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Short Communication

Electrochemical Sensor Based on Molecularly Imprinted Polymer for Determination of Nonylphenol

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Molecularly imprinted polymers were prepared on the surface of acrylamide-functionalized multi-walled carbon nanotubes by thermal polymerization, which using nonylphenol as template molecule, methacrylic acid as functional monomer and ethyleneglycol dimethacrylate as crosslinking agent. The molecularly imprinted polymers were modified on the surface of glassy carbon electrode to prepare electrochemical sensor. The proposed sensor showed a linear range of 0.1 to 30 μM with a detection limit of 0.02 μM. The sensor exhibited good stability, selectivity and high sensitivity to nonylphenol detection. It was successfully applied to detect nonylphenol in water samples.

Keywords: Molecularly imprinted polymers, Electrochemical sensor, Nonylphenol

1. INTRODUCTION

Nonylphenol belongs to a phenolic environmental estrogens. It mainly endangering the endocrine system, immune system and reproductive system of organisms[1-3]. Thus, it is very important to develop nonylphenol determination method. At present, there are some methods for the determination of nonylphenol. They are high performance liquid chromatography[4], capillary electrochromatography[5], enzyme-linked immunosorbent assay[6,7], electrochemical method[8-11], and so on. Among these methods, the electrochemical method has high sensitivity and selectivity, moreover, it is low cost, simple and fast[12].

Molecularly imprinted polymers electrochemical sensor has been developed in recent years. It is a new technology for molecularly imprinted sensing in chemical sensors[13]. The molecularly imprinted sensor is specific for target molecules. Much attention has been paid to develop molecularly imprinted sensors for the detection of drugs, environmental pollutants, etc.

In this work, acrylamide-functionalized multi-walled carbon nanotubes(MWNT) were used as matrix. The nonylphenol molecularly imprinted polymers were grafted on the surface of acrylamide-functionalized MWNT. The molecularly imprinted polymers were dropped on the surface of glassy carbon electrode to prepare electrochemical sensor. The sensor is used for the detection of nonylphenol in water environment.

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%. Nonylphenol, 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 experiments. The working electrode was the MIP or NIP modified glassy carbon electrode. The reference electrode and the counter electrode were saturated calomel electrode and platinum wire electrode, respectively.

2.2 Modification of MWCNT

0.8 g MWCNT was added to the mixed acid (V (HNO_3): V (H_2SO_4) = 1: 3) . After ultrasonication for 10 min, the mixture was refluxed 6 h at 75°C, then diluted with distilled water and filtered. The filter cake is repeatedly washed with distilled water to neutral, and at last drying at 70°C for 24 h to get MWCNT-COOH.

0.5 g MWCNT-COOH was added to the mixed solution of 40 mL $SOCl_2$ and 2 mL DMF , the mixture was refluxed at 70°C for 24h. After the reaction was completed, the unreacted $SOCl_2$ was distilled out. Then, 40 mL DMF and 2 g acrylamide were added, after ultrasonication for 10 min, the mixture was refluxed at 60°C for 12h. After filtration, the filter cake was washed with ethanol and distilled water, and the product was dried at 80°C to obtain MWCNT-AA.

2.3 Preparation of imprinted polymers

0.15 g MWCNT-AA, 0.18 g nonylphenol and 0.33 g MAA were added to 30 mL acetonitrile, after ultrasonication for 10 min and stirring for 2h, 3.2 g EGDMA and 20 mg AIBN were added to the stirring mixture. The mixture was sealed and stirred for 24 h at 60°C, then the product was cooled to room temperature and collected after centrifugation. Then, acetic acid/ethanol solution (V (acetic): V (ethanol) = 1: 9) was used to elute the nonylphenol 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°C, 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 nonylphenol was added.

2.4 Fabrication of the modified electrode

Firstly, the glassy carbon electrode(GCE) was 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 8 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 +0.5 to-0.3 V (step increment of 5 mV, amplitude of 50 mV, pulse period of 0.1 s).

