Supporting Information

Zinc vacancies mediated electron−hole separation in ZnO nanorod arrays for high-sensitive organic photoelectrochemical transistor aptasensor

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Content

1. Materials and Apparatus

1.1 Experimental materials

Zinc acetate ($Zn(Ac)_2$, AR) was purchased from Shanghai Macklin Biochemical Co., Ltd. Methenamine ($C_6H_{12}N_4$, AR), zine nitrate ($Zn(NO_3)_2 \cdot 6H_2O$, AR), Choline chloride ($C_5H_{14}ClNO$, AR), Ethylene glycol ($C_2H_6O_2$), Sodium Dihydrogen Phosphate (NaH_2PO_4, AR), Dibasic Sodium Phosphate (Na_2HPO_4, AR)， Chitosan (CHI, AR, 99.0%)， Glutaraldehyde (GA, AR) and Bovine Serum Albumin (BSA, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Ochratoxin A (OTA), aflatoxin B1 (AFB1) were purchased from Sigma-Aldrich (USA). Other interferents including ochratoxin B (OTB), ochratoxin C (OTC) and T-2 toxin were purchased from Puhuashi Technology Company, Beijing. Phosphate-buffered saline (PBS) of different pH were prepared by mixing 0.1 mol/L stock solutions of NaH_2PO_4 and Na_2HPO_4 at specific ratios, and the washing buffer was prepared by 0.01 mol/L PBS (pH 7.4). Ultrapure water was used throughout the experiment.

OTA aptamer was purchased from Sangon Biological Engineering Technology & Services Co. Ltd, Shanghai, and the sequences as follows:[1] 5'-NH_2-GAT CGG GTG TGG GTG GCG TAA AGG GAG CAT CGG ACA-3'.

1.2 Apparatus

The morphologies of nanomaterials were observed by scanning electron microscopy (SEM, JSM-7800F, Japan) and transmission electron microscopy (HR-TEM, JEOL JEM-AFM, Japan). X-ray diffractometer equipped with (Bruker, Germany) high-intensity Cu Kα (λ = 1.5406) radiation was used to record the X-ray diffraction (XRD) pattern. The absorption spectrum was tested by UV-vis spectrophotometer (UV2550, Shimadzu, Japan) from 200 to 1000 nm with $BaSO_4$ as reflectance sample. X-ray photoelectron spectroscopy (XPS) measurements were measured on Thermo Scientific K-Alpha X-ray photoelectron spectrometer with Al Kα X-rays as the excitation source. Electron paramagnetic resonance (EPR) spectra were recorded at room temperature on an EPR spectrometer (Bruker EMX PLUS). The photoluminescence (PL) spectra of the samples were obtained at room temperature with a FLUOROMAX-4C-TCSPC. The photoelectrochemical (PEC), electrochemical impedance spectroscopy (EIS), and cyclic voltammograms (CV), Mott-Schottky measurements were performed using a conventional three-electrode system (CHI 660E, Chen Hua Instruments Co., Ltd. Shanghai, China). The photo-induced OECT measurements were monitored by a multichannel potentiostat (CHI 1010C, Chen Hua Instruments Co., Ltd. Shanghai, China). All of the electrochemical measurements used Xe lamp (PLS-SXE 300C (BF) Beijing perfect Light Technology Co., Ltd.) as the light irradiation source for the whole detection.

2. Experimental Section

2.1 Preparation of ZnO electrodes.

Vertically aligned ZnO nanorod arrays were directly grown on FTO by a hydrothermal way. First, the F-doped SnO_2 (FTO) electrodes were ultrasonic cleaned, respectively, with toluene, acetone, ethanol and deionized water for 15 min, and then dried with nitrogen. The cleaned FTO electrodes were then coated with ZnO liquid precursors. Subsequently, $Zn(Ac)_2$ (0.0549 g) were added to ethanol (50 mL) to obtain a ZnO liquid precursors. And then the ZnO liquid precursors was spun onto the FTO surface at 500 rpm, 30s; 3000 rpm, 30s using spin coater. After the FTO electrodes were annealed in muffle furnace at 320 ^{o}C for 60 min, they were placed with the conductive surface downward in the growth solution of 40mM methenamine and 40mM zine nitrate and hydrothermally treated under 95 ^{o}C for 5h. Finally, the ZnO electrodes were prepared by washing with deionized water and ethanol and drying in drying oven at 60 ^{o}C for 2 h. The obtained ZnO electrodes were calcined at 450 °C for 2 h in air, named ZnO-450 °C.

