Supporting Information

A portable signal-on self-powered aptasensor for ultrasensitive detection of sulfadimethoxine based on dual amplification of a capacitor and biphotoelectrodes

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Experimental

Reagents.

Cadmium acetate, thiourea, melamine, HNO₃, CuBr, poly (diallyldimethylammonium chloride) (PDDA, MW 100000-200000, 20 % wt. in water), 6-mercapto-1-hexanol (MCH), sulfadimethoxine (SDM), ampicillin (AMP), ibuprofen (IBU), ofloxacin (OFL) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). The SDM aptamer, 5'-GAGGGCAACGAGTGTTTATAGA-3', was synthesized and purified by Sangon Biotech Co., Ltd. (Shanghai, China). Samples of veterinary drugs containing different amounts of SDM were obtained from Huachu Trading Co., Ltd. (Xinxiang, China). Indium tin oxide (ITO) coated glass slides with a surface resistivity of 6–8 Ω /sq were purchased from South China Xiangcheng Science & Technology Co., Ltd. (Guangzhou, China).

Apparatus.

The surface morphology was obtained on a SU 8010 field emission scanning electron microscope (SEM) (Hitachi, Japan) and a Talos F200x transmission electron microscope (TEM) (Thermo Fisher, Netherlands). The crystalline phase was characterized with a Bruker D8 Advance X-ray diffractometer (XRD) (Darmstadt, Germany) using Cu Kα radiation, and the accelerating voltage and applied current were 40 kV and 40 mA, respectively. The energy dispersive spectrum (EDS) and mapping analyses were carried out by using the 4-silicon drift detector (SDD) installed in TEM for exploring elementary component.

All electrochemical and photocurrent measurements were obtained on a CHI660A electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China). A modified electrode, a saturated calomel electrode (SCE), and a platinum wire were employed as the working, reference and counter electrodes, respectively. Electrochemical impedance spectroscopic (EIS) analysis was performed in 0.1 M KCl solution containing 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ at a bias potential of 0.2 V within the frequency range of 0.01 Hz to 100 kHz. The *V-I* curves of the cell were measured with galvanostatic polarization technique.

The power output curves (*P-I* curves) were obtained by plotting the power ($V \times I$) vs. the current (*I*). Two identical portable laser lights with a power of 200 mW at 405 nm were used as the light source to illuminate the photoanode and photocathode. A DMM was used to record the I_{sc} of the PFC which was amplified by the capacitor.

Preparation of g- C_3N_4 /CdS Nanocomposite.

CdS nanoparticles were synthesized using a facilely hydrothermal process.¹ Briefly, cadmium acetate (0.64 g) and thiourea (1.82 g) were added to 60 mL water, and stirred evenly for 0.5 h. Then, the mixture was transferred into a 100 mL Teflon-lined autoclave and reacted at 200 °C for 5 h. The obtained yellow precipitate was centrifuged and washed with water and ethanol for several times, and then dried at 60 °C in a vacuum oven to obtain CdS nanoparticles.

The preparation method of water-dispersible $g-C_3N_4$ was based on our previous work.² Firstly, melamine (5 g) was put into a crucible and calcined at 550 °C for 4 h to obtain bulk C_3N_4 (b- C_3N_4). Then, b- C_3N_4 (1 g) was added to 100 mL of HNO₃ (5 M), and reflux was performed for 12 h at 125 °C. After the reaction was completed, the product was centrifuged and washed with water repeatedly until the supernatant became neutral and dried in an oven at 60 °C. Thus, water-dispersible g- C_3N_4 was obtained for further use.

g-C₃N₄/CdS nanocomposites were synthesized by directly mixing CdS and g-C₃N₄ suspensions. A certain amount of g-C₃N₄ was added to 25 mL of methanol. After ultrasonic treatment for 0.5 h, floral CdS nanoparticles were added to the mixture and stirred for 24 h. Then, the mixture was centrifuged and dried under vacuum at 60 °C.

Construction of PFC.

