Electronic Supplementary Information

From non-electroactive to electroactive species: highly selective and sensitive detection based on dual-template molecularly imprinted electrochemical sensor

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Experimental

1 Chemicals

O-phenylenediamine (OPD) and thionine (TH) were purchased from Sigma-Aldrich Co., LLC. Bensulfuron-methyl (BSM, 98%), terbuthylazine (TB, 98.5%), pyrazosulfuron-ethyl (PSE, 98%), Imidacloprid (IMI, 99.9%), thiacloprid (THI, 98%), and Thiamethoxam (THIM, 99%) were ordered from Aladdin (Aladdin, China). Multi-walled carbon nanotubes (, diameters of 10–30 nm and lengths of 1–2 μm) were purchased from Shenzhen Nanotech Port Co. All other reagents were of at least analytical-reagent grade. And double-distilled deionized water was used for all solutions.

2 Apparatus

Cyclic voltammetry (CV), differential pulse voltammetry (DPV), and Electrochemical impedance spectroscopy (EIS) were performed on CHI 660C workstation (ChenHua Instruments Co., Shanghai, China) with a conventional three-electrode system. A bare or modified glassy carbon electrode (GCE) was served as a working electrode. A saturated calomel electrode and a platinum wire electrode were used as a reference electrode and a counter-electrode, respectively. Field emission scanning electron microscope (FE-SEM) images were obtained on an S-4800 field emission scanning electron microscopy (Hitachi, Japan).

3 Preparation of DMIP/PTH/MWNTs/GCE

The clean GCE was immersed into the carboxyl groups functionalized MWNTs suspension and treated with a constant potential of +1.7 V for 400 s, obtaining the

MWNTs/GCE. poly(thionine) (PTH) modified MWNTs/GCE (PTH/MWNTs/GCE) was prepared by electropolymerizing of 5.0 mmol/L TH in phosphate buffer solution (PBS, 0.1 mol /L, pH 6.0) for 30 cycles with the potential range from -0.4 V to 0.4 V at a scan rate of 50 mV/s. Then PTH/MWNTs/GCE was immersed in a pre-polymerization solution containing the o-phenylenediamine (OPD, 10 mmol/L), bensulfuron-methyl (BSM, 2 mmol/L), and imidacloprid (IMI, 3 mmol/L). The electropolymerization cycles and scan rate were -0.4 V - 0.8 V and 50 mV/s, respectively. Afterwards, the polymer modified electrode was incubated in hydrochloric acid solution (0.5 mol/L) for 15 min to extract the template molecules, which was labeled as DMIP/PTH/MWNTs/GCE. The procedure for the construction of the DMIP/PTH/MWNTs/GCE was illustrated in Scheme 1. As a comparison, non-molecular imprinted polymer (NIP) modified PTH/MWNTs/GCE (NIP/PTH/MWNTs/GCE) was prepared in the same process just in the absence of BSM and IMI.

4 Electrochemical measurements

All electrochemical measurements were performed in PBS (0.1 mol/L, pH 5.0). Chronoamperometry was performed at the potential of 1.7V and the equilibrium time was set at 400s. Selectivity of the sensor was investigated by choosing TB, BSE, THI, and THIM as interferents. Two paddy field water samples were randomly collected from different paddy fields on the outskirts of Wuhu on a same afternoon, which were used as real samples for the detection.

