SUPPLEMENTARY INFORMATION

A cascade-functionalized ZnCdS/Ce-MOF composite gate coupled with self-replicating catalytic hairpin assembly for OPECT sensing of imidacloprid

Bo Zhang,[a,b] Deguo Hou,[b] Xinmeng Chen,[b] Dianping Tang,[c] Chen Zhang,[b,*] Zhenli Qiu,[b,*] Yiting Chen[a,b,*]

[a]*College of Chemistry and Materials Science, Fujian Normal University, Fuzhou, Fujian 350007, China*

[b]*Fujian Provincial University Engineering Research Center of Green Materials and Chemical Engineering, College of Materials and Chemical Engineering, Minjiang University, Fuzhou 350108, PR China.*

[c]*Key Laboratory of Analytical Science for Food Safety and Biology (MOE & FujianProvince), State Key Laboratory of Photocatalysis on Energy and Environment, Department of Chemistry, Fuzhou University, Fuzhou 350108, China*

** Corresponding author.*

E-mail: zhangchen@mju.edu.cn; ZhenliQiu@mju.edu.cn; cyt@mju.edu.cn

TABLE OF CONTENTS

EXPERIMENTAL SECTION

Reagents and materials. The reagents and materials used in this experiment primarily included $Zn(Ac)_2{\cdot}2H_2O_2$ $Cd(Ac_2){\cdot}2H_2O_2$ thiourea, NaOH, absolute alcohol, H_3BTC, $Ce(NO_3)_3{\cdot}6H_2O$ and H_2O_2, all of which were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. N-Hydroxysuccinimide (NHS), 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC),N,N-dimethylformamide, chloroauric acid, and potassium nitrate (KNO_3, AR) were sourced from Sinopharm Chemical Reagent Co., Ltd. Dinotefuran, thiamethoxam, clothianidin, acetamiprid, carbendazim, imidacloprid and sequences of the oligonucleotides listed in Table S1 were obtained from Shanghai Bioengineering Co., Ltd. The ultrapure water used throughout the experiments was supplied by a Direct-Q ultrapure water system (Millipore Corporation, USA).

Table S1. Oligonucleotide sequences used in this study

Oligonucleotide name	Sequence (5' to 3') description
Apt	GTTTTGGTTGTTGTTTGTTGGTGGGTGTA
T	TACACCCACCAACAAACAACAACCAAAAC
H1	TACACCCACCAACAAAGTTTTGGTTGTTGTTTGTTGGTGGGTGTA TTAAACATACCTTTACACCCACCAACAAACAACAACC
H2	GGTTGTTGTTTGTTGGTGGGTGTAAAGGTATGTTTAATACACCCA CCAACAAACAACAACCAAAACCAACAACCAAAAC
Apt-W1	TACACCCACCAACGAACAACCAAAAC
Apt-W2	TACACCCACTAACAAACAACCCAAAAC
Apt-W3	TACACCAACCAACGAACAACCTAAAAC

Apparatus and measurements. Field emission scanning electron microscope (SU8000, Hitachi, Japan); Transmission electron microscope (Talos F200X, FEI, USA); Zeta potential and nanoparticle size analyzer (Zetasizer Nano ZS90, Malvern); X-ray scanner (Minifelx, RIKEN, Japan); Raman spectrometer (DXR2, Thermo); X-ray photoelectron spectrum analyzer (Verios G 4UC, Thermo Fisher Scientific); Nano-laser action instrument (Laser Nano Pro, Tianjin Jiayin Nanotechnology Co., Ltd.); Vertical

electrophoresis tank (DYC-Mini4, Nanjing Yucheng Experimental Equipment Co.); Gel electrophoresis instrument (DYY-600E, Beijing Dongfang Ruili Electrophoresis Equipment Co., Ltd.). Photoelectrochemical measurements (i-t) and cyclic voltammetry (CV) were performed using an electrochemical workstation (CHI-760D, Shanghai Chenhua Instruments Co., Ltd.) combined with a conventional three-electrode system, using Ag/AgCl or saturated glycerol electrodes as reference electrodes, platinum wire electrodes as auxiliary electrodes, and modified ITO electrodes as working electrodes. I-t was performed in a 0.1 M Na_2SO_4 solution. CV was performed in a gold deposition solution containing 0.1 M KNO_3 and 2 mM $HAuCl_4$.

