Supporting Information for

Organic Photoelectrochemical Transistor Detection of Tear Lysozyme

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Experimental section

Reagents and Materials: DNA Oligonucleotides was acquired from Sangon Biotechnology Company, LTD (Shanghai, China) and contained the following sequences: 5'-NH_2-$(CH_2)_6$-ATCTACGAATTCATCAGGGCTAAAGAGTGCAGAGTTACTTAG-3'(aptamer). 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hdrochlo drochloride (EDC), N-Hydroxysuccinimide (NHS), poly(diallyldimethylammonium chloride) solution (PDDA), thioglycolic acid (TGA), lysozyme human and AA were purchased from Sigma Aldrich. $CdCl_2 \cdot 2.5H_2O$ was purchased from Shanghai Jinshan Ting xin Chemical Plant. $Na_2S \cdot 9H_2O$ was purchased from Shanghai Lingfeng Chemical Reagent Co., LTD (Shanghai, China). Monoethanol Amine (MEA) was purchased from Sinopharm Chemical Reagent Co., LTD (Shanghai, China). Phosphate buffer solution (PBS, pH 7.2-7.4) was purchased from Keygen Biotech Co., LTD (Nanjing, China). All aqueous solutions were prepared from ultrapure water (Millipore, 18 MΩ cm).

Experimental Setup and Data Acquisition: PEC and OPECT were measured on a PEC/OPECT detector with a 420 nm wavelength light source (Nandaguang, Nanjing, China). Photocurrent of PEC was measured by the detector with a three-electrodes system (a modified Ti electrode as the working electrode, a saturated Ag/AgCl as the reference electrode, and a Pt slice as the counter electrode) at a constant potential of 0 V (vs saturated Ag/AgCl). The PBS solution containing 0.1 M AA was used as the electrolyte.

For OPECT measurements, the PBS solution containing 0.1 M AA was also used as the electrolyte. For transfer characteristics ($I_{DS} \sim V_G$), the channel current I_{DS} was measured as a function of gate voltage V_G under a constant drain voltage V_{DS} = 0.1 V. The channel current I_{DS} as a function of time ($I_{DS} \sim$ time) was measured under constant gate and drain voltages (V_{DS} = 0.1 V, V_G = 0 V) at a light on/off cycle.

Electrochemical impedance spectroscopy (EIS) was characterized by an impedance analyzer (Bio-Logic SP-150, France) with a standard three electrode system in 0.1 M KCl containing a redox probe of 5.0 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) mixture. The amplitude of the applied voltage was 50.0 mV and the frequency range was from 0.1 Hz to 100 kHz.

The UV-vis absorption spectrums were obtained by Shimadzu UV-3600 UV/vis spectrophotometer (Shimadzu Corporation, Japan). In detail, titanium sheets of 2 cm in length and width were employed to attach CdS QDs for UV-visible absorption characterization. CD spectra were obtained from Chirascan Instrument (Applied Photophysics, Leatherhead, Surrey, U.K.). Atomic force microscopic (AFM) images were recorded by a Bruker Icon atomic force microscope (Bruker Corporation, America).

Synthesis of TGA-stabilized CdS QDs: The synthesis of TGA-stabilized CdS QDs was according to the previous report.[1] Firstly, N_2 was bubbled throughout the 50 mL of $CdCl_2$ aqueous solution (0.01 M concentration) to remove O_2 for 15 min, then 250 μL of TGA was added to the aqueous solution quickly. During this period, NaOH solution (1.0 M concentration) was added to adjust the pH of the above solution to the desired value of 11. After 30 min, 5.0 mL of Na_2S aqueous solution (0.1 M concentration) was added into this solution to obtain TGA-capped water-soluble CdS QDs and the mixed solution was refluxed under N_2 atmosphere at 110 °C for 4 h. Finally, the desired TGA-stabilized CdS QDs were obtained and then the same volume of ultrapure water was added to the reaction mixture and stored in a refrigerator at 4 °C when not in use.

