Supplementary Material

A Multifunctional Core-Shell $CoFe_2O_4$@ZIF-67 Nanocomposite for Simultaneous Detection and Removal of Pb^{2+} in Water

Yingying Wang[a#], Tengda Zhao[a#], Wei Yin[ac], Zhuoxun Liu[a], Shijuan Tian[d], Li zhang[a], Sha Sha[d], Hongling Zhou[a], Huanbao Fa[ab*] , Hang Li[d*], Gang Li[e] , Yuqin Xu[f]

a School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China

b National-Municipal Joint Engineering Laboratory for Chemical Process Intensification and Reaction, Chongqing University, Chongqing 400044, China

c Analytical and Testing Center of Chongqing University, Chongqing 400044, China

d Food Safety Inspection Technology Center of Administration for Market Regulation of Sichuan Province, Chengdu 610014, China

e Food and Drug Inspection and Testing Center of Meishan City, Meishan 620000 , China

f Sichuan Jingwei Food Detection Technology Co.Ltd, Meishan 620010 , China

# These authors contributed equally to this work and should be considered co-first authors

* Corresponding authors.

E-mail addresses: huanbaofa@cqu.edu.cn (H. Fa), LiHang800125@163.com

Telephone:+86 13228612804 (H. Fa) , 13281486301(LiHang)

Fax: +86 023 65678951.

Contents

S1 Experimental section

S1.1Materials and Reagents

All chemicals were of analytical grade and used without further purification. Cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$), ferric chloride hexahydrate ($FeCl_3·6H_2O$), 2-methylimidazole ($C_4H_6N_2$), lead nitrate ($Pb(NO_3)_2$), and Nafion perfluorinated resin solution (5 wt%) were purchased from xxx.

S1.2 Synthesis of $CoFe_2O_4$ Nanoparticles

The $CoFe_2O_4$ magnetic nanoparticles were synthesized via a co-precipitation method. Briefly, solutions of $Co(NO_3)_2·6H_2O$ and $FeCl_3·6H_2O$ (molar ratio 1:2) were mixed under vigorous stirring, the stirring speed is 600 rpm. The pH of the mixture was adjusted to 11-12 using 2mol/L NaOH solution, followed by heating at 80°C for 2 h. The resulting precipitate was collected magnetically, washed thoroughly with ultrapure water and ethanol, and dried in a vacuum oven at 60°C.

S1.3 Synthesis of Core-shell $CoFe_2O_4$@ZIF-67 Nanocomposite

The $CoFe_2O_4$@ZIF-67 composite was prepared through an in-situ growth method. The as-synthesized $CoFe_2O_4$ nanoparticles were dispersed in 50ml methanol by ultrasonication. Then add 7.0g of 2-methylimidazole to the methanol solution and stir for 30 minutes at a stirring speed of 800 rpm. Subsequently, 3.0g of $Co(NO)_3·6H_2O$ was added to the methanol solution, and the mixture was stirred at room temperature for 1 h. Transfer the evenly mixed reaction solution to a PTFE lined reactor and react for 135 minutes at 75 °C .The final product, $CoFe_2O_4$@ZIF-67, was separated by a magnet, washed with methanol, and dried overnight.

S1.4 Fabrication of the Modified Electrode

The glassy carbon electrode (GCE, 3 mm diameter) was sequentially polished with 0.3 and 0.05 μm alumina slurry, followed by sonication in ethanol and water. To prepare the modified electrode, 2 mg of $CoFe_2O_4$@ZIF-67 composite was dispersed in 1 mL of Nafion solution (0.5% in ethanol) by sonication. Then, 6 μL of this suspension was drop-cast onto the clean GCE surface and allowed to dry at room temperature, forming the $CoFe_2O_4$@ZIF-67/Nafion/GCE sensor.

S1.5 Characterization and Measurements

The morphology and elemental composition were characterized by scanning electron microscopy (SEM, Hitachi SU8220) equipped with an energy-dispersive X-ray spectrometer (EDS). Crystal structures were determined by X-ray diffraction (XRD, Bruker D8 Advance). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS50 spectrometer. Magnetic properties were measured using a vibrating sample magnetometer (VSM, LakeShore 7404). Nitrogen adsorption-desorption isotherms were obtained on a Micromeritics ASAP 2460 analyzer. Electrochemical measurements were performed on a CHI760E electrochemical workstation. Adsorption experiments were conducted in batch mode, and the Pb^{2+} concentration was quantified using inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Avio 500).