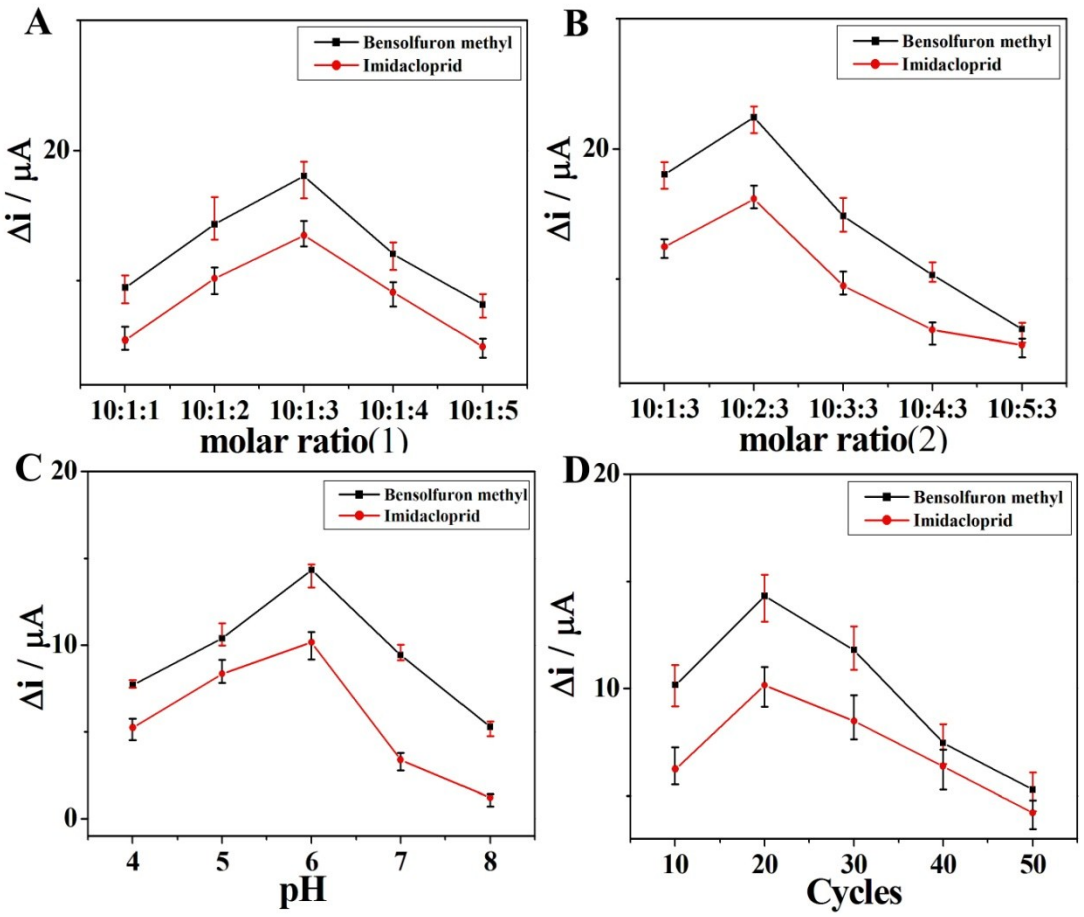

Fig. S1 The optimized condition for the preparation of imprinted sensor (BSM 1×10^{-5}mol L^{-1}, IMI 5.0×10^{-5}mol L^{-1}). (A) The mole ratio between OPD and BSM, (B) the mole ratio between OPD and IMI, (C) the pH value of the pre-polymerization solution, and (D) the electropolymerization cycles for DMIP preparation.

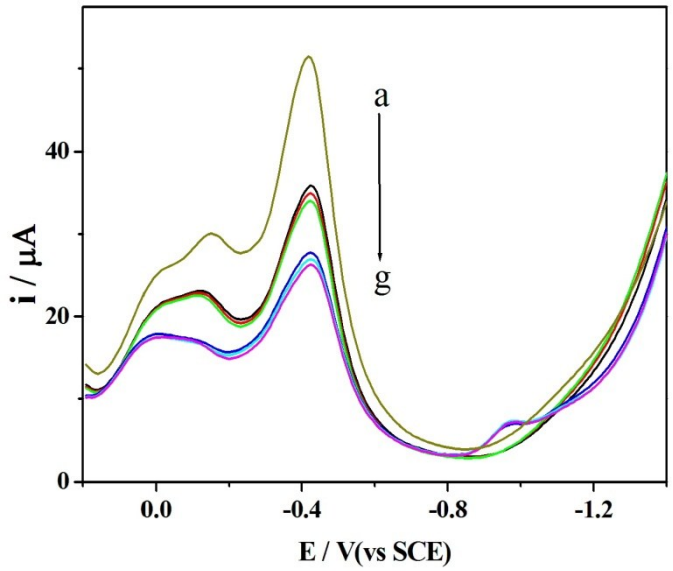

Fig. S2 DPV curves recorded on DMIP/PTH/MWNTs/GCE in (a) blank electrolyte, (b) BSM, (c) BSM and PSE, (d) BSM, PSE, and TB, (e) BSM, PSE, TB, and IMI, (f) BSM, PSE, TB, IMI, and TH, and (g) BSM, PSE, TB, IMI, TH, and THIM. (Concentrations of BSM, PSE, and TB were 1.0×10^{-5} mol/L. Concentrations of IMI, THI, and THIM were 5.0×10^{-5} mol/L.)

Table S1 Comparison of other electrochemical sensors for IMI detection with our work.

Electrochemical sensor	linear range (mol/L)	LOD (mol/L)	Sensitivity (μA/μmol/L)	Reference
tricresyl phosphate-, silicone oil- and n-tetradecane-based carbon paste electrodes	6.6×10^{-6}- 1.2×10^{-4}	-	-	1
nanosilver Nafion®/nanoTiO_2 Nafion® modified GCE	3.0×10^{-7} -3.5×10^{-6}	2.5×10^{-7}	-	2
β-CD polymer/rGO/GCE	5.0×10^{-8} -1.5×10^{-5} 2.0×10^{-5} -1.5×10^{-4}	2.0×10^{-8}	-	3
poly(carbazole)/rGO/GCE	3.0×10^{-6} -1.0×10^{-5}	4.4×10^{-7}	0.0432	4
MIP/rGO/GCE	7.5×10^{-7} -7.0×10^{-5}	4.0×10^{-7}	1.0419	5
GO/GCE	8.0×10^{-7} -1.0×10^{-5}	3.6×10^{-7}	0.8898	6
Nitrogen-doped Graphene/GCE	4.0×10^{-6} -2.0×10^{-5}	5.5×10^{-7}	-	7
Pt-In nanocomposite/MIP/GCE	2.0×10^{-10} -5.0×10^{-8}	1.2×10^{-11}	448	8
GO/GCE	1.0×10^{-5} -2.0×10^{-4}	7.9×10^{-6}	0.38	9
electrochemically pretreated boron-doped diamond electrode	3.0×10^{-5} -2.0×10^{-4}	8.6×10^{-6}	-	10
MIP/PTH/MWCNTs/GCE	1.0×10^{-7} -1.0×10^{-4}	6.5×10^{-8}	0.1592	This work

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Table S2 Application of DMIP/PTH/MWNTs/GCE to determine BSM and IMI in paddy field water.

samples		Added ($\times 10^{-6}$ mol/L)	Detected content by the sensor[a] ($\times 10^{-6}$ mol/L)	Recovery (%)	RSD (%)
1	BSM	0.5	0.47	94.60	3.8
	IMI	1.0	1.04	104.5	2.0
2	BSM	1.0	1.02	102.9	2.3
	IMI	10.0	9.64	96.40	3.1

[a] Average value of three determination