Ultrasensitive photoelectrochemical sensor enabled by target-induced signal quenchers controllable release strategy

Lina Zhang,[a] Jie Xue,[b] Chaomin Gao,*[b] Meiling Xu,[a] Peini Zhao,[b] Shenguang Ge,*[c] and Jinghua Yu[b]

[a]*Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan 250022, PR. China*

[b]*School of Chemistry and Chemical Engineering, University of Jinan, Jinan, Shandong 250022, PR. China*

[c]*Institute for Advanced Interdisciplinary Research, University of Jinan, Jinan 250022, China*

*Corresponding author: Chaomin Gao, Shenguang Ge

E-mail: chm_gaocm@163.com, chm_gesg@163.com

Telephone: +86-531-82767040

Chemical and Apparatus

All reagents were of analytical reagent grade and directly used for the following experiments without further purifications. Fluorine-doped tin oxide (FTO) glasses were used as the substrate with a thickness of 2.2 mm (resistance of <15 Ω/square) which were gotten from Xiamen FTO Photoelectricity Industry. A 0.01 M phosphate buffer solution (PBS, pH 7.4) as the washing buffer solution was obtained through mixing KH_2PO_4 and Na_2HPO_4. The 3-morpholinopropanesulfoinc acid (MOPS) buffer (pH 7.8) was prepared by mixing 10 mM MOPS and 150 mM NaCl. Ultrapure water was obtained from a Millipore water purification system (≥18.2 MΩ·cm, Milli-Q, Millipore). The CEA, PSA, HIgG, AFP, HSA standard solutions and the capture antibodies (CEA-Ab_1, PSA-Ab_1, AFP-Ab_1, HIgG-Ab_1, HSA-Ab_1) were all obtained from Shanghai Linc-Bio Science Co. Ltd (Shanghai, China). N-hydroxysuccinimide (NHS), N-(3-dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDC) and bovine serum albumin (BSA) were obtained from Sigma-Aldrich Chemical Co. (USA). 0.1 mol L^{-1} AA was used as a blank solution for photocurrent measurements, which was degassed by highly pure nitrogen for 10 minutes before the PEC experiments.

Scanning electron microscope (SEM) images were obtained by a QUANTA FEG 250 thermal field emission scanning electron microscopy (FEI Co., USA). A 500 W Xe lamp (CHF-XQ-500W, Beijing Changtuo Co. Ltd.) equipped with monochromator served as the irradiation source. PEC measurements were performed in a home-built PEC system. The i-t curves were measured with a CHI660D electrochemistry workstation (Shanghai CH Instruments Co., China). The phase characterization was performed by X-ray diffraction (XRD) using a D8 advance diffractometer system equipped with Cu Kα radiation (Bruker Co., Germany). X-ray photoelectron spectroscopy (XPS) was obtained from PHI 5000 VersaProbe (UlVAC-PHI Co., Japan). Electrochemical impedance spectroscopy (EIS) was performed on a CHI660B electrochemical workstation (Shanghai CH instruments, China). All the photocurrent measurements were performed at a constant potential of 0.0 V.

The optimization of DNA-Cu NCs concentration

The concentrations of used DNA–Cu NCs were optimized as shown in Fig. S2. As seen, when the concentration range of DNA–Cu NCs was 5-20 mg mL^{-1}, the photocurrent remained almost unchanged due to the presence of excess free MB–Apt. In that case, the target PSA can combine with the free MB–Apt instead of the MB–Apt–DNA–Cu NCs and the DNA–Cu NCs were not liberated, resulting in the unchanged photocurrent response. However, the photocurrent responses decreased and reached the minimum value when the concentration of DNA–Cu NCs increased from 20 to 30 mg mL^{-1}, demonstrating that the DNA–Cu NCs (30 mg mL^{-1}) were excess after conjugating with MB–Apt and there was no free MB–Apt existed. Therefore, the 30 mg mL^{-1} was selected as the optimal concentration of DNA–Cu NCs.

