Supplementary materials

An electrochemical aptasensor based on Co_xP decorated porous carbon microspheres and AuNRs labelled methylene blue as signal labels for sensitive detection of PCB77

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Reagents and Materials

3,3′,4,4′-PCB (PCB77), 2,3′,4,5-PCB (PCB67), 2,2′,3,3′,4-PCB (PCB82), 2,3,3′,4,4′,5,5′-PCB (PCB189), 2,3,3′,4,4′,5′,6-PCB (PCB191) were purchased from American Accustandard Reagent Co., Ltd. (USA). Zinc nitrate hexahydrate, 2-methylimidazole, Cobalt nitrate hexahydrate, sodium dihydrogen phosphate dihydrate and Chloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$) were purchased from Aldrich Industrial Co., Ltd (Shanghai, China). Cetyltrimethylammonium bromide (CTAB), Methylene blue (MB), Tris (2-carboxyethyl) phosphine hydrochloride solution (TCEP), 6-Mercapto-1-hexanol (MCH) were purchased from Shanghai Yuanye Bio-Technology Co., Ltd. (Shanghai, China). Potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) and Potassium ferricyanide ($K_3Fe(CN)_6$) were purchased from Tianjin Guangfu Technology Development Co., Ltd. (Tianjin, China).

During this experiment, cyclic voltammetry (CV) was implemented at a scan rate of 0.1 $V \cdot s^{-1}$ in a solution containing 10 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ and 0.1 M KCl. Electrochemical impedance spectroscopy (EIS) was carried out at frequencies from 0.1 Hz to 100 kHz with a 5 mV amplitude signal in 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ containing 0.1 M KCl. Differential pulse voltammetry (DPV) measurement was performed from -0.6 to 0.1 V with an amplitude of 50 mV and pulse width of 50 ms in 10 mM Tris-HCl. Tris-HCl buffer (10 mM, 1 mM EDTA, pH 7.4) was used as the stock solutions of the oligonucleotides. Potassium ferricyanide solution by mixing 10 mM of $K_3[Fe(CN)_6]$, 10 mM of $K_4Fe(CN)_6 \cdot 3H2O$, and 0.1 M of KCl. All other chemicals were of analytical reagent grade and were used without further purification.

Apparatus

Electrochemical measure was carried out on CHI760E Electrochemical Workstation (Shanghai CH Instrument Co., Ltd., China). All measurements were conducted by using a conventional three-electrode cell containing a 3 mm-diameter Au working electrode, a platinum counter electrode and a saturated calomel reference electrode.

All samples were studied with X-ray diffraction (XRD, CuKα radiation, D/max 2550VB X-ray diffractometer, Rigaku, Japan), Scanning electron microscopy (SEM, Hitachi, Japan) and

Transmission electron microscope (TEM, HT7700, Hitachi, Japan). Aptasensor was incubated by constant temperature and humidity chamber (Shanghai Yiheng Technology Instrument Co., Ltd., China).

Synthesis of ZIF-67

The synthesis of ZIF-67 was modified based on previous literatures.[1] In a typical synthesis, two solutions were first prepared by dissolving 1 mM of $Co(NO_3)_2 \cdot 6H_2O$ and 4 mM of 2-methylimidazole in 25 mL of methanol. Then, the solution of 2-methylimidazole was quickly poured into the solution of $Co(NO_3)_2$ and the resultant mixed solution were stirred evenly for 30 min and aged for 24 h at room temperature. The purple precipitate was centrifuged (5000 rpm, 10 min) and washed several times with methanol. And finally, we collected the purple precipitate after that it is filted and dried at 60 °C for 6 h.

Synthesis of $Zn(PO_4)_x$, $Zn(PO_4)_x$@ZIF-67

The synthesis of $Zn(PO_4)_x$, $Zn(PO_4)_x$@ZIF-67 are based on the previous literature.[2] Briefly, 1.2 mM of zinc nitrate hexahydrate and 0.2 mM of sodium dihydrogen phosphate dihydrate were dissolved ultrasonically in 40 mL of DMF. And then the mixed solution was transferred into a Teflon autoclave at 100 °C for 12 h. After cooling to room temperature, white powder $Zn(PO_4)x$ was collected by washing with anhydrous ethanol, and then drying at 60 °C for 6 h.