Synthesis of ZnCdS . According to the literature method with a slight modification[1]. 0.439 g $Zn(Ac)_2$ $2H_2O_2$ 0.533 g $Cd(Ac)_2$ $2H_2O$ and 0.3806 g thiourea were mixed with 10 mL deionized water (DIW). After stirring a few minutes, 2 mL 4 M NaOH were added dropwise into above solution with strong stirring until forming a homogenous solution. Then, the resulting mixed solution was transferred to 25 mL stainless steel case with PTFE liner, and maintained for 24 h at 180 °C.After cooling naturally, the final powder was collected and rinsed three times with DIW and absolute alcohol, and dried at 80 oC under vacuum for 10 h.

Synthesis of Ce-MOF. Ce(III, IV)-MOF was prepared according to a facile in situ partial oxidation Ce-MOF[2]. Briefly, 0.105 g H_3BTC (0.5 mM) was dissolved in 5mL water-ethanol solution (v/v = 1:1), at the same time, 0.217 g $Ce(NO_3)_3·6H_2O$ (0.5 mM) was dissolved in 5 mL ultrapure water. After that, the $Ce(NO_3)_3·6H_2O$ solution was added to the H_3BTC solution dropwisely under vigorous stirring and was kept in water bath at 60 °C for 1 h. After the reaction, the white precipitate was obtained by centrifugation and rinsing with ultrapure water, followed by drying at 60 °C. In this way, the white product of Ce-MOF was obtained. Later on, 30 mg of the above Ce-MOF was resolved in 6 mL ultrapure water with ultrasonic dispersion. Subsequently, 75 μL of fresh NaOH and H_2O_2 mixed solution was added for in situ partial oxidation. After reaction for 5 min, the suspension turned yellow. Finally, the product of Ce(III, IV)-MOF was collected by centrifugation and dried under vacuum at 60 °C.

Preparation of ITO/ZnCdS/Ce-MOF Gate. First, the ITO substrate was placed in a mixed solution of ultrapure water and ethanol and sonicated for 10 minutes for cleaning. It was then rinsed several times with deionized water and dried. Subsequently, 3 mg of ZnCdS and 2 mg of Ce-MOF were weighed separately and added to 1 ml of deionized water, followed by sonication for 20 minutes to ensure thorough dissolution. Then, 20 μL of the ZnCdS dispersion was drop-cast onto the surface of the ITO substrate and dried in an oven at 60 °C. After removal, 20 μL of the Ce-MOF dispersion was drop-cast onto the surface and reacted in a vacuum oven at 60 °C for 6 hours, yielding the ITO/ZnCdS/Ce-MOF electrode.

Preparation of Gold Nanoparticles. Au NPs were synthesized according to a previously reported method[3]. In a typical experiment, 0.05 mmol $HAuCl_4$ and 20 mg PVP were added to 45 mL water under vigorous stirring. After 5min, 5 mL $NaBH_4$ solution (100 mM) was introduced. The reaction mixture was

stirred atroom temperature for 24 h. In particular, the Au NPs were synthesized by reacting at 80 °C for 3 h and then stirring at room temperature for 24 h.

SRCHA Amplification Strategy. Before the reaction, the mixture of imidacloprid aptamer and T strand, along with the stock solutions of H1 and H2, was heat-treated at 95°C for 5 min, followed by slow cooling to room temperature to form stable DNA duplexes and hairpin structures.First, 100 μL of H2 (1 μM, thiol-modified) was mixed with 100 μL of Au NPs and stirred at room temperature for 30 min. Then, 100 μL of carboxylated magnetic beads (MBs) solution (5 mg/mL) was added to 900 μL of PBS buffer (0.01 M, pH 7.4) containing EDC (2.5 mg/mL) and NHS (2.5 mg/mL). The mixture was allowed to react at room temperature for 15 min to activate the carboxyl groups on the surface of the magnetic beads. The resulting mixture was washed three times with PBS buffer and separated magnetically to obtain the MB-H2-Au NPs structure, which was then redispersed in PBS solution.Subsequently, different concentrations of imidacloprid solution (100 μL), H2 (10 μM, 100 μL), the T-DNA-aptamer duplex (10 μM, 100 μL), and 100 μL of H1 (1 μM) were added at room temperature to 700 μL of PBS solution containing MB-H2-Au NPs for SRCHA amplification for 30 min.The long DNA chains obtained were magnetically separated and then transferred into a mixed solution containing EDC (2.5 mg/mL) and NHS (2.5 mg/mL) for reaction over 15 minutes. Subsequently, 100 μL of glucose (5 mmol/L) was added and allowed to react for 30 minutes. Finally, 20 μL of the resulting product was drop-cast onto the surface of the ITO/ZnCdS/Ce-MOF electrode and allowed to react at room temperature for 20 minutes. The electrode was then gently rinsed with ultrapure water.