S2 EDS and Elemental Mapping

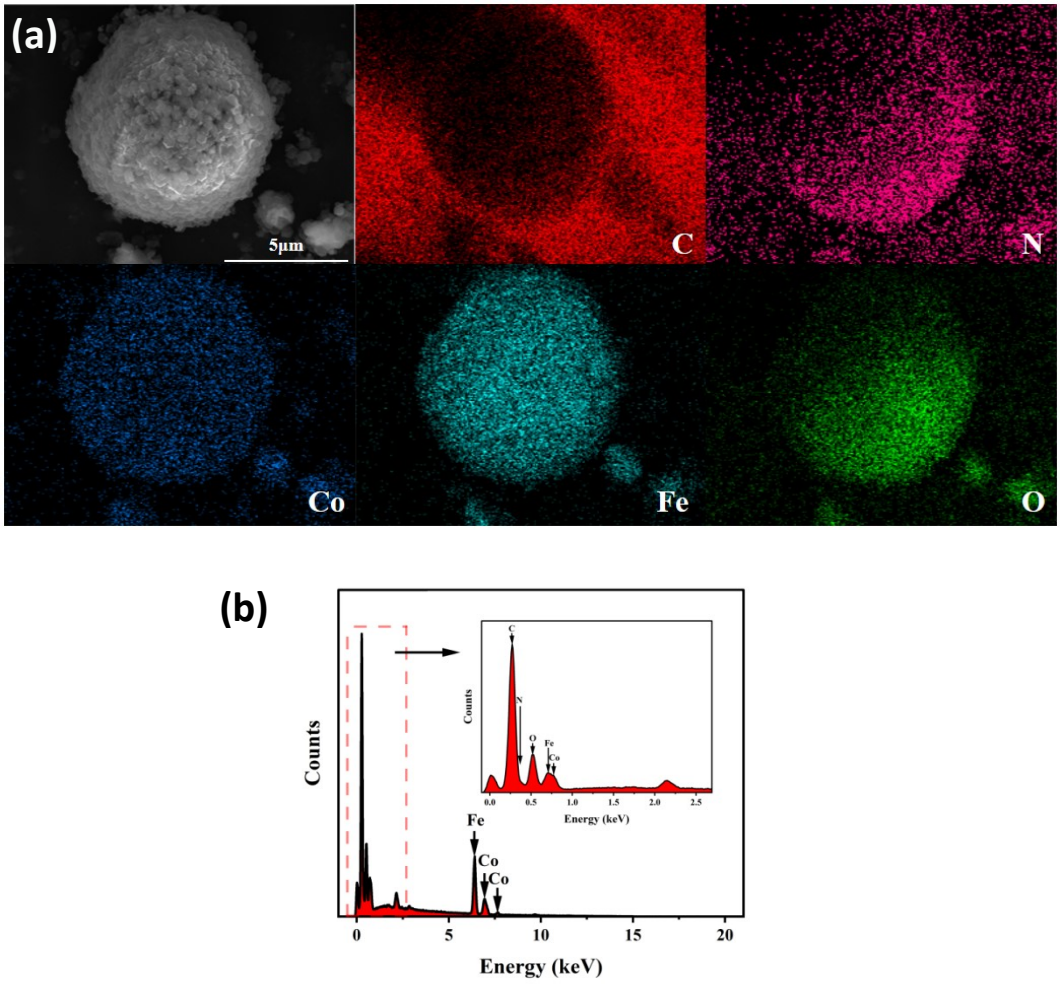


Fig.S1The energy dispersive X-ray image: (a) The energy dispersive X-ray image of $CoFe_2O_4$@ZIF-67; (b) EDS element mappings

Table S1. Element weight and atomic percentage

Element	Weight percentage	Atomic percent
C	55.23	72.40
O	12.65	12.45
Fe	18.50	5.21
Co	6.27	1.67
N	7.36	8.27
Total	100.00	100.00

S3 BET

Table S2 The aperture parameters of the material

material	specific surface (m^2/g)	pore volume (cm^3/g)	Average Pore diameter (nm)
ZIF-67	1647.54	0.72	1.76
$CoFe_2O_4$@ZIF-67	309.32	0.14	1.90

