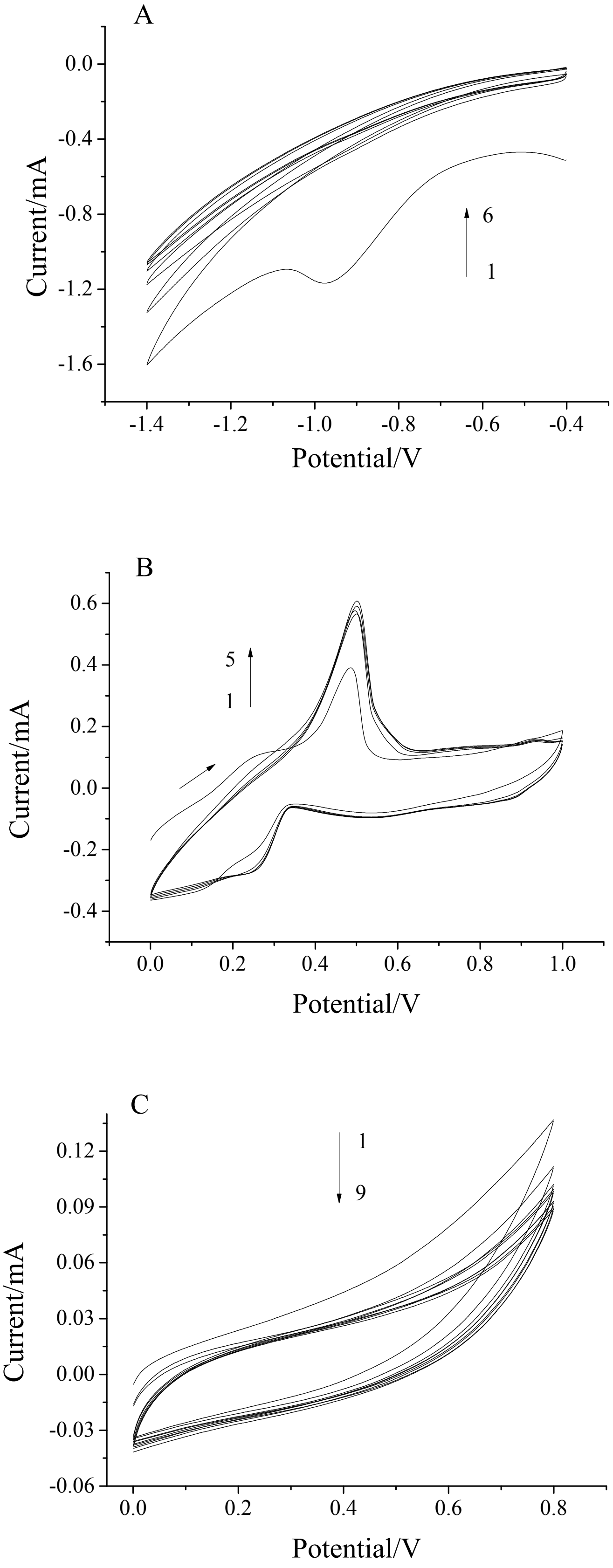

A
Current/mA
0.0
-0.4
-0.8
-1.2
-1.6
-1.4
-1.2
-1.0
-0.8
-0.6
-0.4
Potential/V
6
1
B
Current/mA
0.6
0.4
0.2
0.0
-0.2
-0.4
0.0
0.2
0.4
0.6
0.8
1.0
Potential/V
5
1
C
Current/mA
0.12
0.09
0.06
0.03
0.00
-0.03
-0.06
0.0
0.2
0.4
0.6
0.8
Potential/V
1
9

