Electronic Supplementary Information

Ultrasensitive photoelectrochemical assay of tumor necrosis factor-alpha based on hollow CdS cubes as signal generator and the $NiCo_2O_4$-Au as signal extinguisher

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1. Reagents and materials

$CdCl_2 \cdot 2.5H_2O$, $C_6H_5Na_3O_7 \cdot 2H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, H_2O_2 (30 %), $NH_3 \cdot H_2O$ (25%~28%), glycerol, isopropanol, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). $K_3[Co(CN)_6]$ and $Na_2S \cdot 9H_2O$ were obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Thioacetamide (TAA), 6-mercaptoethanol (MCH), and 4-chloro-1-naphthol (4-CN) were acquired from Maclean Biochemical Technology Co., Ltd. (Shanghai, China). Ascorbic acid (AA) was provided by Guangdong Guangtry Reagent Technology Co., Ltd. (Guangzhou, China). Polyvinylpyrrolidone (PVP, MW: 40K) was purchased from Shanghai Yuanye Bio-Technology Co., Ltd. (Shanghai, China). Tumor necrosis factor-α (TNF-α), heart fatty acid binding protein (h-FABP), and carcinoembryonic antigen (CEA) were provided by Shanghai Sangon Biotech Co., Ltd. (Shanghai, China). The ITO slice used in this work was acquired from Zhuhai Kaivo Electronic Components Co., Ltd. (Zhuhai, China).

2. Instruments

Scanning electron microscope (SEM, ZEISS GeminiSEM 300, Germany) and transmission electron microscope (TEM, FEI Talos-F200S, USA) were used to characterize the morphology of different materials. X-ray diffraction (XRD) analysis was performed on a Rigaku Miniflex-600 X-ray diffractometer (Japan). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific K-Alpha spectrometer (USA). Brunauer-Emmett-Teller (BET) surface area and the pore size

distribution of the materials were investigated by a specific surface and aperture analyzer (JW-BK112, China). All electrochemical experiments were performed on an electrochemical workstation (CHI 660E, China) with a three-electrode system containing a working electrode (the modified ITO electrode), an auxiliary electrode (platinum wire), and a reference electrode (saturated calomel electrode, SCE). The photoelectrochemical investigation was conducted with a 300 W Xe lamp. Here, a 420 nm UV filter was used to avoid possible damage to the biomolecules by ultraviolet light.

3. Preparation of the Cd-PBA cubes

Cd-PBA cubes were synthesized according to the previous literature with minor modifications[1]. 137 mg of $CdCl_2 \cdot 2.5H_2O$, 1.0 g of PVP and 103 mg of $C_6H_5Na_3O_7 \cdot 2H_2O$ were dissolved in 20 mL of H_2O to form solution A. Then, 133 mg of $K_3[Co(CN)_6]$ was dissolved into 20 mL of H_2O to form solution B. Next, solution B was slowly added to solution A and the mixed suspension was aged for 1 h. The obtained product was collected by centrifugation and washed with ethanol several times, which was then dispersed in 100 mL of the mixed solution (containing 50 mL of ethanol and 50 mL of H_2O) to obtain Cd-PBA suspension.

4. Preparation of the $NiCo_2O_4$-Au spheres

The $NiCo_2O_4$ spheres were synthesized as follows[2]: First, 8 mL of glycerol was dissolved into 40 mL of isopropanol to form a transparent solution. Then, 73 mg of $Co(NO_3)_2 \cdot 6H_2O$ and 37 mg of $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in the above solution under magnetic stirring. The solution was then transferred to a Teflon-lined stainless-steel

autoclave and kept at 180 °C for 6 h. After cooling to room temperature naturally, the precipitate was collected by centrifugation, washed with ethanol for several times, and dried in an oven to obtain the NiCo-glycerate spheres (NiCo-GSs). To obtain the $NiCo_2O_4$ spheres, the NiCo-GSs were annealed at 350 °C in the air for 5 min.

For the preparation of $NiCo_2O_4$-Au spheres, 50 mL of $HAuCl_4$ solution (1 mM) was added to the round flask. Then, 50 mg of $NiCo_2O_4$ spheres were added and stirred at room temperature. Next, the mixture was heated to boiling. After that, 38.8 mM of $Na_3C_6H_5O_7$ solution (5 mL) was quickly added under stirring for 10 min. The obtained $NiCo_2O_4$-Au was washed with water several times and redispersed with water to form $NiCo_2O_4$-Au spheres suspension (100 μg mL^{-1}).