Prior to construction, the tin-doped indium oxide (ITO) glass substrates were cleaned by successive sonication in acetone, mixed solution of ethanol, 2 M NaOH (v/v, 1:1) and water, respectively. After being dried with nitrogen gas, the ITO electrodes with an exposed geometric area of 0.071 cm² were coated with 8 μ L of g-C₃N₄/CdS (4 g·L⁻¹) and CuBr (8

 $g \cdot L^{-1}$) suspension sreved as the photoanode and photocathode, respectively, and dried in an oven at 60 °C. The PFC was constructed with the as-prepared photoanode and photocathode, and the electrolyte was 0.1 M phosphate buffer solution (PBS) at pH 5.5. Moreover, the cell had two quartz windows to allow the illumination from the light sources on the anode and cathode.

Capacitor-amplified PFC.

The circuit of the entire sensing system was assembled according to Scheme 1. At first, switches i and ii were turned on to charge the capacitor by PFC. After charging for 40 seconds, switch i was turned off while switch iii was turned on to allow the discharge of capacitor through the DMM. As a result, an amplified short circuit current (I_{sc}) was displayed on DMM, but the signal changed quickly with discharging time. The DMM was connected with a computer through a cable to acquire all instantaneous data employed for plotting the I_{sc} curve accurately by software.

Fabrication of sensor and SDM sensing.

The g-C₃N₄/CdS/ITO was incubated with 2 μ L of 2% PDDA solution containing 0.5 M NaCl to make the electrode positively charged, and then put in an oven at 60 °C for 30 min. Afterwards, 8 μ L of electronegative SDM-binding aptamer (ap) solution (1 μ M) was dropped on the aforesaid electrode and incubated at 37 °C for 2 h to immobilize the aptamer on the electrode via electrostatic attraction. To eliminate the nonspecific binding sites of electrode surface, the ap/g-C₃N₄/CdS/ITO electrode was treated with 2 μ L sealing agent MCH (0.5 mM) at 37 °C for 30 min. To perform the recognition between aptamer and SDM, the MCH/ap/g-C₃N₄/CdS/ITO was incubated with 8 μ L SDM solution with different concentrations, and the reaction was allowed to proceed for 2 h at 37 °C. The electrode was rinsed thoroughly with water after each step to remove excess material that was not attached to the electrode, and dried with N₂ flow. Finally, the electrode served as the photoanode of PFC, and the *I*_{sc} amplified by the capacitor was displayed on DMM.

High Performance Liquid Chromatographic analysis.

High Performance Liquid Chromatographic (HPLC) analysis was performed on an Agilent (USA) 1100 module system with a C18 column. The mobile phase used for HPLC experiment consisted of 0.1% acetic acid: acetonitrile in the ratio 70:30 (v/v). The flow rate was 0.6 mL min⁻¹ while injection volume was 10 μ L. The detection was carried out using UV-vis detector. The column effluents were monitored at absorption wavelengths of 265 nm with column temperature of 35±0.1 °C. All measurements were performed at room temperature.

Results and discussion

Materials characterization.

The as-prepared photoanode materials were characterized by TEM. The results indicate that g-C₃N₄ shows a graphite-like layered structure (Fig. S1A) while CdS shows a flower-like structure with a diameter of *ca*. 200 nm (Fig. S1B). From the high-resolution TEM (HRTEM) image (inset of Fig. S1B), the lattice fringe of CdS can be clearly seen. The interplanar spacing of 0.32 nm can be attributed to the (101) plane of CdS. For the g-C₃N₄/CdS composite (Fig. S1C), the morphology has no obvious change as compared with pure CdS. This might be due to the low content of g-C₃N₄ doped in the composite and thin layer of g-C₃N₄. Nevertheless, both g-C₃N₄ and (101) plane of CdS can be found in the HRTEM image of the composite (Fig. S1D). Meanwhile, the crystal nature of the photoanode materials was analyzed by XRD (Fig. S1E). The XRD pattern of CdS shows primary diffraction peaks at 24.89°, 26.53°, 28.22°, 36.71, 43.75° and 47.95°, which are matched well with the (100), (002), (101), (102), (110) and (103) planes of hexagonal CdS (JCPDS 75-1545).³ This result suggests the high crystalline quality of CdS, consistent with the HRTEM observation. The two diffraction peaks of g-C₃N₄ at 13.17° and 27.52° correspond to the (100) and (002) peaks of the graphitized phase, respectively.⁴ For g-C₃N₄/CdS, the XRD pattern is not significantly

different from that of pure CdS, which should also be due to the low content of $g-C_3N_4$ doped in the composite. Further, the EDS spectrum of the composite (Fig. S1F) displays the sample is composed of C, N, Cd and S elements, corfirming the successful synthesis of the g- C_3N_4 /CdS. The elemental mapping results (Fig. S2) shows that all the elements are homogeneously distributed in randomly selected test areas.