Figure 3

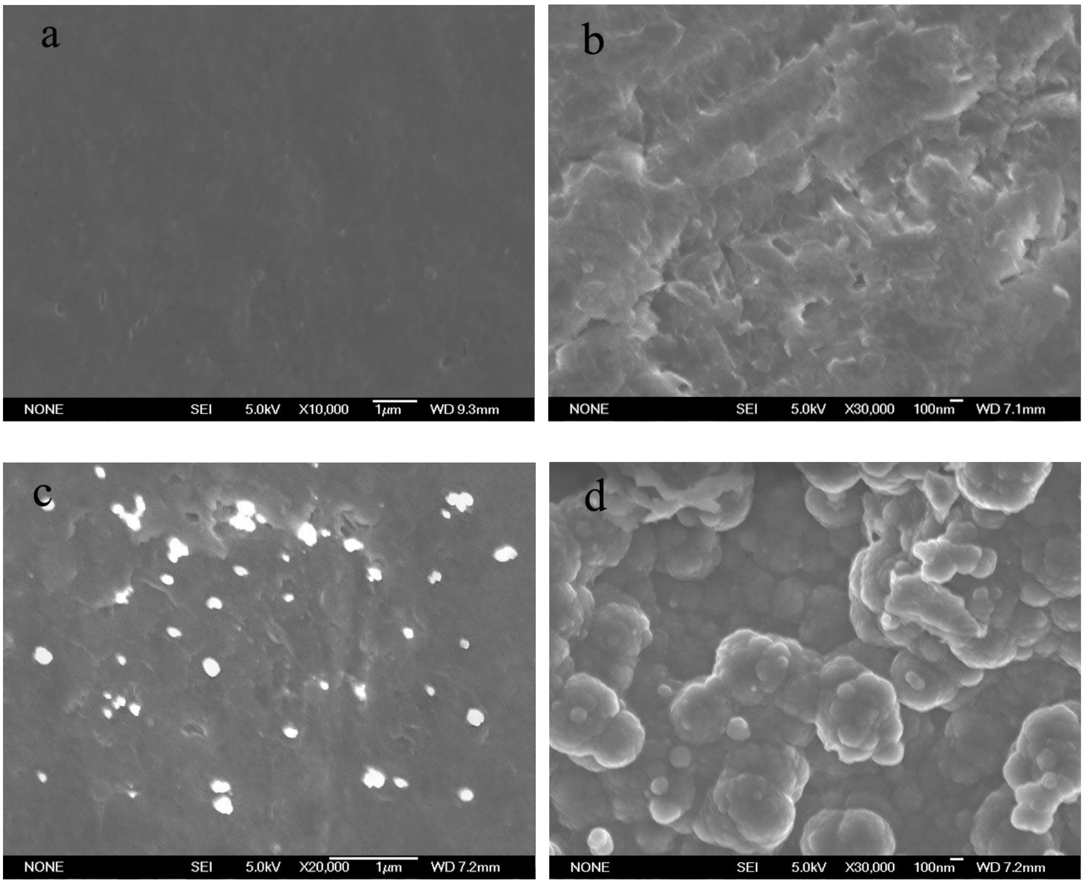

a
NONE SEI 5.0kV X10,000 1μm WD 9.3mm
b
NONE SEI 5.0kV X30,000 100nm WD 7.1mm
c
NONE SEI 5.0kV X20,000 1μm WD 7.2mm
d
NONE SEI 5.0kV X30,000 100nm WD 7.2mm