5. XRD pattern of Cd-PBA cubes

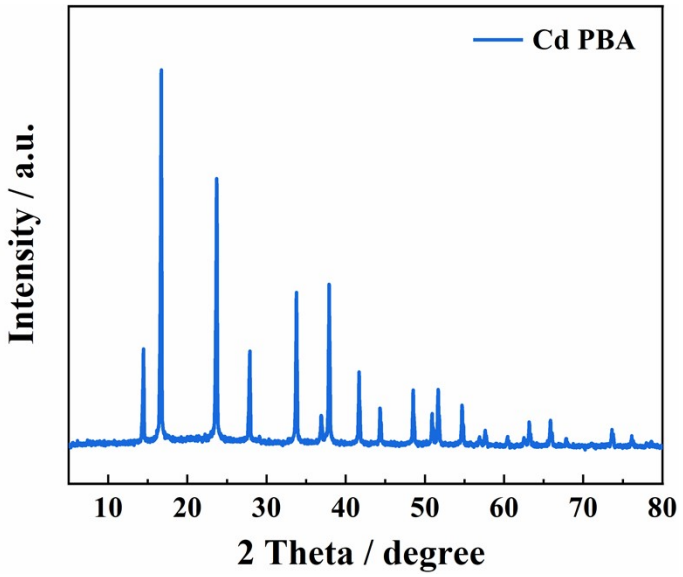

Fig. S1 XRD pattern of Cd-PBA cubes

6. Optimization of experimental conditions

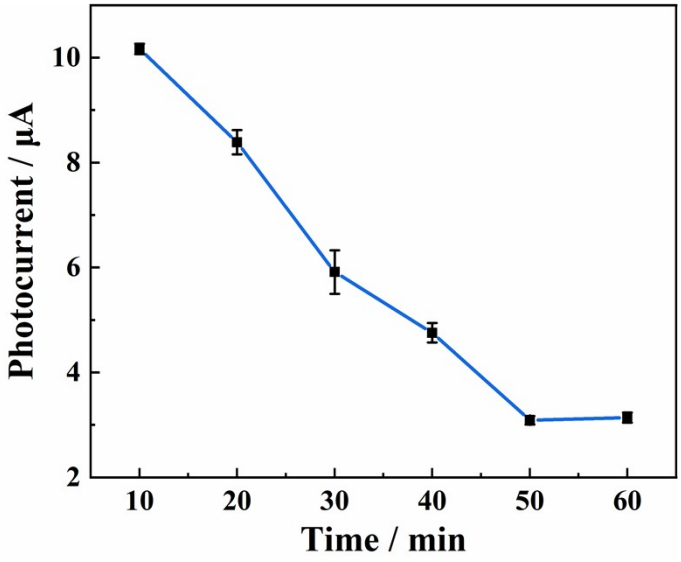

Fig. S2 Effect of the TNF-α incubation time on the photocurrents of the PEC aptasensor, error bars represent three individual experiments.

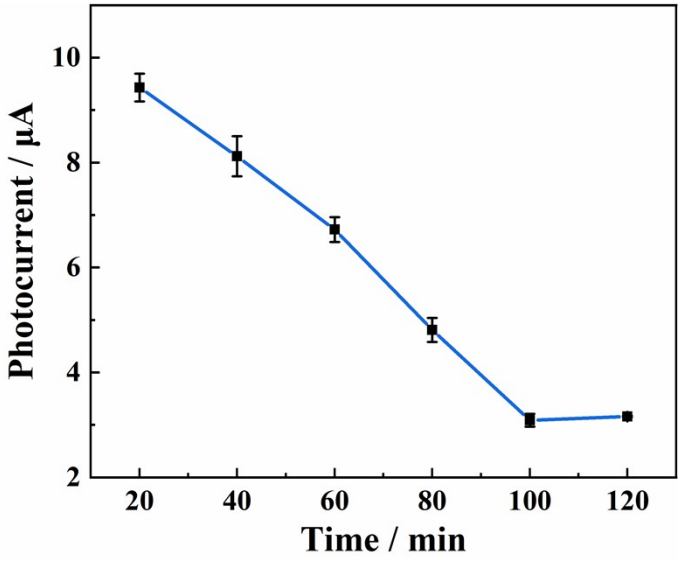

Fig. S3 Effect of the $NiCo_2O_4$-Au@Apt incubation time on the photocurrents of the PEC aptasensor, error bars represent three individual experiments.

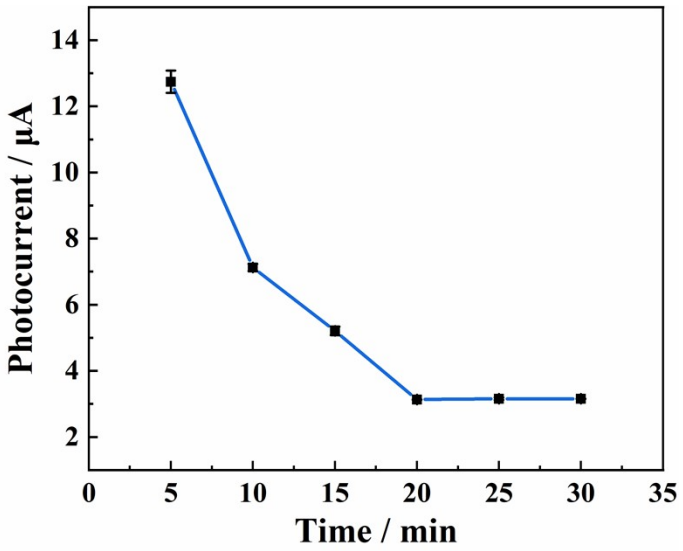

Fig. S4 Effect of the catalytic deposition time on the photocurrents of the PEC aptasensor, error bars represent three individual experiments.

7. Recovery test of TNF-α in serum

Table S1 Determination of TNF-α in 10-fold diluted healthy adult serum samples

Samples	Added	Found	RSD	Recovery
1	10 fg mL^{-1}	0.93 fg mL^{-1}	2.4 %	93 %
2	1 pg mL^{-1}	1.07 pg mL^{-1}	2.8 %	107 %
3	1 ng mL^{-1}	0.95 ng mL^{-1}	0.2 %	95 %

8. References

[1] Zhang, P., Luan, D., Lou, X.W., Fabrication of CdS frame-in-cage particles for efficient photocatalytic hydrogen generation under visible-light irradiation, Adv. Mater.,

2020, 32, 2004561.

[2] Fu, Y., Du, C., Zhang, Q., Xiao, K., Zhang, X., Chen, J., Colorimetric and photocurrent-polarity-switching photoelectrochemical dual-mode sensing platform for highly selective detection of mercury ions based on the split G-quadruplex-hemin complex, Anal. Chem., 2022, 94, 15040-15047.