Additionally, the cathode material of commercial CuBr was also characterized. The SEM image shows the rod-like morphology of CuBr (Fig. S3A). According to XRD analysis (Fig. S3B), five diffraction peaks at 27.12°, 31.40°, 45.02°, 53.40° and 65.54° are indexed to the JCPDS card 06-0292, attributed to the (111), (200), (220), (311) and (400) planes of γ -CuBr.⁵

EIS analysis.

The electrode modification process was monitored by EIS using $[Fe(CN)_6]^{3-/4-}$ as the redox probe (Fig. S5). From the diameter of the Nyquist plot of EIS, the electrontransfer resistance (R_{et}) value of the g-C₃N₄/CdS/ITO electrode is estimated to be 130 Ω (curve a in Fig. S5). When the recognition element aptamer is immobilized on g-C₃N₄/CdS/ITO (curve b in Fig. S5), the R_{et} value increases, to owing the prohibition of electron transfer by low conductive aptamer molecules. After ap/g-C₃N₄/CdS/ITO is incubated with SDM, the R_{et} value increases dramatically (curve c in Fig. S5), showing the formation of the aptamer-SDM complex which further hinders the electron transfer.

Optimization of experimental conditions.

To achieve the best performance of the developed capacitor-amplified self-powered sensor, the experimental conditions were optimized. Firstly, the effect of $g-C_3N_4$ content in g- C_3N_4/CdS composite on the photocurrent response of the photoanode was investigated (Fig. S8). The result indicates that the photoanode modified with 4% g- C_3N_4 encapsulated CdS exhibits the optimal photoelectrocatalytic activity. Afterward, the effects of $g-C_3N_4/CdS$ concentration on photoanode and CuBr concentration on photocathode on the P_{max} responses S-6

of the fabricated PFC were researched. The results show that g-C₃N₄/CdS concentration of 4 g L⁻¹ (Fig. S9) and CuBr concentration of 10 g L⁻¹ (Fig. S10) are the optimum concentrations for constructing the PFC. Moreover, the effect of aptamer concentration on the P_{max} response of PFC was studied. As shown in Fig. S11, the P_{max} decreases in the aptamer concentration range of 0.1 to 1.0 µM because more aptamer molecules are assembled on the photoanode. When the concentration of aptamer is greater than 1 µM, the P_{max} levels off, implying that the aptamer molecules assembled on the photoanode are saturated. Finally, the influence of charging time for the capacitor was studied. As illustrated in Fig. S12, both the $I_{\text{sc-max}}$ and voltage values of the capacitor increase with increasing the charging time until 40 s. Accordingly, 4% g-C₃N₄ content in g-C₃N₄/CdS composite, 4 g L⁻¹ g-C₃N₄/CdS on photoanode, 10 g L⁻¹ CuBr on photocathode, 1 µM aptamer and 40 s charging time of the capacitor were used as the optimal conditions for the sensor in this work unless otherwise indicated.



Fig. S1. TEM images of (A) g-C₃N₄, (B) CdS and (C) g-C₃N₄/CdS nanocomposites. Inset of Fig. 1B shows HRTEM image of CdS. (D) HRTEM image of g-C₃N₄/CdS. (E) XRD patterns of g-C₃N₄, CdS and g-C₃N₄/CdS. (F) EDS spectrum and (G) Elemental mapping of g-C₃N₄/CdS.



Fig. S2. Elemental mapping of $g-C_3N_4/CdS$.



Fig. S3. (A) SEM image and (B) XRD pattern of CuBr. The inset of A shows high magnification image.



E / **V Fig. S4.** Polarization curves of (a) $g-C_3N_4/CdS/ITO$ photoanode and (b) CuBr/ITO photocathode in 0.1 M PBS (pH 5.5) under photoirradiation at 2 mV s⁻¹.



