Electronic Supplementary information for

An Ultrasensitive Energy-transfer Based Photoelectrochemical Protein Biosensor

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Experimental

Materials and apparatus. The ITO slices (type N-STN-S1-10, China Southern Glass Holding Co., Ltd.) were used as the working electrode. $CdCl_2 \cdot 2.5H_2O$ was obtained from Shanghai Jinshan Tingxin Chemical. Rchloroauric acid ($HAuCl_4$) was purchased from Nanjing Reagent Company (Nanjing, China). $NaBH_4$ was purchased from Tianjin Chemical Reagent Institude. $Na_2S \cdot 9H_2O$ was obtained from Shanghai Lingfeng Chemical Reagent Co., LTD (Shanghai, China). Tris(2-carboxyethyl) phosphine hydrochloride(TCEP), PDDA (20%, w/w in water, molecular weight (200000-350000)) were obtained from Sigma-Aldrich. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) was purchased from Fluka. *N*-Hydroxysuccinimide(NHS), ascorbic acid (AA), thioglycolic acid (TGA) and monoethanolamine (MEA) were purchased from Sinopharm Chemical Reagent Co.,LTD (Shanghai, China). Thrombin from bovine plasma was obtained from Sigma-Aldrich. All the synthetic oligonucleotides were purchased from Shenggong Bioengineering Ltd. Company (Shanghai, China) and the corresponding sequences were summarized in Table 1. All other reagents were analytical grade and were used as received. All aqueous solutions including phosphate buffer solution (PBS) were prepared using ultra-pure water (Milli-Q, Millipore).

Table 1 The corresponding sequences of anti-thrombin aptamers

Aptamer1	5'-NH_2-TAA GTT CAT CTC CCC GGT TGG TGT GGT TGG-3'
Aptamer2	5'-AGT CCG TGG TAG GGC AGG TTG GGG TGA CT_{37}-SH-3'

PEC measurements were performed with a homemade PEC system equipped with a 500 W Xe lamp and a monochromator. Photocurrent was measured on a CHI 750a electrochemical workstation (China) with a three-electrode system: a modified ITO electrode with a geometrical area of $0.25\ ^2\pi$ cm^2 as the working electrode, a Pt wire as the counter electrode, and a saturated Ag/AgCl electrode as the reference electrode. All the photocurrent measurements were performed at a constant potential of 0 V (versus

Ag/AgCl). A 0.1 M PBS containing 0.1 M AA was used as the blank solution for photocurrent measurements, which was degassed by highly pure nitrogen for 15 min before PEC experiments and then kept over a N_2 atmosphere for the entire experimental process. Transmission electron microscopy (TEM) was performed with a JEOL model 2000 instrument operating at 200 kV accelerating voltage. The UV−Vis absorption spectra were obtained on a Shimadzu UV-3600 UV−Vis-NIR photospectrometer (Shimadzu Co.).

Synthesis of TGA-Stabilized CdS QDs. The utilized CdS QDs was synthesized according to the previous report with a slight modification. Briefly, 250 μL of TGA was added to 50 mL of 1.0×10^{-2} M $CdCl_2$ aqueous solution, and N_2 was bubbled throughout the solution to remove O_2 for 30 min at 40 °C. During this period, 1.0 M NaOH was added to adjust the above solution to the desired value of pH 11. Then, 5.5 mL of 0.1 M Na_2S aqueous solution was injected into this solution to obtain TGA-capped water-soluble CdS QDs, and the reaction mixture was refluxed under N_2 atmosphere for 4 h. This procedure produced CdS QDs with a Cd to S (Cd/S) ratio of 1:1.1. Finally, the desired TGA-stabilized CdS QDs were obtained and then diluted with the same volume of water and stored in a refrigerator at 4 °C for further use.

Fabrication of Electrode. The PDDA/CdS multilayer film was grown by alternately dipping of the freshly cleaned ITO slices into a solution of 2% PDDA containing 0.5 M NaCl and the as-obtained CdS QDs solution for 10 min, respectively, and this process was repeated four times to obtain desired photocurrent intensity. The films were carefully washed with doubly distilled water after each dipping step.