Figure 4

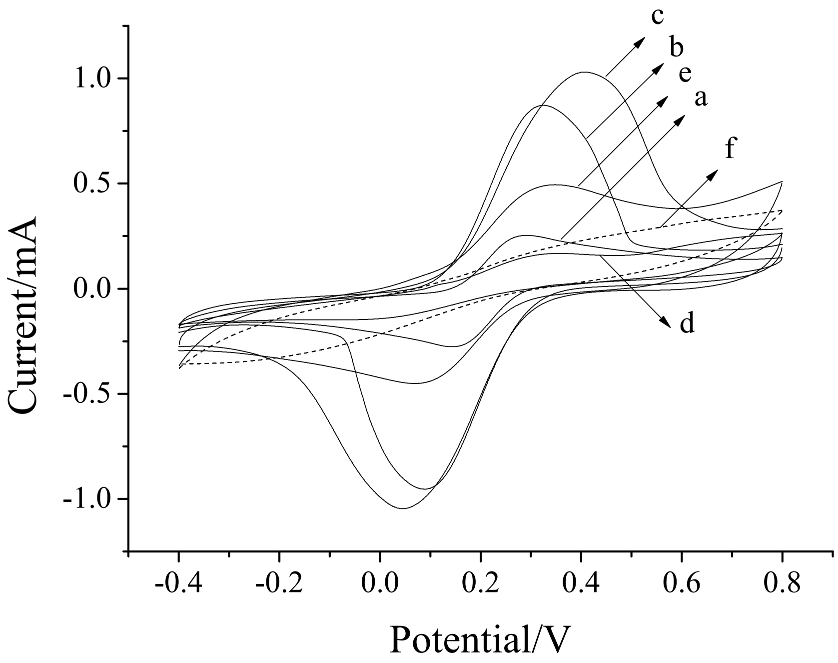


Figure 5

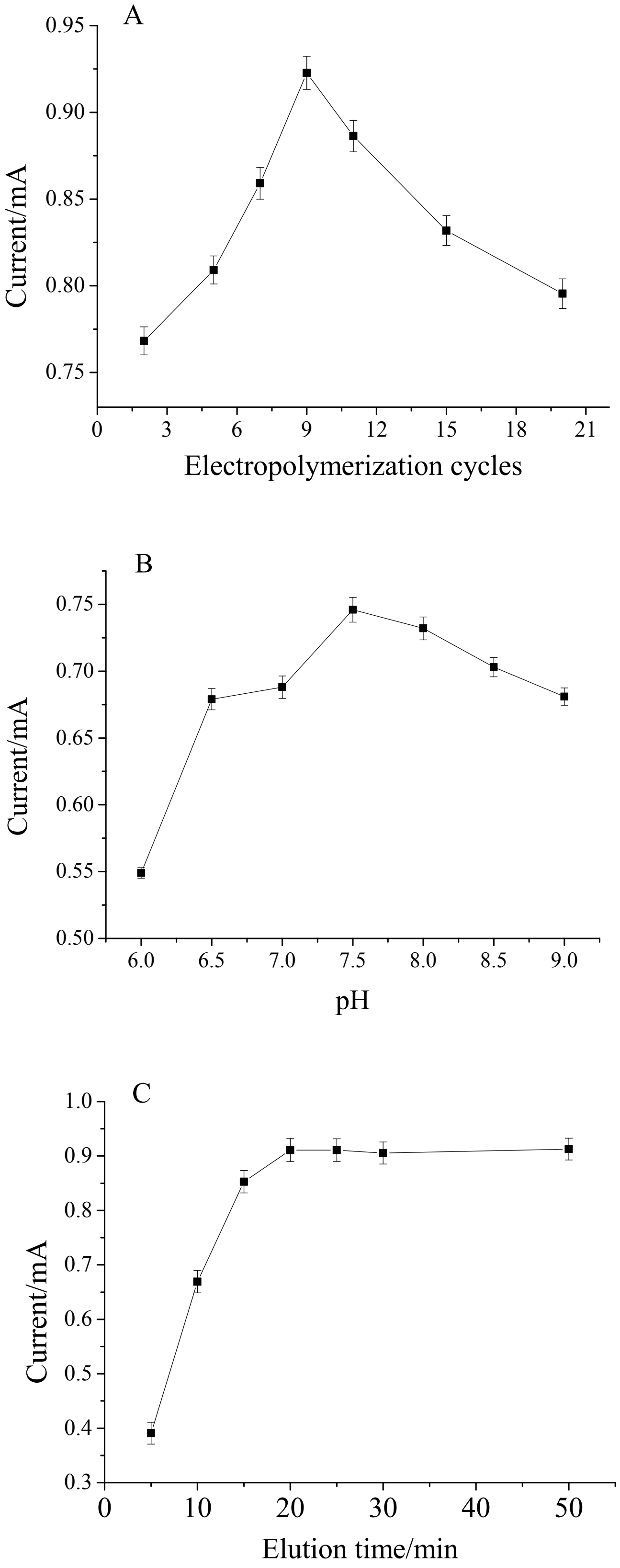

A
Current/mA
0.95
0.90
0.85
0.80
0.75
0
3
6
9
12
15
18
21
Electropolymerization cycles
B
Current/mA
0.75
0.70
0.65
0.60
0.55
0.50
6.0
6.5
7.0
7.5
8.0
8.5
9.0
pH
C
Current/mA
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0
10
20
30
40
50
Elution time/min