Device Fabrication: Soda-lime glass was first sonicated in acetone, ethanol and ultrapure water for 10 min, respectively. Cr/Au electrodes was deposited on the surface of the soda-lime glass through a metallic shadow mask with a magnetron sputtering film deposition system (Kurt J. Lesker PVD75 Proline SP, America). The thickness of Cr was 10 nm and the Au was about 100 nm. The channel length and width of the devices were 0.2 mm and 6.0 mm, respectively. Then the patterned substrate was treated with oxygen plasma. After that, PEDOT:PSS was spin-coated at 3500 rpm on the surface of the channel to form a layer of thin film. Finally, the device was annealed at 180 °C for 1h in the glove box, which filled with high purity Ar. When not in use, the device was stored in the glove box filled with Ar.

Fabrication of the Gate Electrode: A modified Ti electrode with a diameter of 0.5 mm and a length of 3 mm was used as the G-electrode of the device. Ti wires were sonicated in acetone, ethanol and ultrapure water, respectively. Subsequently, the cleaned Ti wires was treated with

$HF-HNO_3-H_2O$ mixed solution (1:4:5 in volume) for 30 s, thoroughly washed by ultrapure water and dried with N_2. The clean Ti wires were immersed in 2% PDDA solution containing 0.5 M NaCl for 10 min, then the Ti wires were immersed in the obtained CdS QDs solution for 10 min, and the above steps were repeated once. After each soaking step, the Ti electrodes were carefully washed with ultrapure water.

Aptamer Immobilization: The aptamers were immobilized onto CdS QDs/Ti G-electrode via amide bond, the amino groups on the aptamers and carboxyl groups on CdS QDs were coupled. Firstly, the solution containing 20 mg/mL EDC and 10 mg/mL NHS was used to treat the as-prepared CdS QDs/Ti G-electrode for 50 min at room temperature. After washing with PBS carefully, 10 μL aptamer solution (0.1 μM concentration) was added to a centrifuge tube with a capacity of 200 μL, then CdS QDs/Ti G-electrode was soaked in the aptamer solution and incubated at 4 °C for 12 h. Subsequently, the G-electrode was cleaned with PBS solution to remove the non-immobilized DNA probes. Then, the excess carboxyl groups of CdS QDs was blocked by 1 mM MEA at 4 °C for 2 h. Finally, PBS solution was employed to rinse the G-electrode carefully.

Lysozyme detection: For the lysozyme detection, 10 μL lysozyme targets with different concentrations were added to a centrifuge tube with a capacity of 200 μL, then the G-electrode which immobilized aptamer were immersed into the lysozyme solution for 1 h incubation at 37 °C. Afterwards the uncombined lysozyme targets should be washed away by the PBS solution (3 times). To determine the specificity for lysozyme detection, the aptamer/CdS QDs/Ti gate electrode was incubated with 2 μg/mL lysozyme and 100 μg/mL IgG, IgA, BSA, HAS, respectively.

In order to verify the stability of the as-fabricated OECT device in PBS containing 0.1 M AA, we measured the transfer curves for 2000 min. As shown in Figure S1, the transfer curves measured in different time were quite consistent.

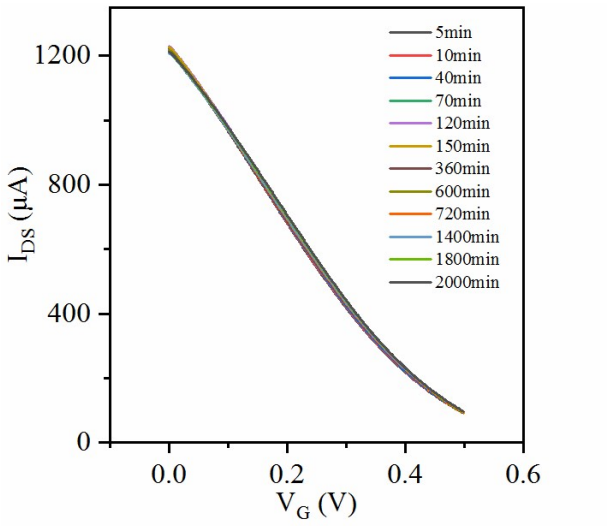

Figure S1. Transfer characteristics of an OECT measured in PBS containing 0.1 M AA at different time within 2000 min. G-electrode: Ag/AgCl. V_{DS} = 0.1 V.

