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Supplementary information

Electrochemiluminescence Sensor Based on Ag/ZnO Nanomaterial-Enhanced GPTMS/FeCdS@FeIn₂S₄ for Sensitive Analysis of CD44

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Materials.

InCl₃, 3-glycidoxy propyl trimethoxy silane (GPTMS), FeSO₄·7H₂O, 2-Methylimidazole, and Zn(NO₃)₂·6H₂O were purchased from Macklin Reagent Co., Ltd. (Shanghai, China). Ethanol was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Cd(CH₃COO)₂, AgNO₃, bovine serum albumin (BSA), and thioacetamide (TAA) were purchased from Aladdin Reagent (Shanghai, China). CD44 and anti-CD44 antibodies were purchased from Lin's Biotechnology Co., Ltd., Shanghai. All of the above chemicals are analytical reagent grade and can be used without further purification. Phosphate buffered solution (PBS) was prepared by using 1/15 M Na₂HPO₄ and 1/15 M KH₂PO₄ solution. 2.5 mM K₃Fe(CN)₆/K₄Fe(CN)₆ and 0.1 M KNO₃ solution were used as electrolyte for electrochemical impedance spectroscopy (EIS). Ultrapure water (18.25 MΩ cm, 24 °C) was used for all the experiments.

Apparatus.

Scanning electron microscope (SEM) images were obtained using a field emission SEM (Zeiss, Germany). morphological feature of the sample was observed using a JEM 2100F high-resolution transmission electron microscope (HRTEM, JEOL, Japan) Electrochemical impedance spectroscopy (EIS) measurements were performed using IM6e Electrochemical Interface (Zahner, Germany). UV-Vis absorbance spectra and diffuse reflectance ultraviolet-visible light spectra (DRS) were obtained on a UV-vis spectrophotometer (Cary 500 Scan Spectrophotometers, Varian, and U.S.A). The UV-vis absorption was characterized by TU-1909 spectrophotometer (Beijing Puxi Instrument Co., Ltd., China). X-ray photoelectron spectroscopy (XPS) measurements were performed with Axis Supra (Shimadzu, Japan). Fluorescence (FL) spectra were collected on a LS-45/55 PL spectrometer (PerkinElmer, America). X-Ray Powder Diffraction (XRD) was performed with D8 advance X-ray diffractometer (Bruker AXS, Germany). Fourier transform infrared spectroscopy (FTIR) was recorded on a VERTEX 70 spectrometer (Bruker, Germany). The ECL measurements were performed using an MPI-F flow-injection chemiluminescence detector (Xi'an Remax Electronic Science Tech.Co.Ltd., China) with the voltage of the photomultiplier tube (PMT) set at 700 V in the detection process. In this work, a three-electrode system was used to test the immunosensor system, which Ag/AgCl as reference electrode, platinum electrode as counter electrode, and the electrode with different modification states as working electrode.

SEM images of materials.



Fig. S1 SEM images of (A) FeCdS, (B) FeIn₂S₄

EDS pattern of FeCdS@FeIn₂S₄.



Fig. S2 EDS pattern of FeCdS@FeIn₂S₄

XPS gross spectrum of FeCdS@FeIn₂S₄.



Fig. S3 XPS gross spectrum of FeCdS@FeIn₂S₄

EDS pattern of Ag/ZnO.



Fig. S4 EDS pattern of Ag/ZnO

XPS spectra of Ag/ZnO.



Fig. S5 XPS spectra of Ag/ZnO (A) total spectrum; (B) Ag 3d spectrum; (C) Zn 2p spectrum; (D) O 1s spectrum

Fluorescence emission spectrum and UV absorption spectrum.



Fig. S6 (a) Fluorescence emission spectrum of Ag/ZnO, (b) UV absorption spectrum of FeCdS@FeIn₂S₄

Optimization of conditions for ECL immunosensor.



Fig. S7 (A) FeCdS@FeIn₂S₄ concentration, (B) Ag/ZnO concentration, (C) K₂S₂O₈ concentration, (D) pH of PBS

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Electrode	$R_s(\Omega)$	$R_{\text{et}}(\Omega)$	$C_{d1}(F)$	$Z_{\rm w}$
GCE	30.94	127.7	5.918×10-4	0.001151
GCE/Ag/ZnO	38.46	185.6	5.634×10 ⁻⁴	0.001214
GCE/Ag/ZnO/Ab ₁	66.77	591.7	4.211×10 ⁻⁶	0.002033
GCE/Ag/ZnO/Ab ₁ /BSA	78.07	1299	3.999×10-6	0.001671
GCE/Ag/ZnO/Ab ₁ /BSA/CD44	178.8	1854	6.041×10 ⁻⁶	0.001684
GCE/Ag/ZnO/Ab ₁ /BSA/CD44/GPTMS/FeCdS@ FeIn ₂ S ₄ -Ab ₂	52.18	2734	6.052×10-6	0.001374

Equivalent circuit component simulation parameters.

Table S1 Analogue parameters of equivalent circuit originals

other detection methods				
Detection method	Linear range	Detection limit	Defenences	
	(ng/mL)	(fg/mL)	Kelefences	
FL	0~100	35	1	
EC	$0.5 \sim 500$	1400	2	
ECL	$0.002\sim 250$	1000	3	
ECL	$0.1 \sim 1000$	79200	4	
ECL	$0.00001 \sim 100$	0.00916	This work	

Table S2 Comparison of the performance of the constructed immunosensor with

Comparison for the performance of the proposed and referenced methods.

Detection	of	CD44	in	human	serum.
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	Added	Detected (ng	Recovery	RSD
Samples (ng/mL)	(ng/mL)	/mL)	(%)	(%, <i>n</i> = 11)
1.5	0.5	1.98	96.00	2.6
	1.34	2.88	102.99	3.4
	2.5	4.06	102.40	1.5
	3.66	5.11	98.63	4.6
2.5	1.25	3.71	96.80	2.4
	2.44	4.98	101.64	3.7
	3.65	6.1	98.63	2.3
	4.5	6.89	97.56	4.3

Table S3 Detection of CD44 in human serum

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