Synthesis of Au NPs. Au NPs with average diameter 5 ± 1 nm were prepared through the reduction of $HAuCl_4$ by sodium $NaBH_4$. Briefly, 0.6 mL of 0.1 M ice cold $NaBH_4$ was added to 20 mL of aqueous solution containing 2.5×10^{-4} M $HAuCl_4$ under stirring,

and the solution immediately turned to an orange-red color, indicating the formation of Au NPs. Then the solution was kept under stirring in the ice bath for 10 min and for another 3 h at room temperature with the color changing from orange-red to wine red. The nearly monodispersed Au NPs had an average diameter of 5 ± 1 nm as characterized by TEM and thus the final concentration of the Au colloid solution was estimated to be 6×10^{-8} M. The prepared Au NPs were kept in a refrigerator at 4 ºC for further use.

Supplementary data

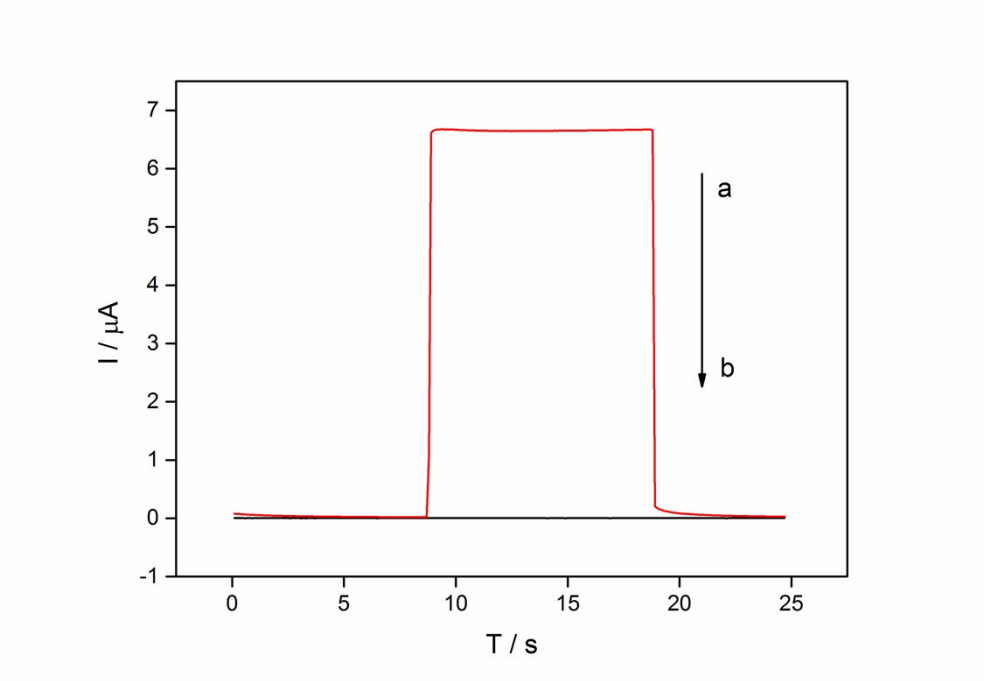

Fig. S1 The photocurrent response before (a) and after (b) CdS QDs modification on the ITO electrode.