As shown in Figure S2, the corresponding output curves measured after 2000 min in PBS containing 0.1 M AA reflected the sensitive response of the device toward varying V_G. The transfer curves and output curves show that the regulation performance of OECT is basically not affected by 0.1 M AA.

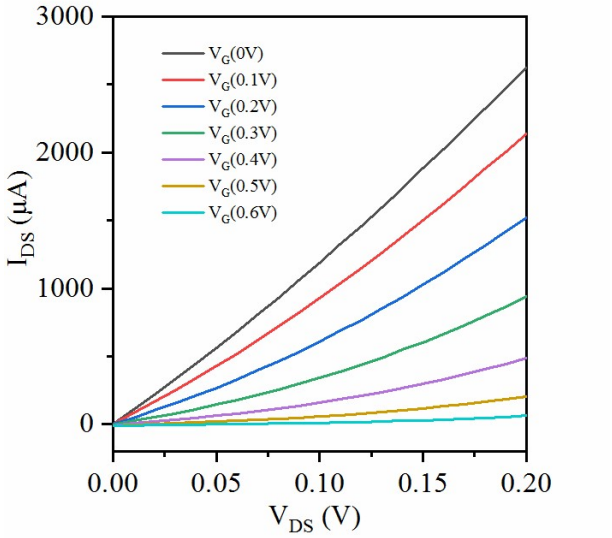

Figure S2. Output characteristics of the OECT measured in PBS containing 0.1 M AA after 2000 min.

Figure S3 shows the operational stability of the channel current response of the device upon applying varying potential steps from 0.1 V to 0.5 V. As shown, the current responses were recorded as the repeated potential switched on and off more than 25 times over 1000 s and the device generated reproducible signal responses without any noticeable decrease within this period.