3. RESULTS AND DISCUSSION

3.1 CV of the modified electrodes

CV is an effective method to study the electron transfer at a modified electrode [14]. Fig. 1 shows the CV of different modified electrodes in 2.0 mM $K_3[Fe(CN)_6]$ solution containing 0.1 M KCl. A couple of redox peaks were found at MWCNT-MIP /GCE (curve 1) related to the redox of $K_3[Fe(CN)_6]$, which suggested that the cavities in the MIP after template removal acted as channels for electron transport. Curve 2 shows the CV of MWCNT-MIP /GCE after incubation with 0.2 mM nonylphenol. The peak current of this redox peaks were lower than those observed in curve 1, which indicated that the binding of nonylphenol in MIP film resulted in blockage of the cavities, and hence hindered the diffusion of $K_3[Fe(CN)_6]$.

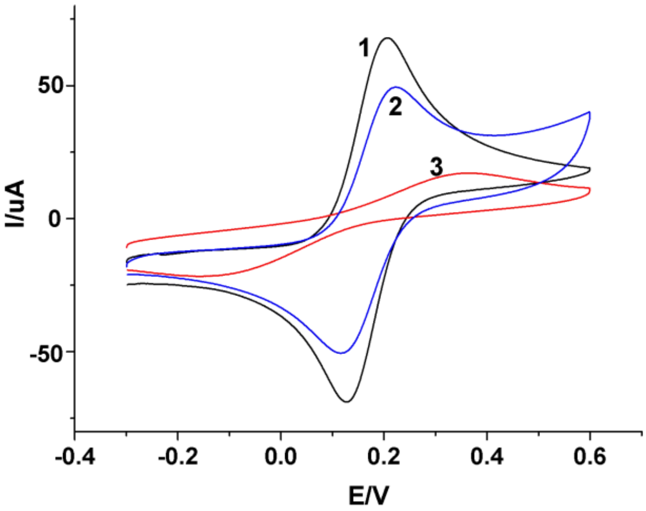
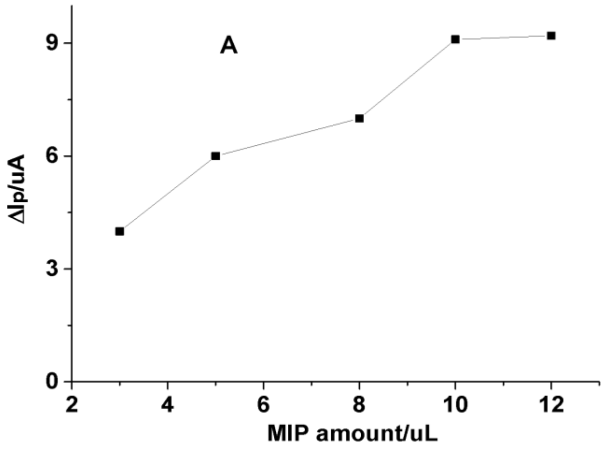


Figure 1. Cyclic voltammograms of 2.0 mM $K_3[Fe(CN)_6]$ at MWCNT-MIP/GCE(1), MWCNT-MIP/GCE after incubation with nonylphenol (2), and MWCNT-NIP/GCE (3).

The electrochemical behavior of the NIP film modified electrode was also evaluated by CV. For the CV of MWCNT-NIP /GCE(curve 3), the peaks were very poor and peak current very low, it was because that the polymer film had lower electron transfer rate and electrical conductivity, which limited diffusion of $K_3[Fe(CN)_6]$ to the electrode surface.

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. 2A, the peak current difference(ΔIp) increases with increasing the MIP amount, but 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.