The optimization of experimental conditions

The incubation time between antibody and antigen was optimized as shown in Fig. S5. As seen, the photocurrent intensity decreased as the increasing of incubation time from 0 to 40 min and reached a constant state after 40 min. Therefore, 40 min was selected as the appropriate incubation time. What's more, the value of pH plays a vital role in the performance of designed PEC sensor. The effect of pH on photocurrent intensity was shown in Fig. S6. The intensity increased with the increasing pH value and reached a maximum value at pH 7.4. Thus pH 7.4 was used in the further study.

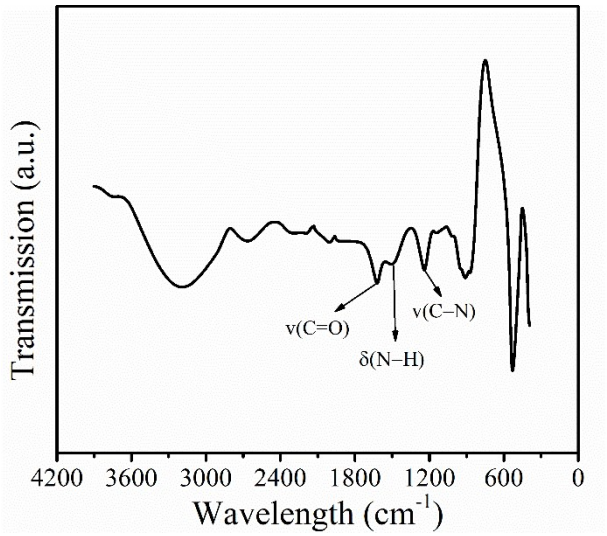

Fig. S1. FTIR spectra of MB-Apt.

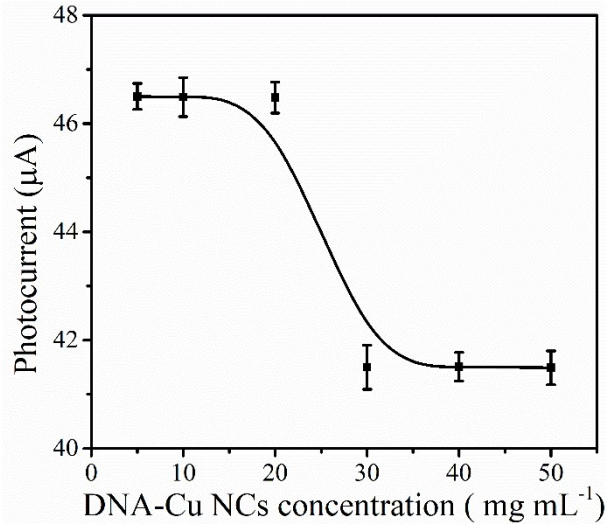

Fig. S2. The optimization of DNA-Cu NCs concentration.

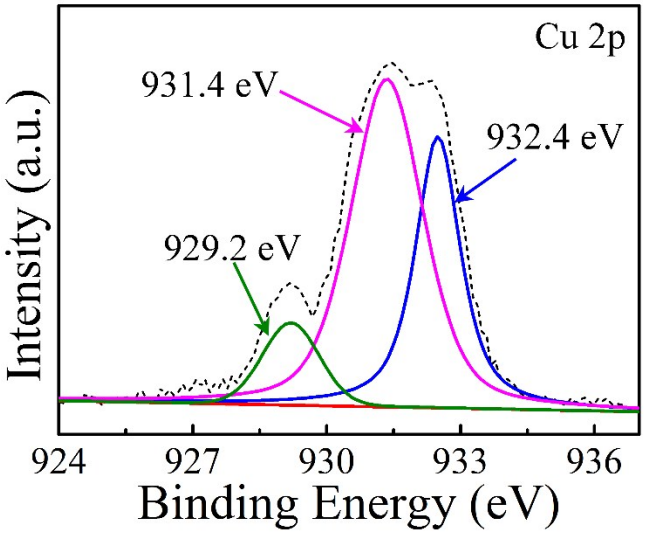

Fig. S3. The high-resolution XPS spectra of Cu 2p.