Polypropylene gel electrophoresis(PAGE). The DNA (2 uL) was thoroughly mixed with loading buffer (1 uL), and this mixed sample was upsampled into a 12% polyacrylamide gel. Electrophoresis was carried out in an electrophoresis tank with 1×TBE as electrolyte, and the electrophoresis apparatus was set to 200 V for 45 min. After electrophoresis, the gel was stained with 4S Red Plus in a thermostatic oscillator protected from light for 90 min. Finally, the gel could be photographed and recorded by a fully automated gel imaging system.

PARTIAL RESULTS

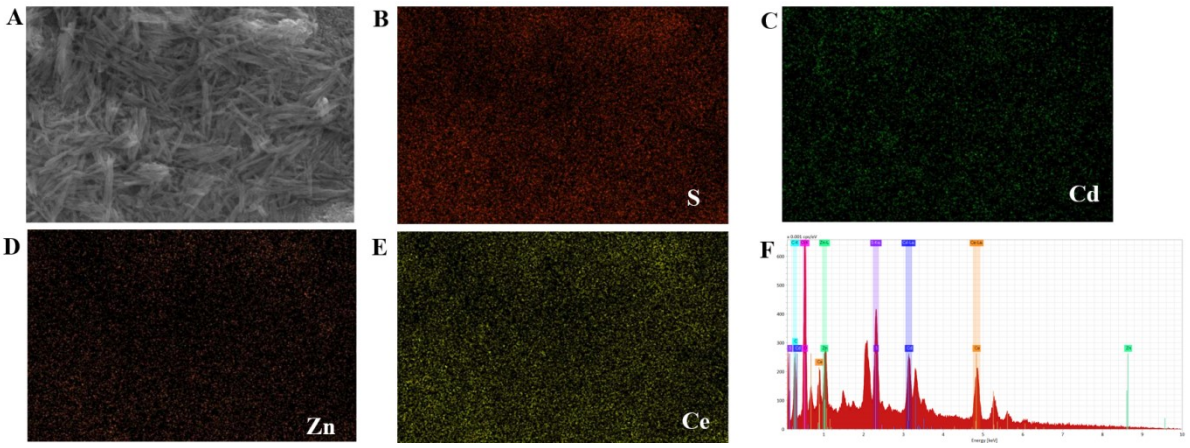


Fig. S1 (A) EDS elemental mapping of ZnCdS/Ce-MOF; (B) S element; (C) Cd element; (D) Zn element; (E) Ce element; (F) EDS spectrum and elemental mapping images of ZnCdS/Ce-MOF.