S4 VSM

Table S3 Room-temperature hysteresis loop parameters

material	$CoFe_2O_4$	$CoFe_2O_4$@ZIF-67
saturation magnetizationMs (emu/g)	51.12	43.86
coercivityHc (Oe)	685.30	718.90
remanenceMr (emu/g)	16.74	14.06

S5 Optimization of Experimental Parameters

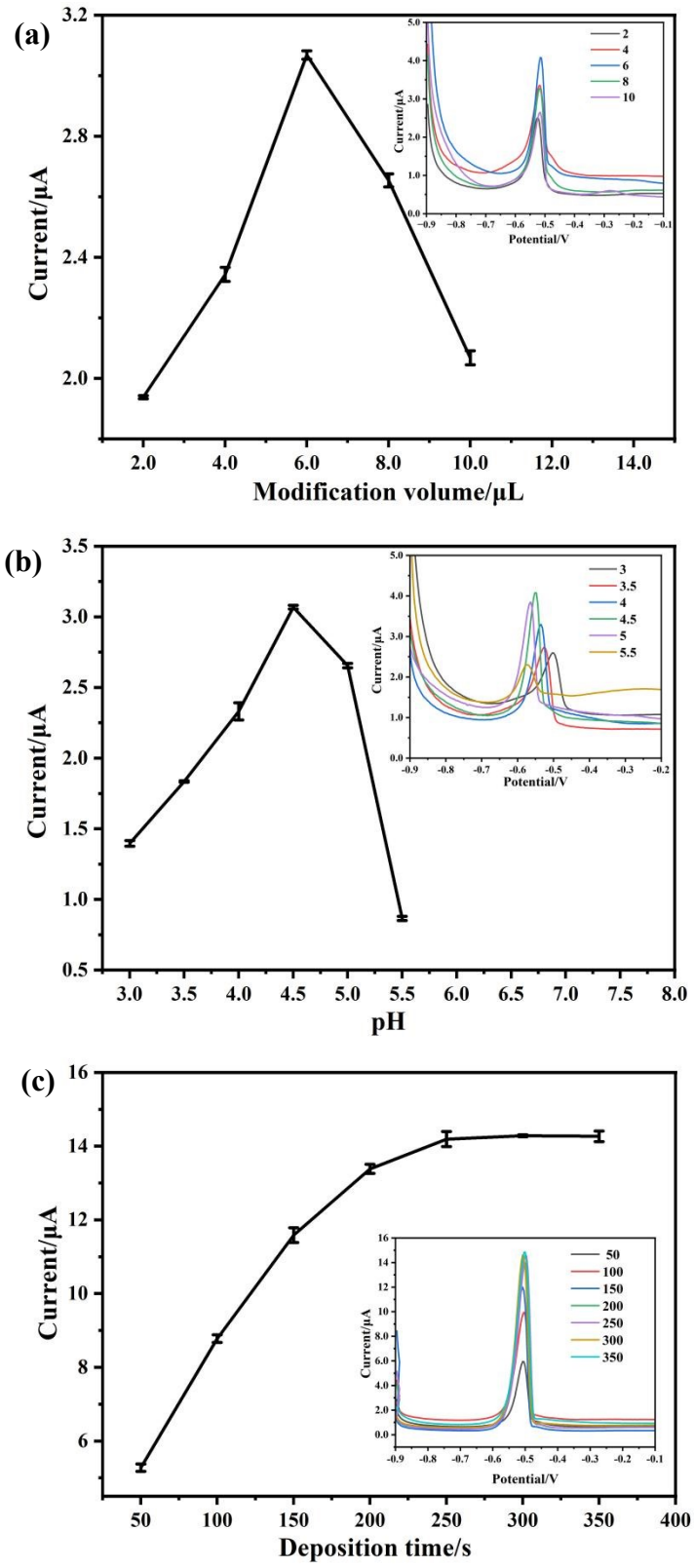


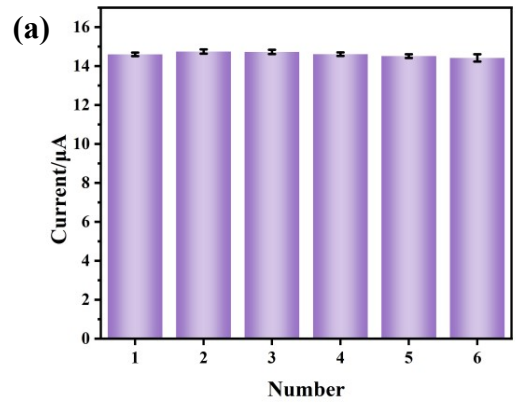
Fig.S2 (a) $CoFe_2O_4$@ZIF-67 The effect of coating amount on the current response of Pb^{2+}(b) The influence of pH on the current response of Pb^{2+}(c) The influence of sedimentation time on the current response of Pb^{2+}