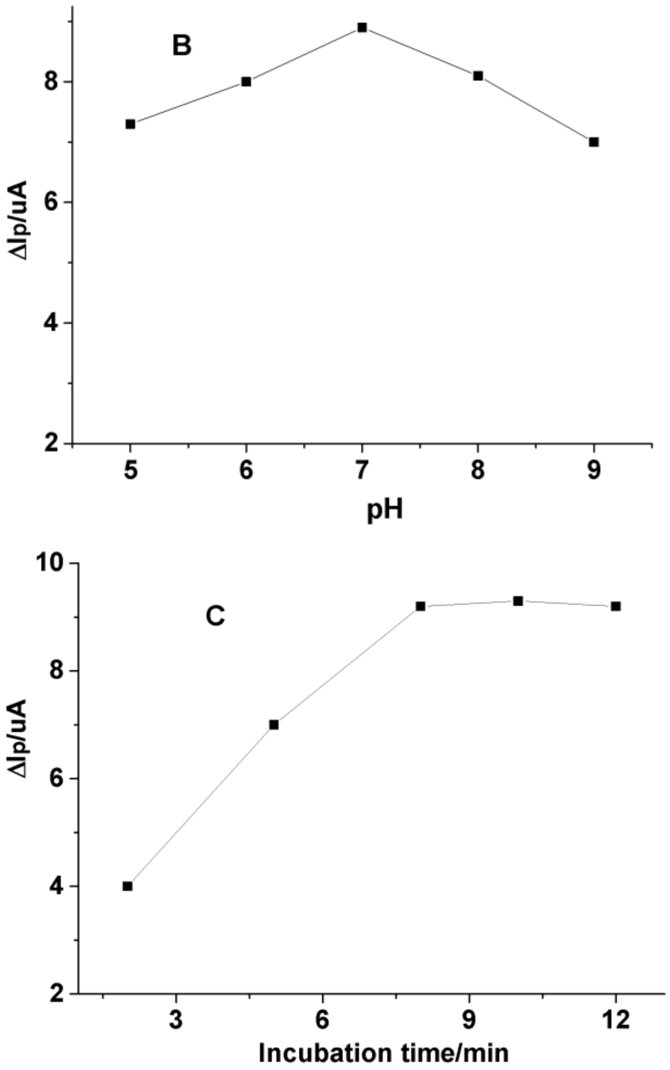


Figure 2. The effect of MIP amount(A), the pH (B) and the incubation time(C) on the ΔIp of MWCNT-MIP/GCE.

The pH value of electrolyte solution has an important influence on the MIP film. The pH effect of the solution was investigated from 5–9. As shown in Fig.2B, the maximum ΔIp was obtained at around pH = 7. Thus, the electrolyte solution pH = 7 was selected in the following measurements.

The effect of incubation time was studied in the range from 2 to 12 min. As shown in Fig. 2C, the ΔIp increases with increasing incubation time and achieved balance at 8 min, indicating that adsorption equilibrium was achieved. The results are similar with the previous reports [15, 16]. Therefore, the incubation time of 8 min was applied in the following measurements.

3.3 Determination of nonylphenol

Differential pulse voltammetry (DPV) was used for the determination of nonylphenol. Fig. 3A shows DPVs of the MWCNT-MIP /GCE at different concentrations of nonylphenol. As can be seen, the peak currents decreased with increasing concentration of nonylphenol.