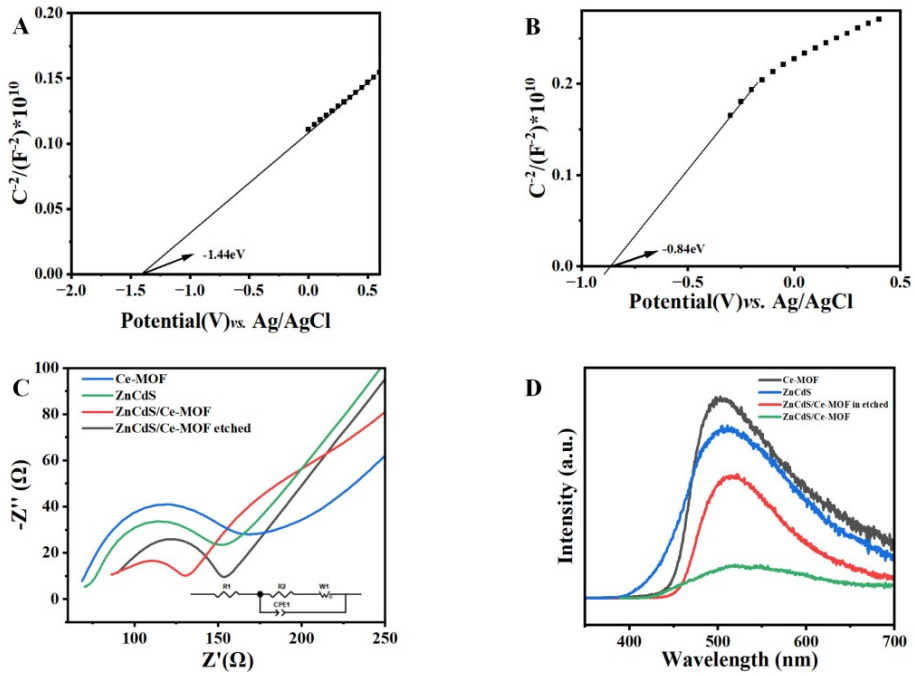


Fig. S2 (A) Mott-Schottky curve of ZnCdS; (B) Mott-Schottky Curve of Ce-MOF; (C) EIS Nyquist plots and (D) Photoluminescence spectroscopy of ZnCdS,Ce-MOF, ZnCdS/Ce-MOF, and the etched ZnCdS/Ce-MOF.

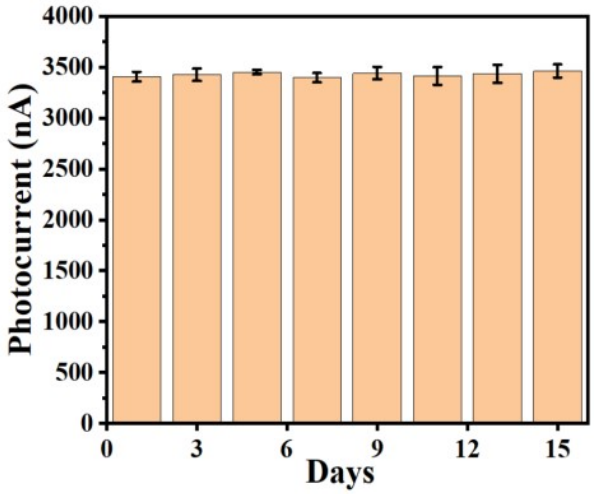


Fig. S3 Stability of the ZnCdS/Ce-MOF modified electrode over 15 days.

Table S2. Inter-day reproducibility of ZnCdS/Ce-MOF modified electrodes

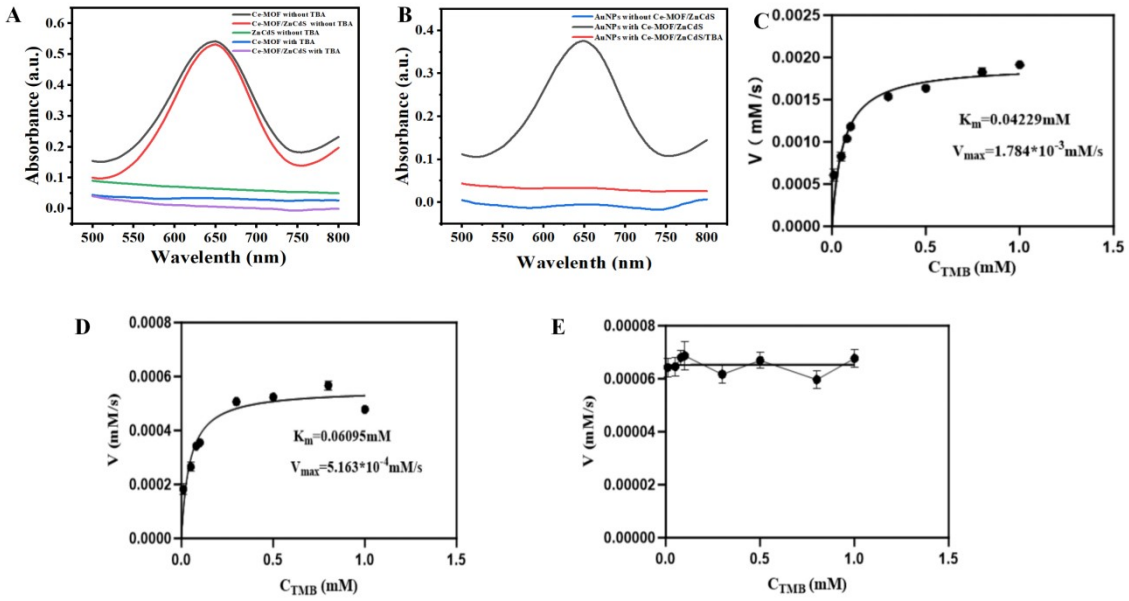
Day	Response 1 (nA)	Response 2 (nA)	Response 3 (nA)	Mean±SD (nA)	RSD (%)
1	3398	3415	3406	3406.3±8.5	0.25
2	3409	3374	3392	3391.7±17.5	0.52
3	3412	3389	3401	3400.7±11.5	0.34
4	3405	3393	3418	3405.3±12.5	0.37
5	3423	3387	3402	3404±18.1	0.53