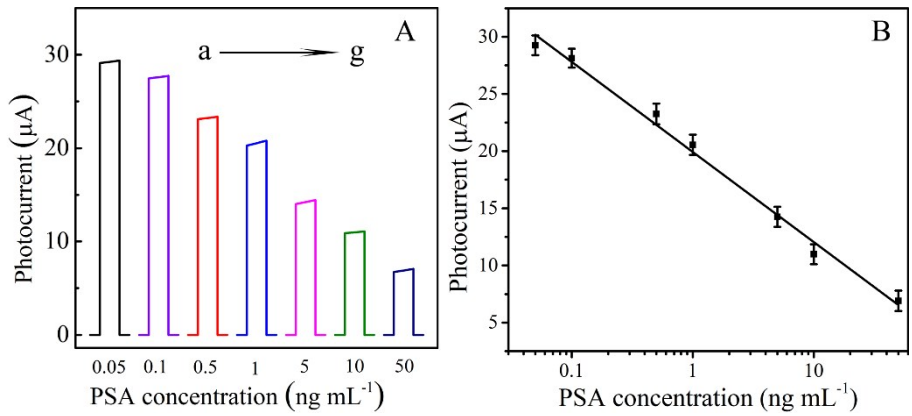

Fig. S4. (A) Photocurrent response and (B) linear calibration curves of CdS based PEC sensor with different PSA concentrations (the concentration was increasing from a to g: 0.05, 0.1, 0.5, 1, 5, 10, 50 ng mL^{-1}).

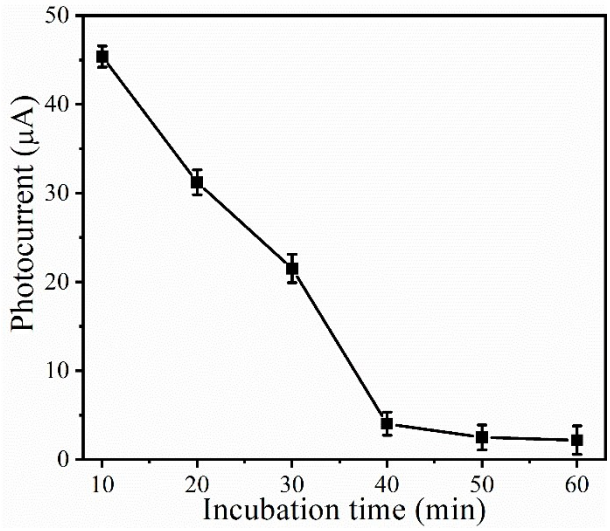

Fig. S5. The effect of incubation time of antigen with antibody on photocurrent response.

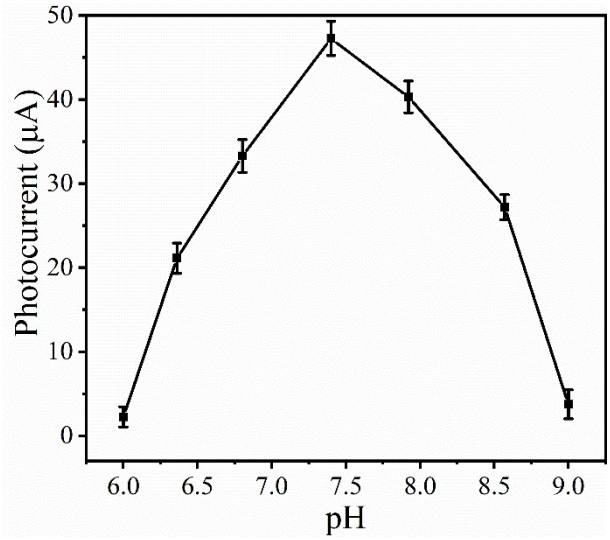

Fig. S6. The effect of pH on the photocurrent response.