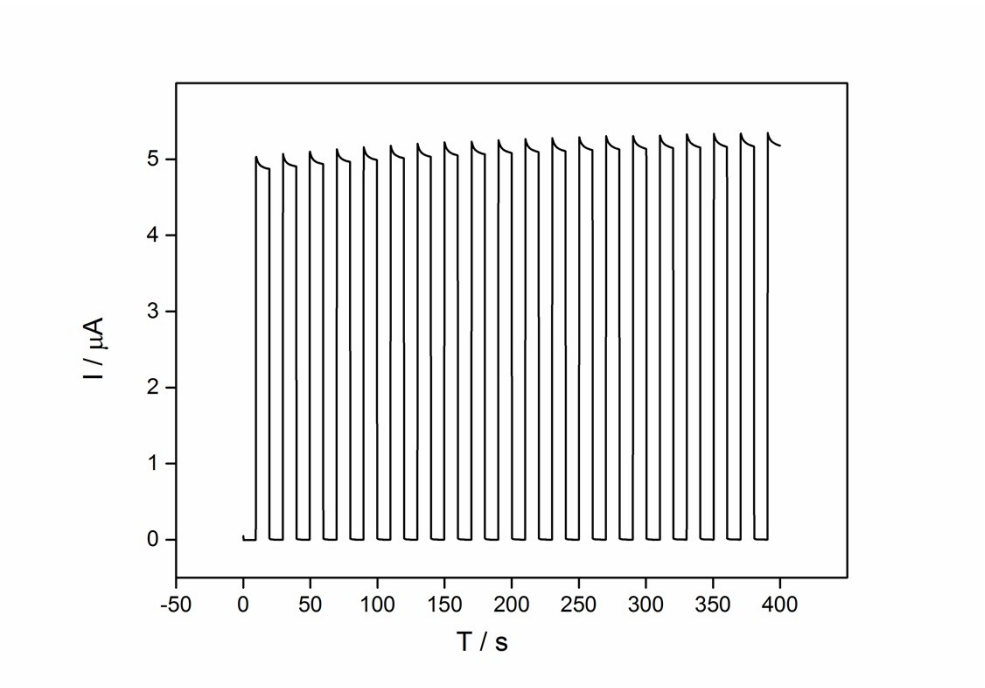

Fig. S2 Time-based photocurrent response of $(PDDA\text{-}CdS)_4$ bilayers on a modified ITO electrode.

