Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Construction of a label-free electrochemical immunosensor based on Co_9S_8/Co_3C@C dual-heterojunction for the detection of diethylstilbestrol

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Reagents

The glassy carbon electrode (GCE) was acquired from Xuzhou Xinke Instrument Co. Ltd., China. The silver/silver chloride electrode (Ag/AgCl) and platinum electrode (Pt) were gained from Wuhan Gaoss Union Co. Ltd., China. Prostate-specific antigen (PSA), carcinoembryonic antigen (CEA), alpha-fetoprotein (AFP), serum components (glucose, dopamine, and ascorbic acid), diethylstilbestrol (DES) antigen and DES antibody were collected from Saiao Biotechnology Co. Ltd., (Shanghai, China). Thioglycollic acid (TGA) were obtained from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China). Bovine albumin (BSA), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) were obtained from Aladdin Reagent Database Inc. (Shanghai, China). Cobalt(II) nitrate hexahydrate $Co(NO_3)_2 \cdot 6H_2O$ and dimethylimidazole were also purchased from Aladdin Reagent Co., Ltd. $Na_2S \cdot 9H_2O$ was obtained from Shanghai McLean Biochemical Technology Co., Ltd.

Apparatuses

All pelectrochemical measurements and electrochemical impedance spectroscopy (EIS) analysis were performed on a CHI760D electrochemical workstation (Chenhua Instrument Shanghai Co., Ltd., China). Transmission electron micrographs (TEM) were measured on an H-800 microscope (Hitachi, Japan). X-ray diffraction (XRD) patterns were obtained by using D8 focus diffractometer (Bruker AXS, Germany). The Tecnai G2 F20 microscope (America) has been employed to perform high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS). And the ESCALAB 250XI detected the X-ray photoelectron spectroscopy (XPS).

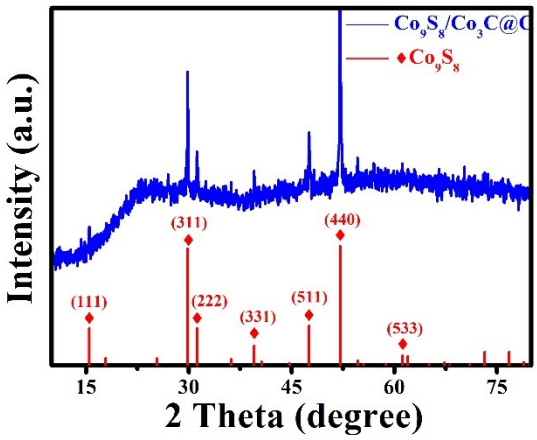

Figure S1 XRD patterns of synthesized $Co_9S_8/Co_3C@C$

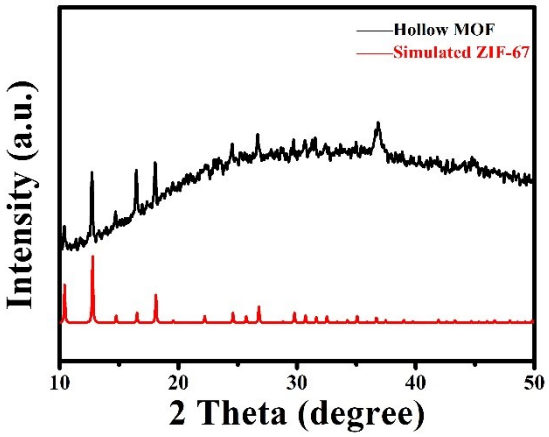

Figure S2 XRD result of hollow MOF.

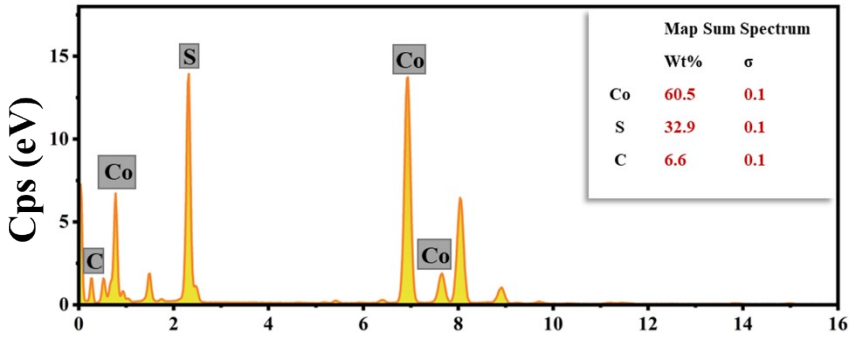

Figure S3 HAADF-STEM image and corresponding elemental mappings.

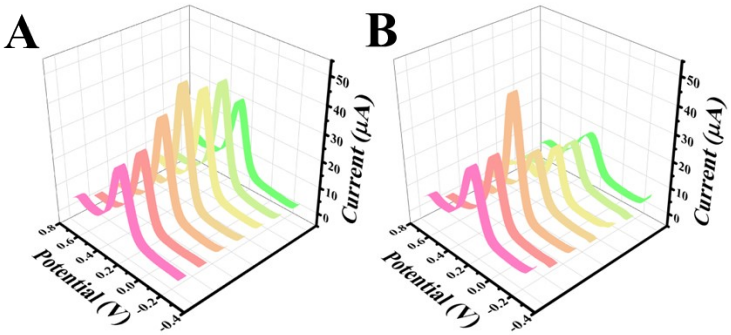

Figure S4 Optimization of experimental conditions with (A) Co_9S_8/Co_3C@C and (B) pH on the response of the immunosensor to 1.2 ng/mL DES.

Table S1 Simulation parameters of the equivalent circuit components.

Electrode	R_s, Ω	R_{ct}, Ω	C_{dl}, F	Warburg, Yo, S·sec^5
GCE	55.81	116	5.603×10^{-6}	0.0001881
GCE/CC	33	567.7	5.725×10^{-6}	0.001624
GCE/CC/Ab	38.14	1175	4.908×10^{-6}	0.0008404
GCE/CC/Ab/BSA	58.47	1734	4.71×10^{-6}	0.0005067
GCE/CC/Ab/BSA/DES	45.92	2000	4.456×10^{-6}	0.0003183

Table S2 The developed immunosensors for detecting DES compared to other published immunosensor.

Materials	Detection method	Linear range (ng/mL)	LOD (fg/mL)	Reference
MIP-CdSe/CdS/ZnS QDs	Fluorescence	50~2×10^4	4×10^3	[1]
$Cu_3(BTC)_2$-Ag NPs	Electrochemical immunosensor	500~5000	1.67×10^3	[2]
AuNPs	Competitive immunoassay	16~500	1.3×10^7	[3]
Au/UiO-66(NH_2)/CdS	Photoelectrochemical immunosensor	1×10^{-4}~20	60	[4]
CdTe NC/rGO	Electrochemiluminescence	0.002~2	1×10^3	[5]
DIB-Cl	HPLC-FLD	1.5~300	5×10^5	[6]
This work	Electrochemical immunosensor	0.000384~6	3.24	

Table S3 Reproducibility result of the immunoassay for 1.2 pg/mL of DES.

Methods	Found (ng/mL)	Average (ng/mL)	RSD (n = 5, %)	Variance (s^2)
DPV	47.40, 47.00, 48.75, 49.68, 48.39	48.24	2.22	0.92

The results were showed in Table S3, and the RSD of the method is less than 5.0%. The results implied that the variance of the DPV method results performed a good degree of precision and indicating the system error can be ignored.

References

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