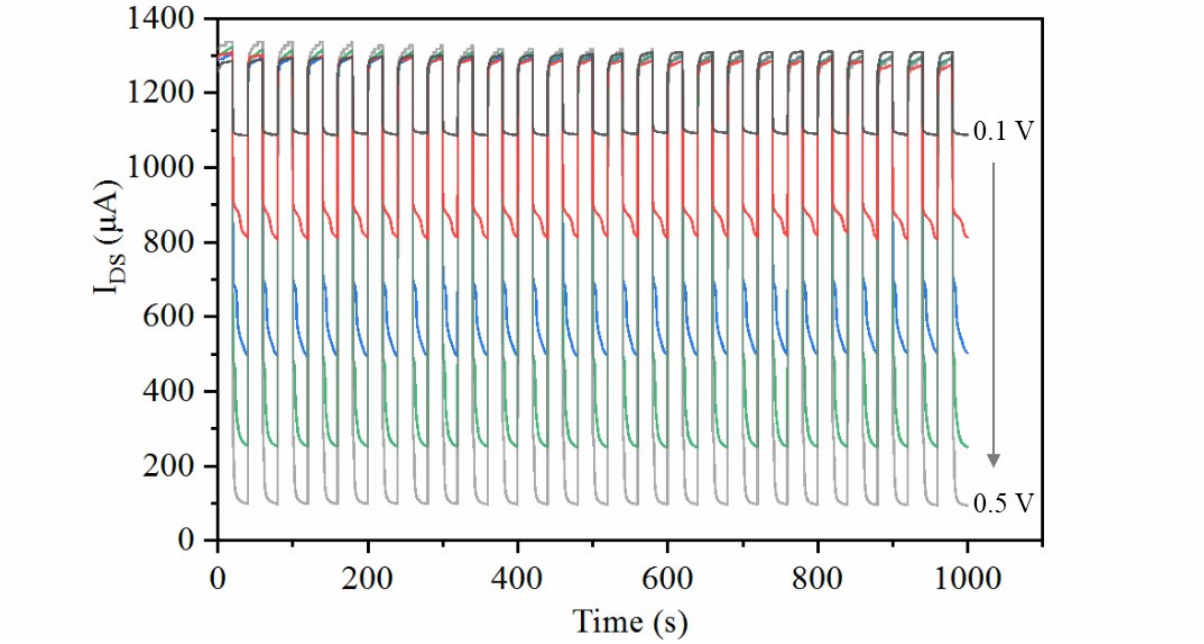

Figure S3. The channel current of the OECT measured in PBS containing 0.1 M AA by applying the potential (0.1 V-0.5 V) to Ag/AgCl G-electrode.

To characterize the PEC property of the as-prepared CdS QDs, photocurrent stability of CdS QDs/Ti e lectrode measured in traditional PEC analysis. As shown in Figure S4, CdS QDs/Ti electrode exhibited fast and stable photocurrent generation upon illumination, indicating not only the good PEC property of the CdS QDs but also the excellent contact between the CdS QDs and the titanium wires as the current collector.

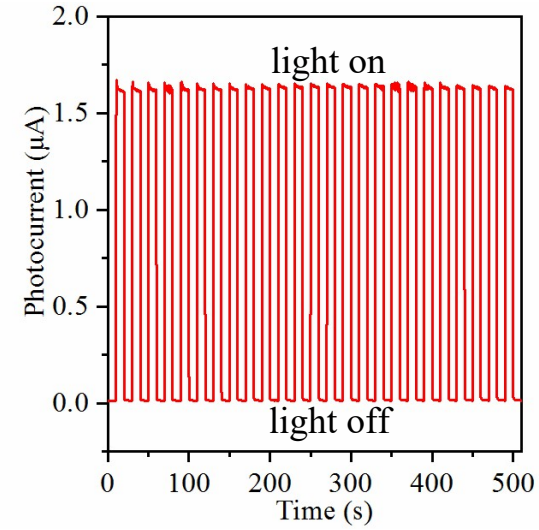

Figure S4. Photocurrent stability of CdS QDs/Ti electrode measured in traditional PEC analysis.

The image shows the assembly process more intuitively. The measured linewidth of sample has errors due to the size of the probe of AFM, which is the widening effect of AFM.[2] The accurate data of AFM is the measured sample height. As shown in Figure S5, (a) CdS on mica slide; (b) binding with aptamers; (c) after combination with the lysozyme, the height of the samples change obviously.