 Z / Ω Fig. S5. Nyquist plots of different modified photoanode: (a) g-C₃N₄/CdS/ITO, (b) ap/g-C₃N₄/CdS/ITO and (d) ap/g-C₃N₄/CdS/ITO incubated with 200 nM SDM.



Fig. S6. (A) *V-I* and (B) *P-I* curves of PFCs consisted of different electrodes: (a) $g-C_3N_4/CdS/ITO$ photoanode and CuBr/ITO photocathode, (b) CdS/ITO photoanode and CuBr/ITO photocathode, (c) $g-C_3N_4/CdS/ITO$ photoanode and Pt cathode.



Fig. S7. The I_{sc-max} reading photos by DMM of (A) capacitor that is not charged by PFC, (B) individual PFC, and (C) capacitor is charged by PFC. The insets of A-C show the switch conditions on the circuit when testing; and the marked switches are turned on while the unmarked switch is turned off.



Fig. S8. Effect of $g-C_3N_4$ content in complex $g-C_3N_4/CdS$ on the photocurrent response.



Fig. S9. Effects of g-C₃N₄/CdS concentration on photoanode on the P_{max} of the fabricated PFC.





Fig. S11. Effect of Aptamer concentration on the P_{max} response of the sensor.



Fig. S12. Effect of charging time for the capacitor on the I_{sc-max} and voltage signals read out by DMM.

Table S1. Contrast of determination property for the fabricated SDM self-powered sensor								
witł	other detection methodologies.							
	Detection strategy	Lincority rongo / nM	I ODa / mM	Dof				

Detection strategy	Linearity range / nM	LOD ^a / nM	Ref.
Photoelectrochemical sensor	1-100	0.55	6
Optical images of liquid crystals	32-644	32	7
Photoelectrochemical aptasensor	0.5-80	0.1	8
Electrochemical aptasensor	1-1000	1	9
colorimetric aptasensor	0.16-3.22	0.16	10
PFC-based self-powered sensor	0.1-500	0.057	This work

^aLOD: limit of detection

Sample	Label content	Detected by	RSD	Detected by	Relative
No.	(g/100 g)	sensor (g/100 g)	(%)	HPLC (g/100 g)	error (%)
1	10.00	9.572	4.28	9.122	4.93
2	15.00	15.23	5.44	15.91	-4.27
3	30.00	29.68	3.72	29.30	1.30

Table S2. Detection of SDM content in different veterinary drug samples with the proposed self-powered sensor (n = 3).

References

- 1 S. Han, Y. C. Pu, L. Zheng, J. Z. Zhang and X. Fang, J. Mater. Chem. A, 2015, 3, 22627-22635.
- 2 Y. Liu, K. Yan and J. Zhang, ACS Appl. Mater. Inter., 2016, 8, 28255-28264.
- 3 M. Shaban, M. Mustafa and A. M. El Sayed, *Mater. Sci. Semicon. Process.*, 2016, **56**, 329-343.
- 4 Q. Zhu, B. Qiu, M. Du, J. Ji, M. Nasir, M. Xing and J. Zhang, ACS Appl. Mater. Inter., 2020,
 8, 7497-7502.
- 5 T. Subashini, B. Renganathan, A. Stephen and T. Prakash, *Mater. Sci. Semicon. Process.*, 2018, **88**, 181-185.
- 6 O. K. Okoth, K. Yan, Y. Liu and J. Zhang, Biosens. Bioelectron., 2016, 86, 636-642.
- 7 J. Du, Q. Jiang, X. Lu, L. Chen, Y. Zhang and X. Xiong, Analyst, 2019, 144, 1761-1767.
- 8 X. Dang, H. Zhao, X. Wang, T. Sailijiang, S. Chen and X. Quan, *Microchim. Acta*, 2018, 185, 345.
- 9 Z. Yang, X. Ding, Q. Guo, Y. Wang, Z. Lu, H. Ou, Z. Luo and X. Lou, Sens. Actuators, B, 2017, 253, 1129-1136.
- 10 X. X. Chen, Z. Z. Lin, C. Y. Hong, Q. H. Yao and Z. Y. Huang, Food Chem., 2020, 309, 125712.