1 **Supplementary Information**

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3 **A quenching electrochemiluminescence energy resonance**

4 **transfer system based on CdS and COFs for ultrasensitive**

5 **detection of CA242**

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Additional experimental section

CA242, anti-CA242, and other cancer antigens used in this work were bought from Shanghai Linc-Bio Science Co. Ltd. 2,5-dimethoxyterephaldehyde (DMTP) and 1,3,5-Tris(4-aminophenyl) benzene (TAPB) were obtained from Anhui Zesheng Technology Co., Ltd., Cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$), sodium suifide 9-hydrate ($Na_2S \cdot 9H_2O$), Tris (2-carboxyethyl) phosphine hydrochloride (TCEP) (3-aminopropyl) triethoxysilane were obtained from Shanghai Macklin Biochemical Technology Co., Ltd. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS) and Bovine serum albumin (BSA, 96-99%) were obtained from Shanghai Aladdin Biochemical Technology Co.Ltd. Phosphate buffer solution (PBS, 0.1 mol/L KH_2PO_4, and 0.1 mol/L Na_2HPO_4) was used during the electrochemical measurements.

X-ray diffraction (XRD) patterns were performed with D8S-3 advance X-ray diffractometer (Bruker AXS, Germany), transmission electronmicroscopy (TEM) images were taken by Tecnai G2 F20S-TWIN transmission electron microscope (Field Electron and Ion Co., United States). Scanning electron microscopy (SEM) images were taken by Quanta FEG250 field emission environmental electron microscope (Field Electron and Ion Co., United States). The F-4500 fluorescence spectrophotometer (Japan) was used to complete fluorescence emission spectrum. The electrochemical data were obtained by using CHI-660 electrochemical analyzer in standard three-electrode system with a glassy carbon electrode (GCE, diameter 4 mm) as the working electrode, The fluorescence emission spectrum was measured by F-380 fluorescence spectrophotometer. All the chemical reagents were analytical grade and were directly used without further purification.
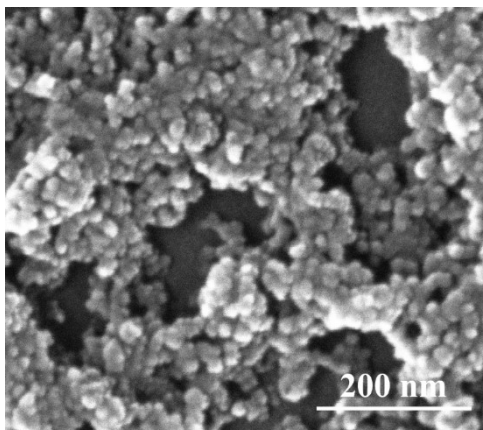
Characterization of CdS NCs

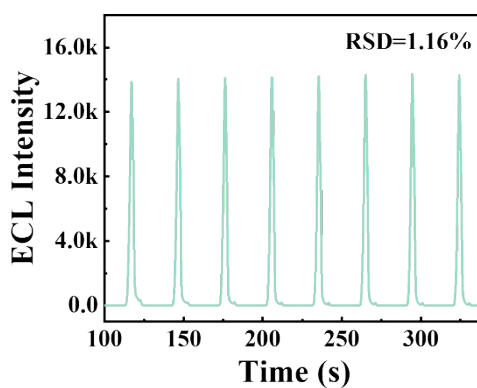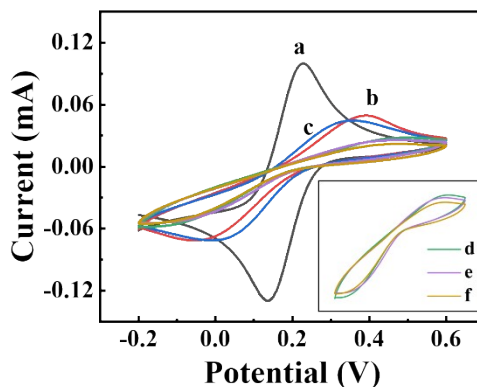**Fig. S1.** SEM image of CdS NCs.