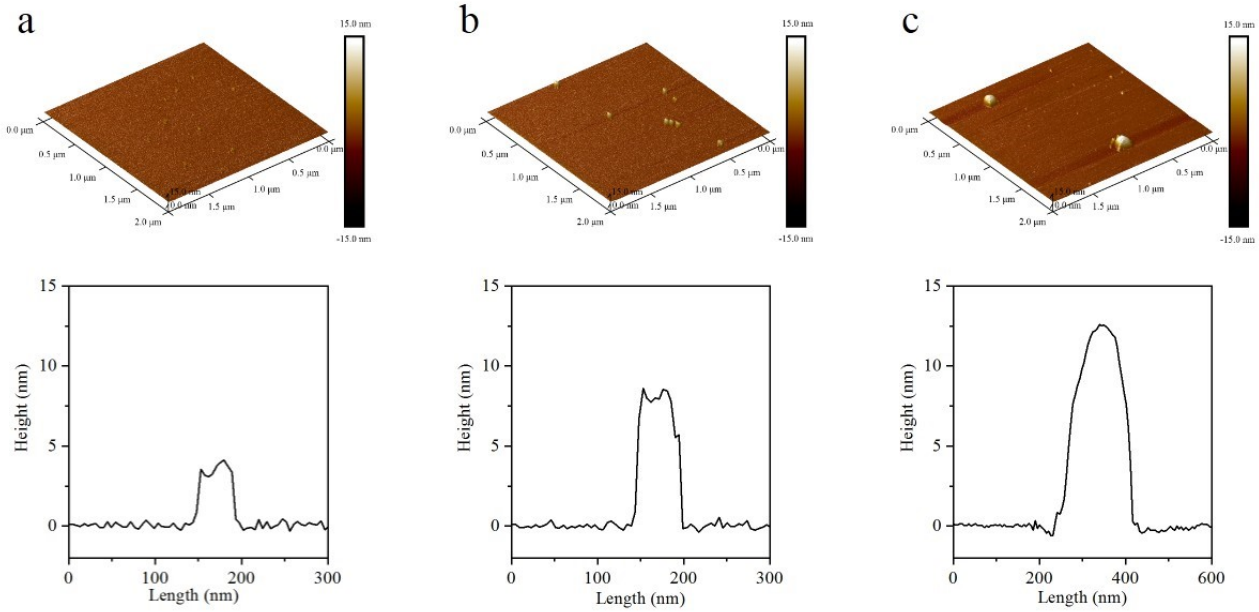

Figure S5. AFM image of (a) CdS QDs on mica slide; (b) binding with aptamers; (c) after combination with the lysozyme. The lower panels show the corresponding cross sectional height profile

As shown in Figure S6, the aptamer concentration was optimized as 0.1 μM to modify the CdS QDs/Ti electrode for subsequent biosensor application.

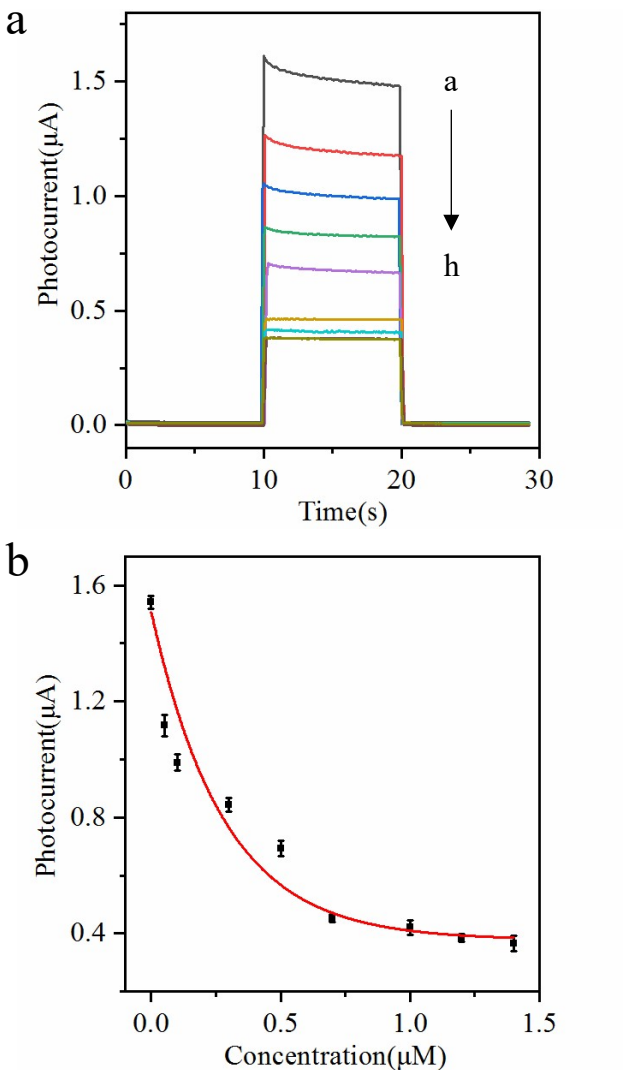

Figure S6. (a) Partakers concentrations optimization in traditional PEC bioanalysis and the concentration corresponding to (curves a-h) 0, 0.05, 0.1, 0.3, 0.5, 0.7, 1.0, 1.2, and 1.4 μM, respectively. (b) The corresponding calibration curve.