Figure 6

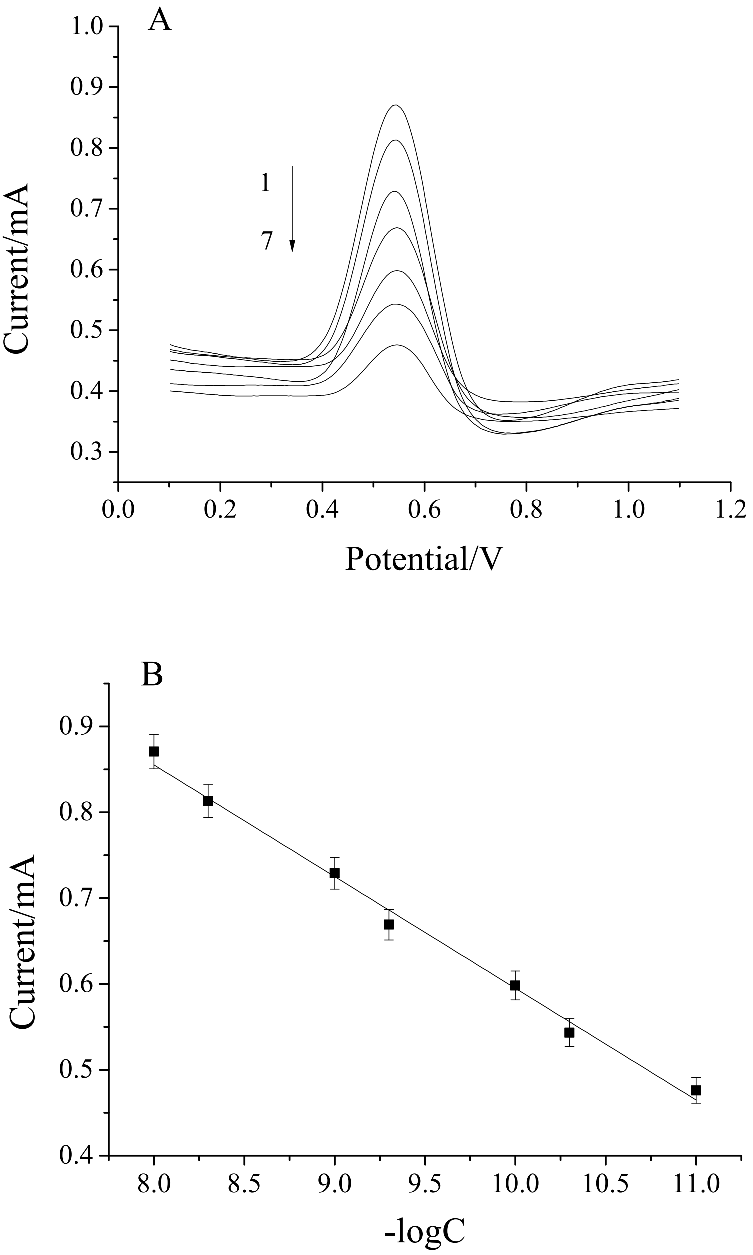

A
Current/mA
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
1
7
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Potential/V
B
Current/mA
0.9
0.8
0.7
0.6
0.5
0.4
8.0
8.5
9.0
9.5
10.0
10.5
11.0
-logC