Table S3. Inter-electrode reproducibility of ZnCdS/Ce-MOF modified electrodes

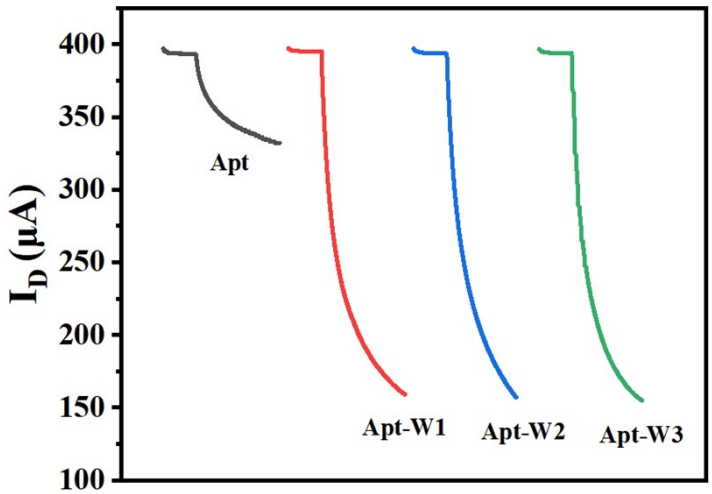
No.	Measurement 1	Measurement 2	Measurement 3	Mean±SD (nA)	RSD (%)
1	3375	3379	3385	3379.3 ± 4.51	0.13
2	3389	3395	3400	3394.7 ± 4.51	0.13
3	3403	3410	3417	3410.0 ± 5.72	0.17
4	3427	3423	3429	3426.3 ± 4.90	0.14
5	3385	3396	3400	3393.7 ± 8.58	0.25
Overall Statistics				3400.5 ± 16.57	0.49

Table S4 Cd^{2+} Release Concentrations Measured by AAS

Simple Number	Sample Description	Cd^{2+} concentration (μg/L)	RSD (%) (n=3)
1	Blank	----	----
2	ZnCdS/Ce-MOF	1.2 ± 0.08	6.5
3	The etched ZnCdS/Ce-MOF	24.6 ± 1.5	6.1



141 Fig S4. (A) Absorbance tests of ZnCdS/Ce-MOF under different experimental conditions; (B) Absorbance tests of Au NPs
142 under different conditions; (C) Reaction kinetic curves of Ce-MOF/ZnCdS; (D) Reaction kinetic curves of Ce-MOF; (E)
143 Reaction kinetic curves of ZnCdS.
144



145
146 Fig S5. The sequence specificity of the SRCHA system.