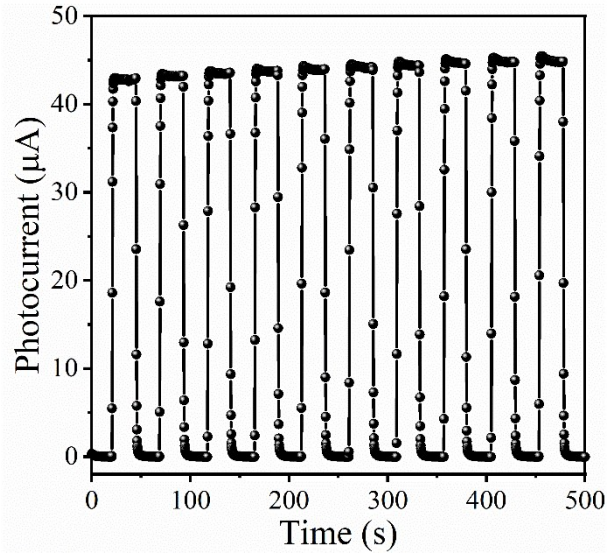

Fig. S7. The photoelectrode stability of photoelectrode.

Table S1. The sequences of used DNAs.

Name	Sequence (from 5′ to 3′)	Description
Apt	NH_2-$(CH_2)_6$-TTT AAT TAA AGC TCG CCA TCA AAT AGC TTT	Recognition element
C-apt-poly(30T)	GGA GCT TTA ATT AAA GCA AGT-poly(30T)	Initiator

Table S2. Decay parameters and average lifetime according to a biexponential fitting model of the PL decay curves obtained from the samples.

Samples	τ_1 (ns)	τ_2 (ns)	A_1	A_2	τ_{ave} (ns)
CdS	0.35	7.2	0.83	0.052	4.21
PSATs/CdS	0.12	1.5	0.19	0.046	1.16

Table S3. Comparison of different sensors for the detection of PSA.

System	Detection range (ng mL^{-1})	The detection limit (pg mL^{-1})	Reference
EC	0.5-40	200	[1]
ECL	0.5-40	100	[2]
FL	0.1-100	27	[3]
PEC	0.01-20	3.8	[4]
PEC	0.005-100	1.7	This work

ECL: electrochemiluminescent; FL: fluorescence; EC: electrochemistry; PEC: photoelectrochemical

Table S4. The assay results of the proposed sensor and CAEA for human clinical serum samples.

	Method; concentration [mean ± SD, ng mL^{-1}, n = 4]		
Sample (TB)	PEC sensor	CAEA	t_{exp}
1	4.32 ± 0.51	3.90 ± 0.25	1.65
2	12.91 ± 0.16	12.85 ± 0.14	0.63
3	35.24 ± 0.30	34.93 ± 0.32	1.58
4	62.67 ± 0.75	63.09 ± 0.58	0.99

References:

1. N. Zhao, Y. He, X. Mao, Y. Sun, X. Zhang, C.Z. Li, Y. Lin, G. Liu, *Electrochem. Commun*, 2010, **12**, 471–474.
2. H. Yang, Z. Li, M. Shan, C. Li, H. Qi, Q. Gao, J. Wang, C. Zhang, *Anal. Chim. Acta* 2015, **863**, 1–8.
3. D.D. Xu, Y.L. Deng, C.Y. Li, Y. Lin, H.W. Tang, *Biosens. Bioelectron*. 2017, **87**, 881–887.
4. K. Zhang, S. Lv, Z. Lin, D. Tang, *Biosens. Bioelectron*. 2017, **95**, 34–40.