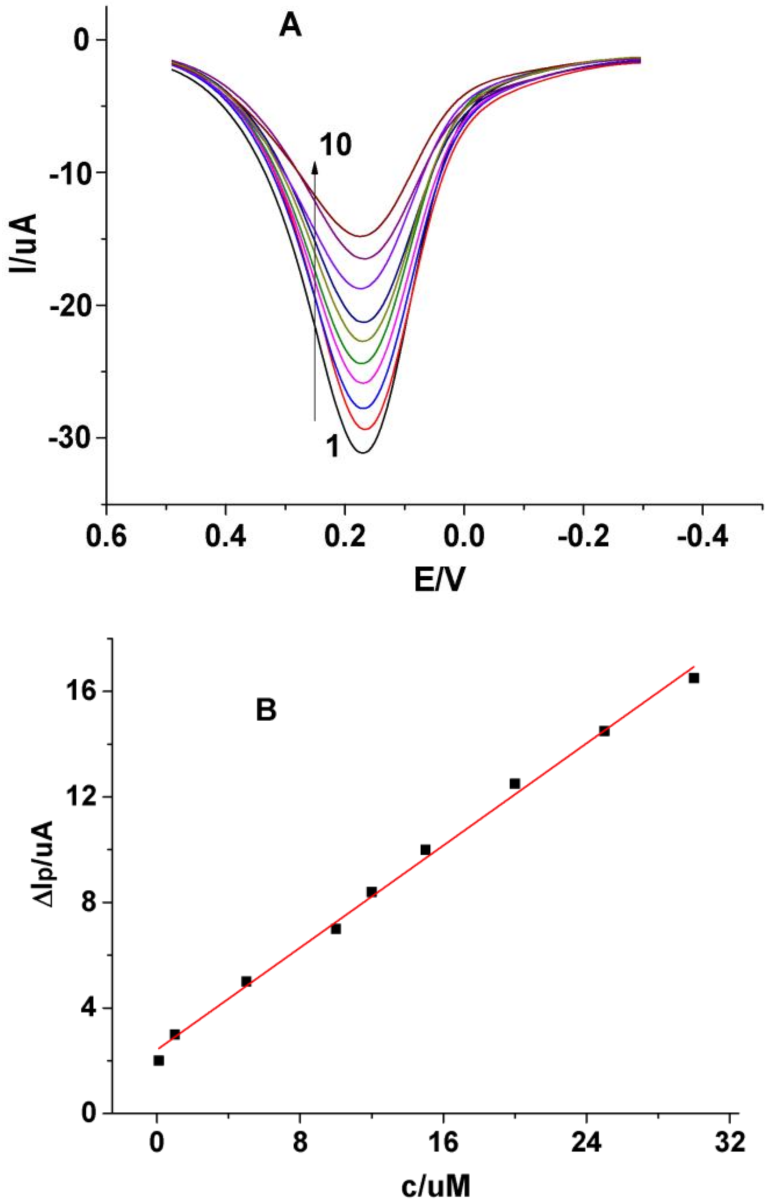


Figure 3. (A) DPVs of the MWCNT-MIP/GCE with different concentrations of nonylphenol. From 1-10: 0; 0.1; 1; 5; 10; 12; 15; 20; 25; 30μM. (B) Plot of the *Δ*Ip *vs* concentration of nonylphenol.

As shown in Fig. 3B, the *Δ*Ip are linearly to the concentrations of nonylphenol in the range of 0.1 to 30 μM, with a detection limit of 0.02 μM. The linear regression equation can be expressed as ΔIp (μA) = 2.416 + 0.4839c (μM), with a correlation coefficient $r = 0.9955$.

The comparison of the proposed method with other electrochemical methods for determination of nonylphenol was illustrated in Table 1. The results showed that the proposed method has a wide linear range and a low detection limit, which makes it suitable for the determination of nonylphenol.

Table 1. Comparison of the proposed method with other electrochemical methods for determination of nonylphenol.

Modified electrode	Linear range (µM)	LOD(µM)	References
AuNPs - CNTs /GCE	0.05 - 4	0.023	[17]
TiO_2 - AuNPs /GCE	0.95 - 480	0.32	[18]
CTAB/CP	0.1- 25	0.01	[19]
FGNS/GCE	0.5 - 30	0.058	[20]
MWCNT-MIP/GCE	0.1 – 30	0.02	this work

3.4. Selectivity of the MWCNT-MIP /GCE

The selectivity of the MWCNT-MIP /GCE was evaluated. For the determination of 10 µM nonylphenol, the concentration of 20 times of hydroquinone, catechol and 100 times of NH_4^+, Mg^{2+}, Na^+, SO_4^{2-} did not affect the determination of nonylphenol. Therefore, the MWCNT-MIP /GCE showed good selectivity in the determination of nonylphenol.

3.5. Real sample analysis

Determination of nonylphenol in real water samples was performed to investigate the applicability of the proposed sensor. Local lake water samples were collected and filtered through a membrane for the electrochemical measurements. After adding 5 and 12 µM nonylphenol to the filtered lake water, the concentrations of nonylphenol were found to be 4.7 and 11.5 µM, respectively. The recovery range from 94% to 95.8%. The RSD for the results was less than 4.8%. The results showed the applicability and reliability of the MWCNT-MIP /GCE for the determination of nonylphenol in real samples.

4. CONCLUSION

In this work, we presented a molecularly imprinted electrochemical sensor, which using acrylamide-functionalized multi-walled carbon nanotubes as carrier, nonylphenol as template molecule, methacrylic acid as functional monomer and ethyleneglycol dimethacrylate as crosslinking agent. The sensor was used for the detection of nonylphenol, and the detection range was 0.1 to 30 µM with a detection limit of 0.02 µM. The proposed sensor was applied for the detection of nonylphenol in lake water with good recovery.

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