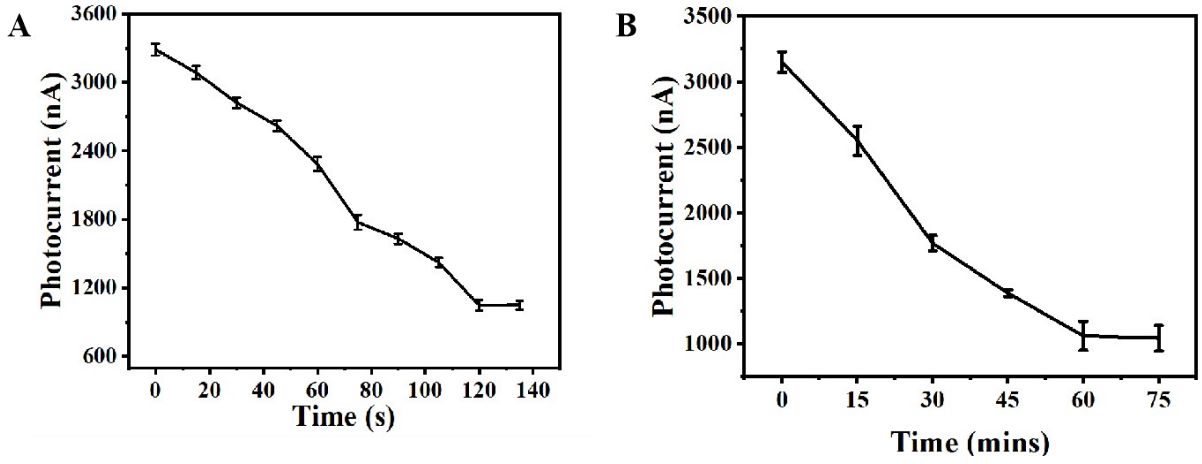


Fig. S6. (A) CHA reaction time; (B) SRCHA amplification time.

Optimization of experimental conditions

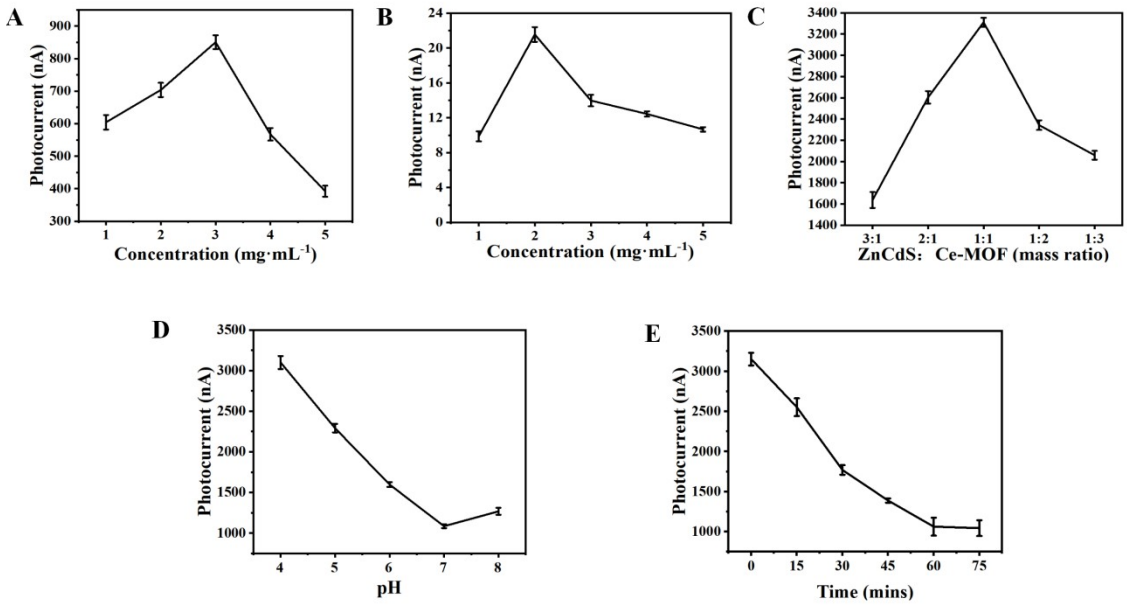


Fig S7. Optimization of (A) ZnCdS concentration; (B) Ce-MOF concentration; (C) ZnCdS:Ce-MOF mass ratio; (D) effect of pH; (E) SRCHA amplification time.