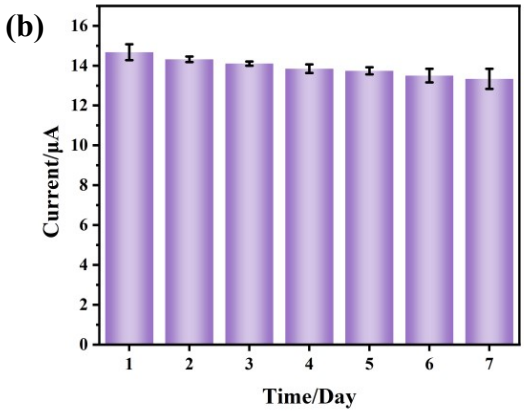
S6 Comparative Analysis

Table S4 Performance comparison of different modified eletrodes for detection of Pb^{2+}

modified electrode	linear range (μM)	sensitivity (μA·mM^{-1}·cm^{-2})	detection limit (μM)	Ref.
$NiCo_2O_4$/GCE	0.2-1.2	26.11	0.0890	32
$MnFe_2O_4$/GO/GCE	0.2-1.1	33.90	0.0883	33
$[Ru(bpy)_3]^{2+}$-GO Au GCE	0.05-0.25	24.12	0.3500	34
$CoMn_2O_4$/CNT/GCE	0.01-0.85	-	0.0040	35
Ni-MOF-modified GCEs	0.5-6	-	0.5080	36
$CoFe_2O_4$@ZIF-67/GCE	0.01-40	32.17	0.0093	This work

S7 Repeatability, Stability, and Anti-interference Ability





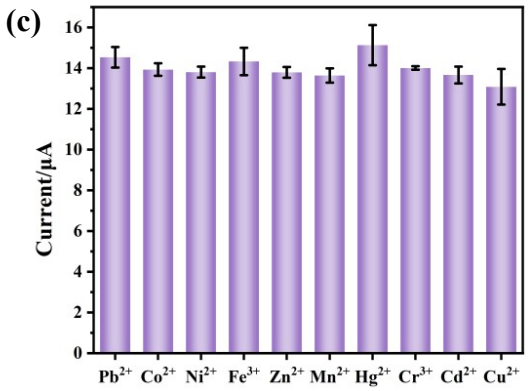
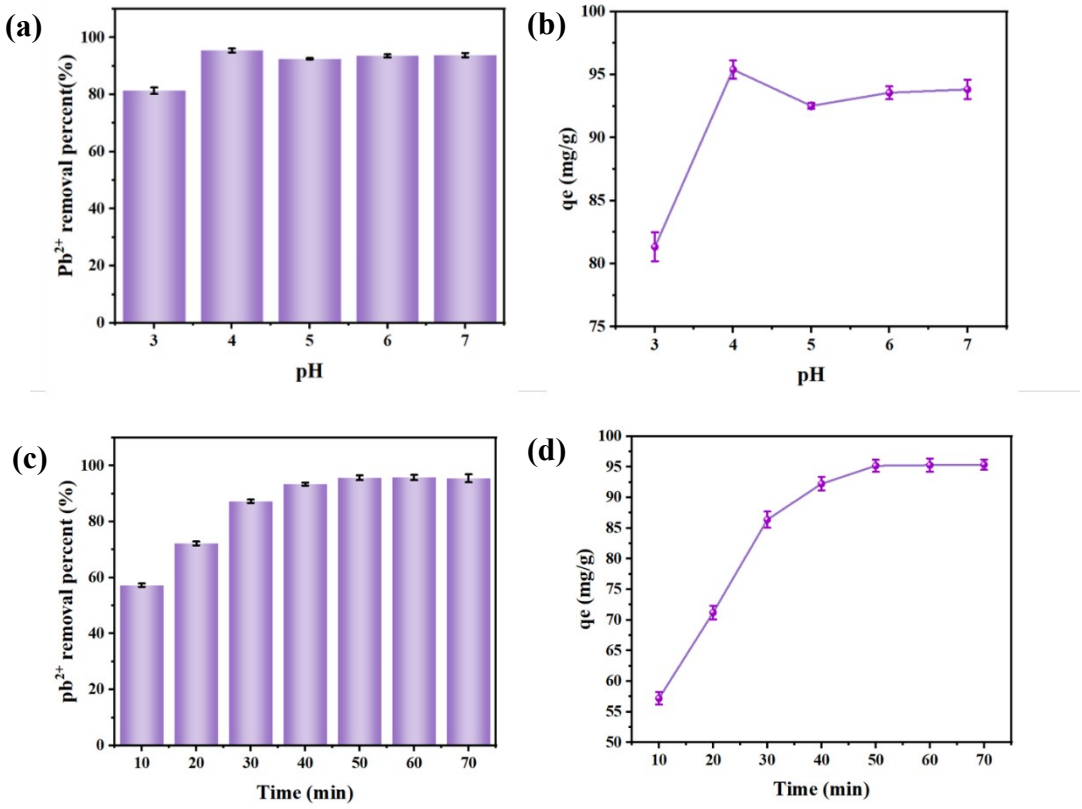