ECL stability of CdS/GCE

Fig. S2. The CdS/GCE continuous scanned for 8 cycles in PBS containing 40 mM H_2O_2.
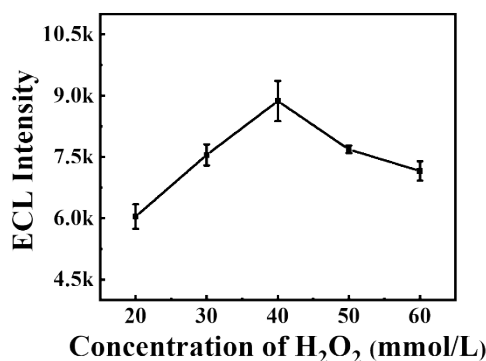
Electrochemical characterization of the immunosensor

Fig. S3. (B) CV of (a) bare GCE, (b)CdS/GCE, (c) Ab1/CdS/GCE, (d) BSA/Ab1/CdS/GCE, (e) CA242/BSA/Ab1/CdS/GCE, (f) Ab2-

67   COFs/CA242/BSA/Ab1/CdS/GCE.

68   **Optimization experiments**

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70   **Fig. S3.** The optimizations of H_2O_2 concentration.

71   **Limit of detection**

72   The limit of detection can be calculated by a most common way and the equation

73   as follow[1]:

74    $$X_L = X_{b1} + kS_{b1},$$

75   where X_L is derived from the smallest measure, X_{b1} is the mean of the blank

76   measures, S_{b1} is the standard deviation of the blank measures and k is a numerical factor

77   chosen according to the confidence level desired. A value of 3 for k in equation is

78   strongly recommended, and it usually corresponds to a confidence level of about 90%

79   in a practical sense. The values for X_L and S_{b1} cannot usually be determined from theory

80   but must be found experimentally by making a sufficiently large number of

81   measurements. In this work, after making twenty ECL measurements of blank, the X_{b1}

82   = 10798.6 and S_{b1} = 66.3 was calculated. According to $X_L = X_{b1} + 3S_{b1}$, the X_L =

83   10997.5 was obtained, and the fitting equation of this proposed biosensor is I = 8185.75

84   - 752.41×lg c. Thus, the LOD of this proposed biosensor is $c_L = 10^{(10997 - 8185.75)/(-752.41)}$

85   ≈ 0.000183 U/mL.

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92 **Table S1.** Comparison of different methods for the detection of CA242

Detection method	Linear range(U/mL)	Limit of Detection(U/mL)	Reference
Electrochemical biosensor	0.01-100	20	2
Electrochemical biosensor	0.001-10000	0.0015	3
AlphaLISA	0.16-400	0.16	4
Electrochemiluminescence biosensor	0.005-100	0.0019	5
Electrochemical biosensor	1-150	0.04	6
Electrochemiluminescence biosensor	0.001-1000	0.000537	7
Electrochemiluminescence biosensor	0.001-1000	0.000183	this work

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94 **Table S2.** The recovery analysis results (bovine serum sample).

Concentration of CA242 in the sample (U/mL)	The addition (U/mL)	The detection (U/mL)	RSD (%, n=3)	Recovery (%)
0.55	1	1.73, 1.56, 1.52	6.9	105.4
	2	2.33, 2.59, 2.46	5.3	95.6
	3	3.41, 3.71, 3.91	3.0	104.0

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96 **Table S3.** The recovery analysis results (human serum sample).

Concentration of CA242 in the sample (U/mL)	The addition (U/mL)	The detection (U/mL)	RSD (%, n=3)	Recovery (%)
0.55	1	1.53, 1.61, 1.48	4.3	99.3
	2	2.54, 2.29, 2.67	7.6	97.5
	3	3.60, 3.74, 3.81	3.0	105.7

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