Figure 7

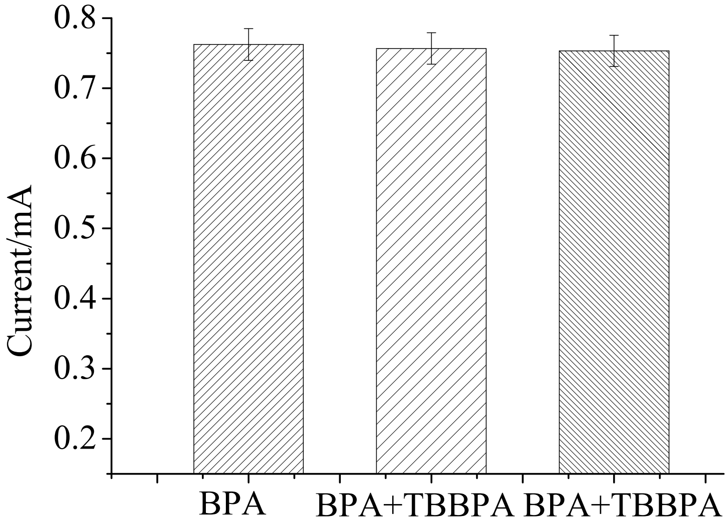


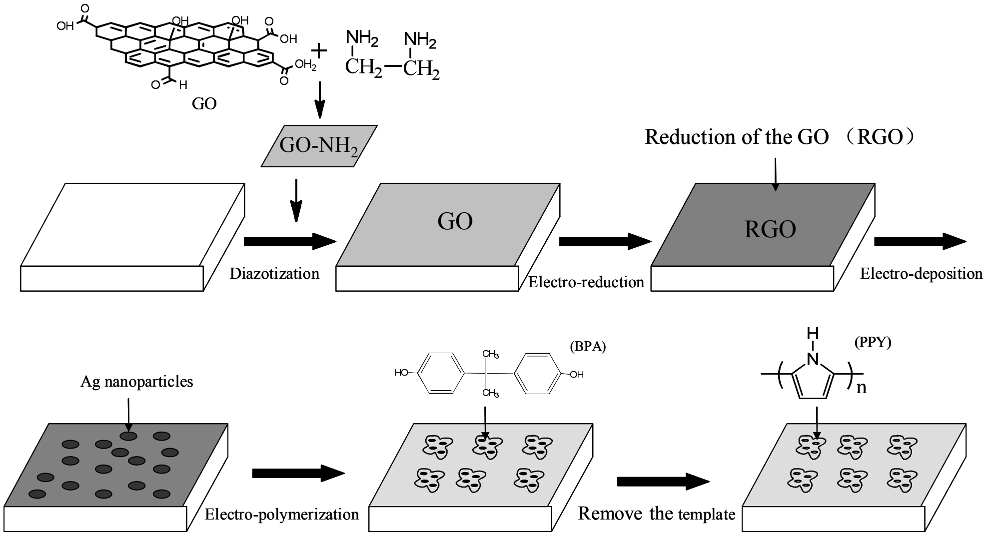
Table 1

Sample (water solution)	Measured (μmol L^{-1})	Added (μmol L^{-1})	Found (μmol L^{-1})	RSD (%)	Recovery (%)
PVC drinking cup	1.02	1.00	2.08	3.87	103.0
PC nursing bottle	0.56	0.50	1.02	4.23	96.2
PVC food package	0.86	1.00	1.80	4.16	96.7
Soil	0.01	0.05	0.056	3.99	93.3

Table 2

Electrodes	Linear range (mol L^{-1})	Detection Limit (mol L^{-1})	Reference
SBA-MIPs-electrode	1.0×10^{-7}-5.0×10^{-4}	3.2×10^{-8}	[29]
SWCNT–CD/GCE	1.1×10^{-8}-1.9×10^{-4}	1.0×10^{-9}	[30]
CS–Fe_3O_4/GCE	5.0×10^{-8}-3.0×10^{-5}	8.0×10^{-9}	[31]
N-GS /GCE	1.0×10^{-8}-1.3×10^{-6}	5.0×10^{-9}	[32]
MIPs-graphene-Ag/CE	5.0×10^{-11}-1.0×10^{-8}	3.2×10^{-12}	This work

Graphical abstract



A highly sensitive and selective imprinted electrochemical sensor based on Ag nanoparticles and graphene modified carbon electrode was prepared for the determination of bisphenol A in aqueous solution.