As shown in Fig. S7A, the photocurrent gradually increased as the concentration of ZnCdS rose from 1 mg mL^{-1} to 3 mg mL^{-1}. However, when the concentration reached 4 mg mL^{-1}, the photocurrent decreased significantly, indicating that an excessively high concentration impeded electron transfer and thereby adversely affected the photocurrent. Thus, 3 mg mL^{-1} was selected as the optimal concentration for ZnCdS. From Fig. S7B, five different concentrations of Ce-MOF were tested. The results showed that the photocurrent response was strongest at a concentration of 2 mg mL^{-1}, which was therefore chosen as the optimal concentration for Ce-MOF in subsequent experiments. The test results of the sensor varied

significantly under different experimental conditions. Therefore, various experimental parameters were optimized to ensure accurate and reliable results in the final testing. As shown in Fig. S7C, the photocurrent initially increased and then decreased, reaching its maximum when the mass ratio of the two materials was 1:1. At this ratio, the synergistic effect between ZnCdS and Ce-MOF was strongest. Thus, a ZnCdS-to-Ce-MOF mass ratio of 1:1 was selected as the optimal condition for subsequent experiments. In Fig. S7D, as the pH increased from acidic to neutral, the photocurrent gradually decreased, indicating more efficient progression of the SRCHA reaction. When the pH was further increased to 8, the photocurrent rose again, suggesting that the DNA reaction was inhibited. Therefore, pH 7.0 was selected as the optimal reaction pH. As illustrated in Fig. S7E, the SRCHA amplification first triggers the formation of the H1+H2 duplex structure, which is a key step in the entire biorecognition event. Therefore, the optimal amplification time for SRCHA was investigated. As the amplification time increased, the resulting photocurrent decreased, indicating a more complete reaction of the final product on the electrode. When the time reached 60 minutes, the change in results plateaued, suggesting that the SRCHA amplification was fully complete. Consequently, the SRCHA amplification time was determined to be 60 minutes.

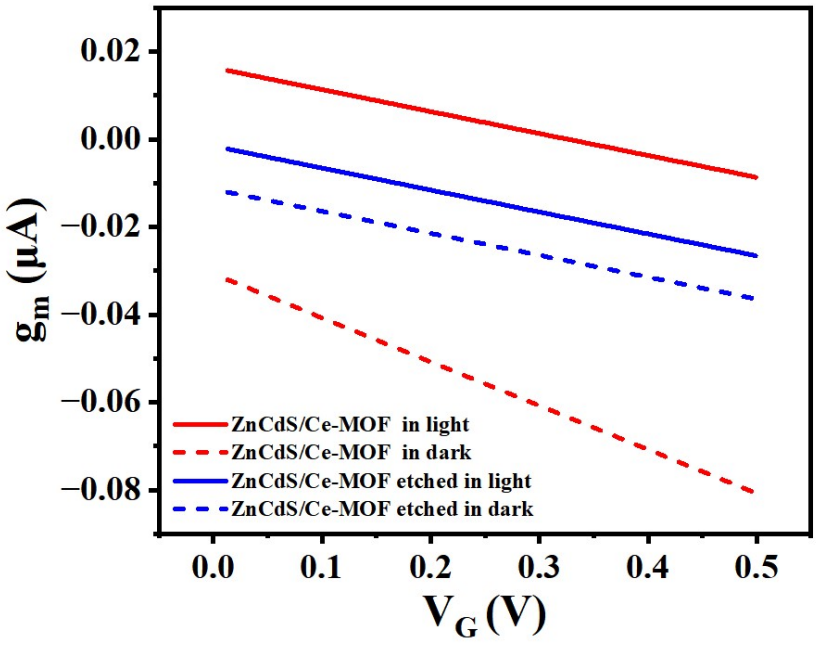


Fig. S8 The transconductance (gm) values of ZnCdS/Ce-MOF and etched ZnCdS/Ce-MOF under dark and illuminated conditions.

References

1. J. Song, H. Zhao, R. Sun, X. Li and D. Sun, *Energy Environ. Sci.*, 2017, **10**, 225-235.
2. Y. F. Zhang, Q. Wang, D. X. Xue and J. Bai, *Inorg. Chem.*, 2020, **59**, 11233-11237.
3. J. Chen, Q. Ma, M. Li, D. Chao, L. Huang, W. Wu, Y. Fang and S. Dong, *Nat. Commun*, 2021, **12**, 3375.