Under the 420 nm light illumination, CdS QDs absorb photons with energy higher than that of its bandgap, resulting in the excitation of electrons from the valence band (VB) to the conduction band (CB) and thus the formation of electron-hole pairs. As AA is a strong electron donor, the recombination of electron-hole pairs is effectively inhibited, leading to the continuous and stable photocurrent, as shown in Figure S7.

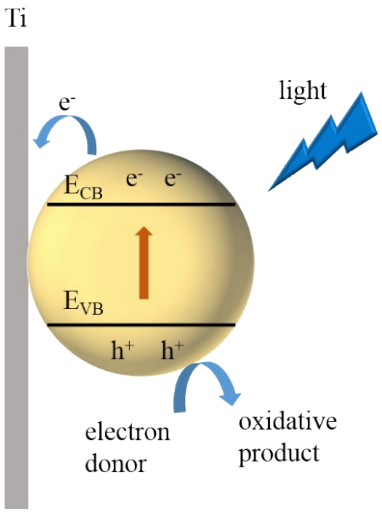

Figure S7. Schematic of the charge transfer between CdS QDs and Ti G-electrode.

As shown in Figure S8, the I_{DS} responses of six aptamer/CdS QDs/Ti G-electrodes fabricated in the same batch confirmed a good repeatability, with highly identical current signals caused by light irradiation.

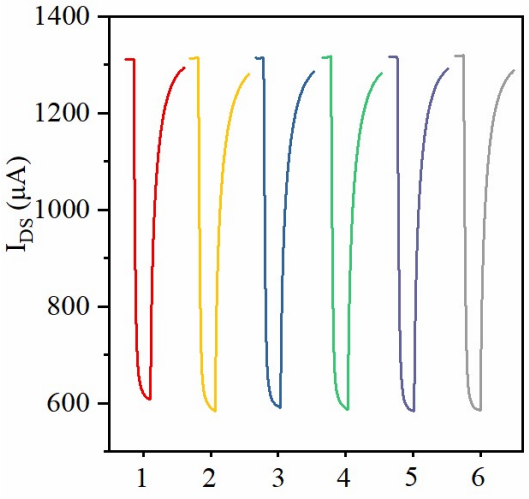

Figure S8. The channel current responses of six aptamer/CdS QDs/Ti G-electrodes.

ELISA was utilized to determine the content of target in human tears, and the results are compared with those measured in our work. Figure S8 shows the standard curve for analysis of lysozyme concentration in human tears.

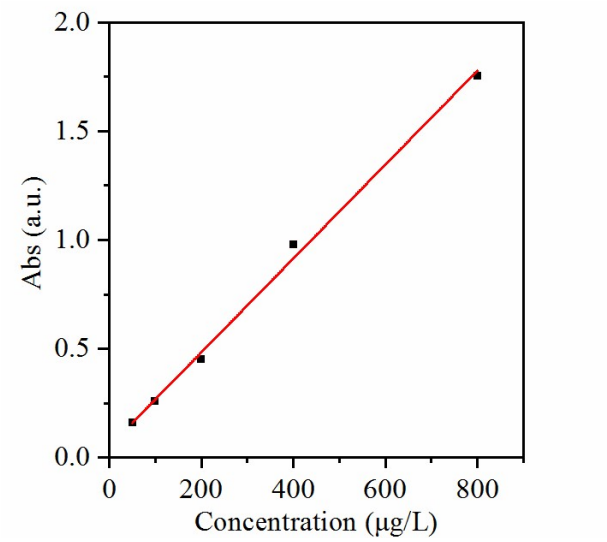

Figure S9. ELISA standard curve for analysis of lysozyme concentration in human tears.

Reference

1. Z. Y. Ma, J. B. Pan, C. Y. Lu, W. W. Zhao, J. J. Xu and H. Y. Chen, Chem. Commun., 2014, **50**, 12088-12090.
2. C. Bustamante, J. Vesenka, C. L. Tang, W. Rees, M. Guthold and R. Keller, Biochemistry, 1992, **31**, 22-26.