Fig. S3 Reproducibility (a), Stability (b) and Anti-interference (c) of $CoFe_2O_4$@ZIF-67/nafion/GCE

S8 Optimization of Adsorption Conditions



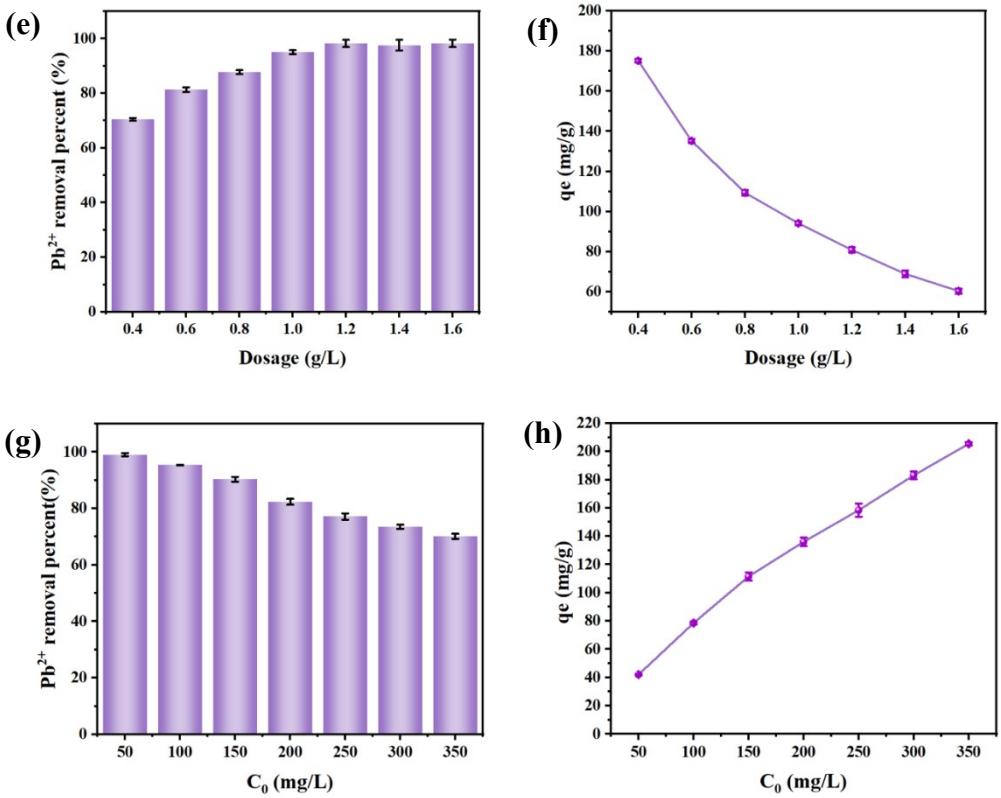


Fig. S4 Removal rates (a) and adsorption capacity (b) of different pH，Removal rates (c) and adsorption capacity (d) of different adsorption time，Removal rates (e) and adsorption capacity (f) of different dosage，Removal rates (g) and adsorption capacity (h) of different initial concentration