The composite precursor was obtained by in-situ growth of Co-based zeolite imidazolate skeleton ZIF-67 on the $Zn(PO_4)_x$ microspheres. Firstly 0.55 g of our previously prepared $Zn(PO_4)_x$ powder and 3.84 g of cobalt nitrate hexahydrate were dissolved into 220 mL of anhydrous methanol under magnetic stirring to form a Solution A. Concurrently, 4.33 g of 2-methylimidazole was dissolved in 220 mL of anhydrous methanol under magnetic stirring to form a Solution B. Then, Solution B was quickly poured into solution A and stirred vigorously at room temperature for 2 hours. After centrifugation, washing and drying, light purple $Zn(PO_4)_x$@ZIF-67 was obtained from the above mixed solution.

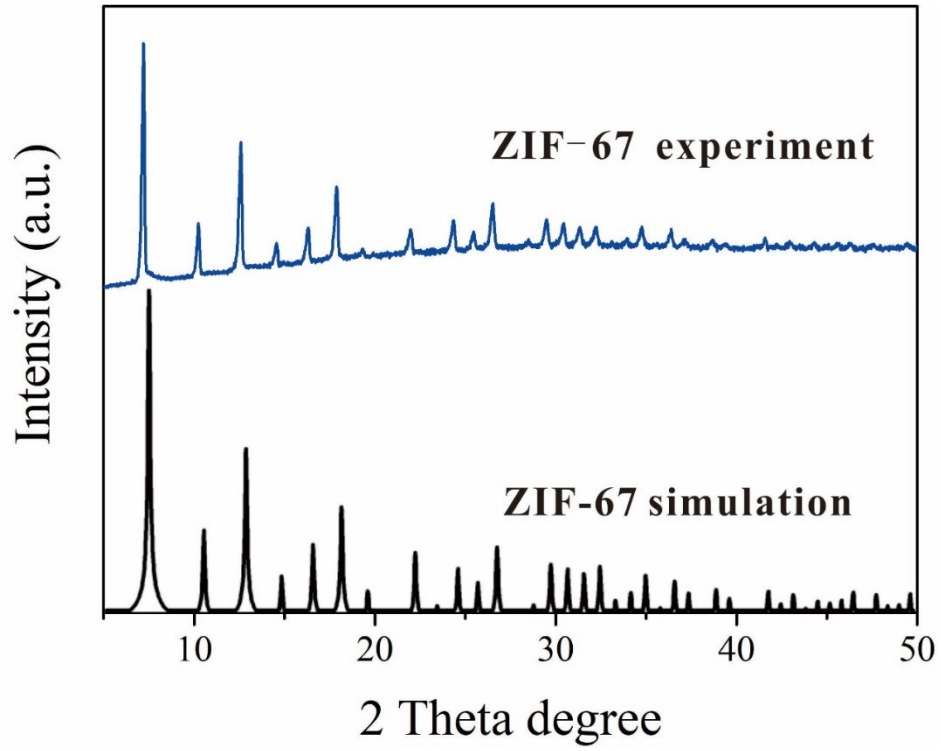

Fig. S1. XRD pattern of the precursor ZIF-67 and the simulated ZIF-67.

Detection limit calculation

In this work, The limit of detection (LOD) was calculated according to IUPAC recommendation(IUPAC 1976), the analyte's signal at the detection limit (Sdl) is given by:

$$Sdl = Sreag + k * \sigma reag,$$

Sreag is the electrochemical signal for a blank, σreag is the known standard deviation for the blank's electrochemical signal (n=10).

k is a numerical factor chosen according to the confidence level desired. (The k value of this experiment is 3)

The electrochemical signal response values (I) used to calculate LOD were presented in Table. S1. The limit of detection is calculated as 0.059 $ng \cdot L^{-1}$ by the above data, formula and calibration curves.

Table S1 The electrochemical signal response values (I) of the zero-dose for ten times

Number	*I* (-μA)	Average	SD	RSD (%)
1	12.18			
2	10.90			
3	11.32			
4	10.05			
5	10.43			
6	11.24	11.02	0.661076	6.00
7	10.62			
8	10.37			
9	11.04			
10	12.02			

Supporting information references

1 H. Hu, B. Guan, B. Xia and X. W. Lou, *J. Am. Chem. Soc.*, 2015, **137**, 5590-5595.

2 L. Xiao, R. Xu and F. Wang, *Talanta*, 2018, **179**, 448-455.