Photoelectrochemical aptasensor for the detection of 17β-estradiol based on In_2S_3 and CdS co-sensitized cerium doped TiO_2

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1 Reagents and Apparatus

Cerous nitrate ($Ce(NO_3)_3$❿$6H_2O$), sodium sulfide hydrate (Na_2S❿$9H_2O$), cadmium acetate dihydrate ($Cd(CH_3COO)_2$❿$2H_2O$) and ascorbic acid (AA) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd, China. Indium chloride ($InCl_3$) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Tetrabutyl titanate (TBOT) and hioglycolic acid (TGA) were obtained from Tianjin Kermel Chemical Reagent Co. 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) were obtained from Aladdin Reagent Database Inc. (Shanghai, China). Bovine serum albumin (BSA) and 6-Mercapto-1-hexanol (MCH,⩾99%) were obtained from Beijing J&K Chemical Reagent Co., Ltd. The aptamer with following sequence: 5'-GCT-TCC-AGC-TTA-TTG-AAT-TAC-ACG- CAG-AGG-GTA-GCG-GCT-CTG-CGC-ATTCAA-TTG-CTG-CGC-GCT-GAA-GCG-CGG-AAG-C-3' was obtained from Shanghai Sangon Biological Co., Ltd which was diluted to 2 μM in phosphate buffered saline and preserved at 4°C. 17β-estradiol (E2) was purchased from BeiJing Kwinbon Biotechnology CO., LTD.

All the experiments mentioned in the paper were conducted with ultrapure water (18.25 MΩ·cm) which obtained from a Millipore water purification system. All the reagents used in the experiments were analytically pure without any extra dispose.

All photoelectrochemical experiments were conducted with the electrochemical workstation (Zahner Zennium PP211, Germany). The surface morphology of the sample was carried out through scanning electron microscopy (SEM, S-3400).

Electrochemical impedance spectroscopy (EIS) analysis was performed with an RST5200F electrochemical workstation (Zhengzhou Shiruisi Technology Co., Ltd, China). Transmission electron microscope (TEM, JEOL JEM 2100 Plus microscope) was employed to confirm the microstructure of the materials. The presented elements of the composite were obtained using Energy Dispersive X-ray Spectroscopy (EDS). X-ray diffraction (XRD) patterns were gathered through D8 focus diffractometer (Bruker AXS, Germany). UV–vis diffuse reflectance spectrum measurements were performed on Shimadzu UV-3101PC spectrometer (Japan).

2 Synthesis of CdS

CdS nanoparticles were prepared through a hydrothermal method [1]. In brief, the solution containing 20 mL of 0.1 mol/L $Ce(NO_3)_3$❿$6H_2O$ and 20 mL of 0.1 mol/L $Cd(CH_3COO)_2$❿$2H_2O$ were mixed intensely under room temperature for 1 h. Then the received mixture was poured into the reaction kettle and kept at high temperature (180 °C） and high pressure for 24 h. The final product was centrifuged with ultrapure water and ethanol to remove excess reagent. The product was dried at 50 °C and seal saved.

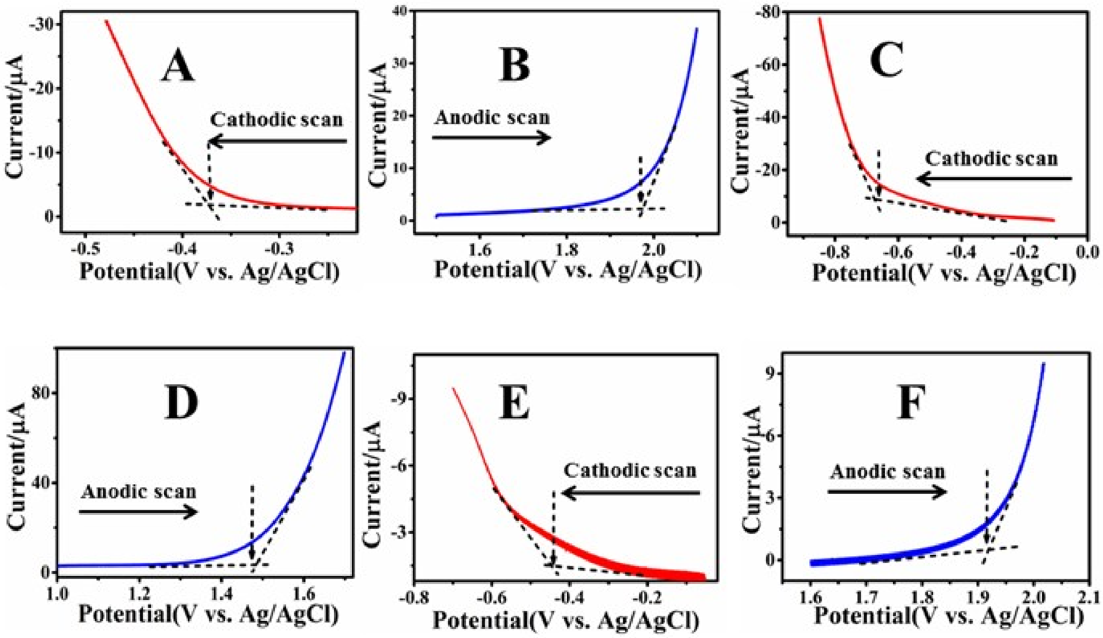

Fig. S1 Cathodic and anodic linear potential scan for (A) and (B) Ce:TiO_2; (C) and (D) In_2S_3; (E) and (F) CdS; Experiments were conducted in the deaerated 0.2 mol/L Na_2SO_4 solution

Table. S1 The results of E2 detection in real water sample

Water Samples	Addition content (ng/mL)	Detection content (ng/mL)	RSD(%)	Recovery(%)
Tap water	1.00	0.87, 0.93, 0.98, 1.03, 0.88	7.21%	93.8%
	5.00	4.90, 4.91, 5.09, 4.83, 4.85,	2.09%	98.3%
	10.00	8.9, 9.75, 9.73, 9.82, 9.71	4.00%	95.8%
Lake water	1.00	1.07, 1.19, 0.98, 1.13, 1.17	7.67%	110.8%
	5.00	5.12, 5.32, 5.19, 5.25, 5.43	2.27%	105.2%
	10.00	10.53, 10.44, 10.62, 10.29, 10.09	2.01%	103.9%

References

1. R. Xu, D. Wei, B. Du, W. Cao, D. Fan, Y. Zhang, Q. wei and H. Ju, *Biosens. Bioelectron.*, 2018, **122**, 37-42.