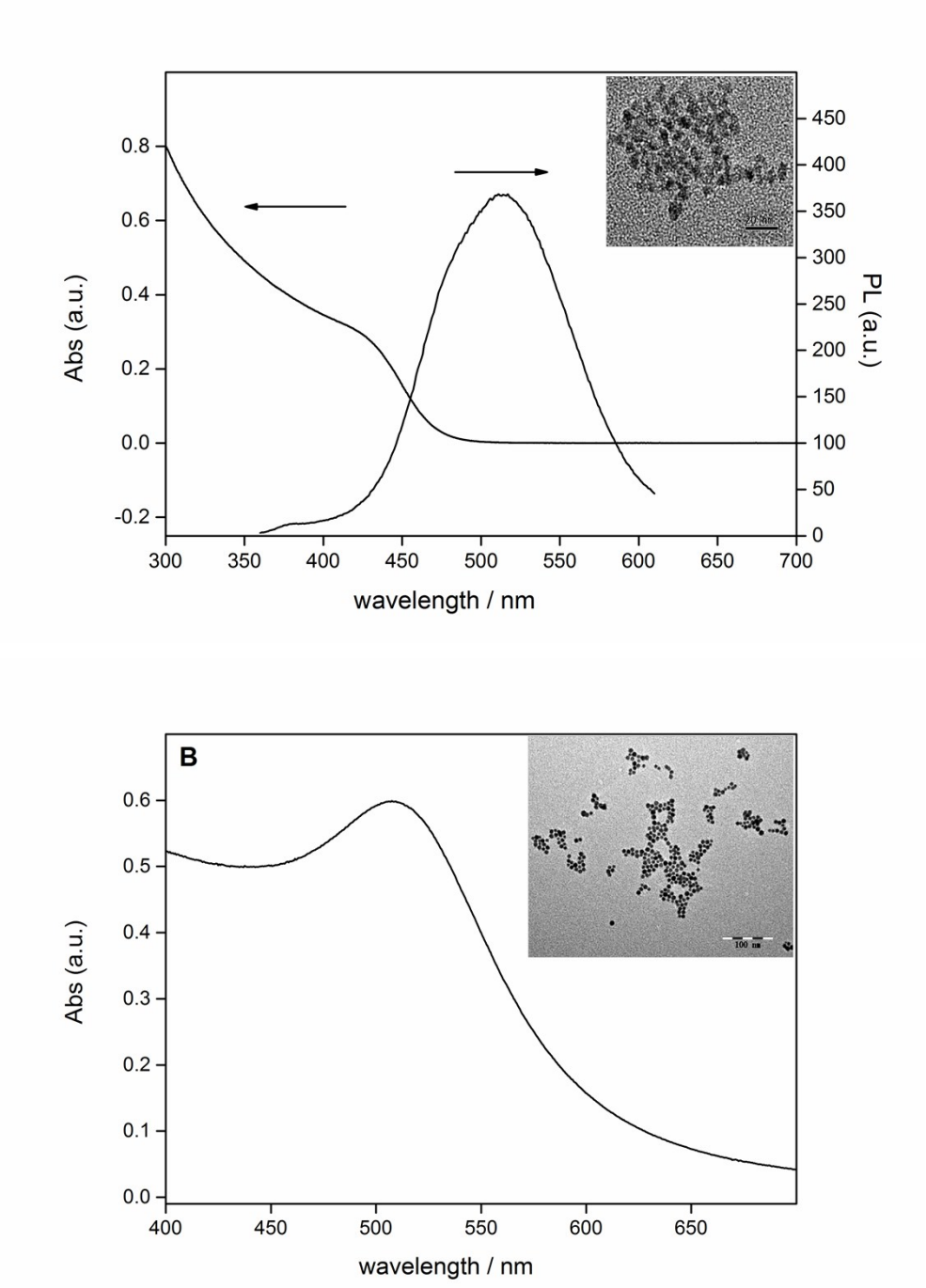

Fig. S3 (A) The UV-Vis absorption spectrum and the PL spectrum of CdS QDs, excitation wavelength: 410 nm. (B) The UV-Vis absorption spectrum of Au NPs. The insets are the TEM of CdS QDs and Au NPs respectively.

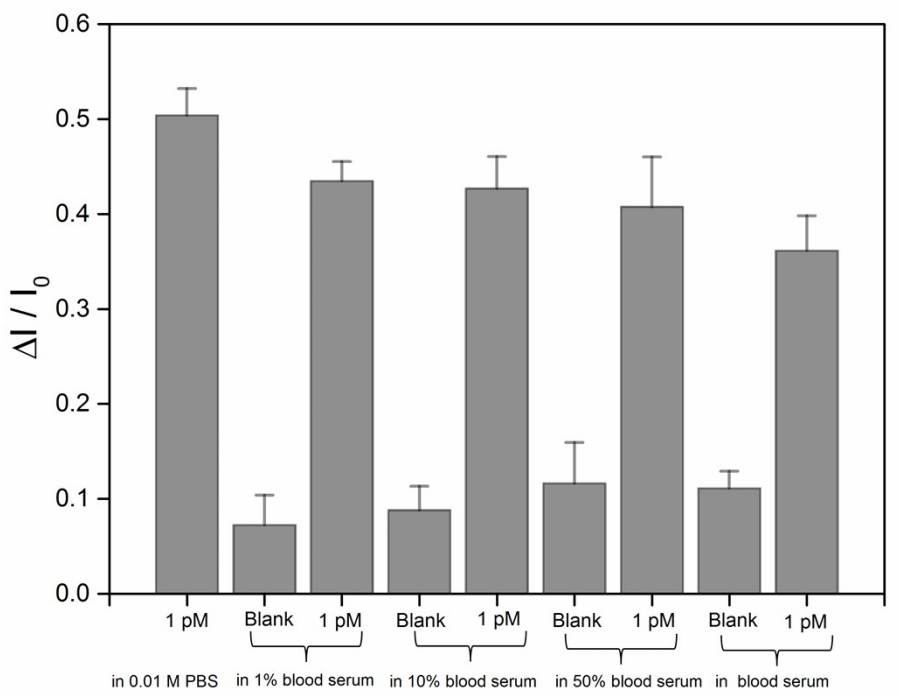

Fig. S4 Variance ratio of photocurrent caused by thrombin (concentration was 1 pM) in 0.01 M PBS, 1% blood serum1, 10% blood serum, 50% blood serum (diluted with 0.01 M PBS), blood serum (from normal human)respectively. $\Delta I=I_0-I$, I_0 is the photocurrent of MEA/aptamer1/CdS/ITO, and I is the photocurrent of Au/aptamer2/thrombin/MEA/aptamer1/CdS/ITO. The photocurrent measurement was carried out in 0.10 M PBS containing 0.10 M AA. The working potential was 0.0 V and the light wavelength was 410 nm.