2.2 Preparation of $Zn_{1-x}O$ electrodes.

The DES was formed at room temperature by combining choline chloride (Meryer, 99%) and ethylene glycol (Sigma–Aldrich, 99.8%) in a 1:2 molar ratio. The ZnO-450 °C electrode was immersed in DES solution, and the temperature was raised to 80°C and kept for 10 h. Then take the ZnO-450 °C electrode out of the DES and rinse it repeatedly with Milli-Q water, named $Zn_{1-x}O$.

2.3 Preparation of channel device of the OPECT sensor.

Firstly, screen printing device specifications were customized from Qing Dao Technology Co., Ltd. as designed, in which the length and width of the channel were 6mm*0.2mm. Conductive carbon paste was printed on polyethylene glycol terephthalate (PET) substrate to make source electrode and drain electrode. Then the PEDOT:PSS was printed on the top of the channel through screen printing technology to form the layer of thin film. Last, these devices were sealed with polyethylene plastic (PE) film for later use.

2.4 Fabrication of the OPECT aptasensor.

All aptamer molecules were dissolved in PBS (0.1 M, pH = 7.4). Aptamer probes were immobilized onto the ZnO NEAs gate electrodes via the classic coupling reaction between the amino ($-NH_2$) groups on aptamer probes and aldehyde (-CHO) groups on glutaraldehyde (GA). Firstly, 10 μL chitosan solution (CHI, 0.1%) with $-NH_2$ was coated onto the electrodes surface and placed the electrodes under an infrared light to dry. The gate electrodes were further modified with 20 μL glutaraldehyde (GA, 2.5%) by incubating at room temperature for 1 h to combine the $-NH_2$ on CHI with -CHO on GA, then washed with PBS carefully. Subsequently, aptamer solution (20 μL, 3 μM) with $-NH_2$ was added to the surface of the gate electrode and incubated at 4 °C overnight (6 h) to obtain Apt/ $Zn_{1-x}O$. Then bovine serum protein (BSA, 20 μL, 3%) was further modified on the electrode surface and incubated at room temperature for 30 min to seal unbound -CHO groups of GA. Finally, the electrodes were washed with PBS solution and dried at room temperature.

For the hybridization reaction, aptamer targets (OTA toxin, 20 μL) with different concentrations were dropped on the Apt/ $Zn_{1-x}O$ gate electrodes for 45min incubation at 37 °C. Then, the OTA/Apt/ZnO NEAs gate electrodes were obtained by washing carefully three times with PBS solution to remove the unhybridized OTA toxin.

2.5 Electrical measurements

OPECT devices were tested in the electrolyte of PBS solution (0.1M, pH 7.4). For transfer characteristics (I_{DS}-V_G), the channel current I_{DS} was measured as a function of gate voltage V_G under a constant drain voltage $V_{DS} = -0.2$ V. The channel current I_{DS} as a function of time (I_{DS}-time) was measured under constant gate and drain voltages ($V_{DS} = -0.2$ V, $V_G = 0$ V) under illumination.

For the traditional PEC measurements, the PBS solution (0.1M, pH 7.4) was also used as the electrolyte. The photocurrent was measured with a three-electrodes system (a modified FTO electrode as the working electrode, a saturated calomel electrode as the reference electrode, and a Pt wire as the counter electrode) at a constant potential of 0 V. The photovoltage, electrochemical impedance spectroscopy (EIS), cyclic voltammograms (CV) and Mott-Schottky were also tested using a three-electrode system (a modified FTO electrode as the working electrode, a saturated calomel electrode as the reference electrode, and a Pt wire as the counter electrode). The EIS tests were recorded in 0.1 M KCl solution containing $Fe(CN)_6^{3-/4-}$ (5 mM) in a frequency range from 0.1 Hz to 100 kHz; The open circuit potential was used as a DC bias potential, on which amplitude of the AC potential was 5 mV. All the modified FTO electrodes ensure the same quality of material in the same working area.

2.6 The detection process of actual sample.

The preprocessing of the actual sample solution are as follows. The corn kernels were purchased from a local market. After full crushing, the 25 g of corn flour was mixed with 5 g of NaCl evenly and then transferred into a volumetric flask and diluted to 100 mL with 80% methanol. Subsequently, the mixture was homogenized and extracted at high speed for 2 min. After filtration, the extract was diluted 5 times for future use. Prior to the addition of standard solution at each concentration, the liquid chromatography−mass spectrometry was used to ensure that there was no OTA contamination. Subsequently, OTA toxin standard solutions were spiked into the diluted milk, yielding final concentrations of 10 $pg \cdot L^{-1}$, 100 $pg \cdot L^{-1}$ and 5 $ng \cdot L^{-1}$. Finally, the recoveries of three different concentrations of OTA toxin in the spiked corn flour samples were obtained using the OPECT aptasensor.

3. Results and Discussion

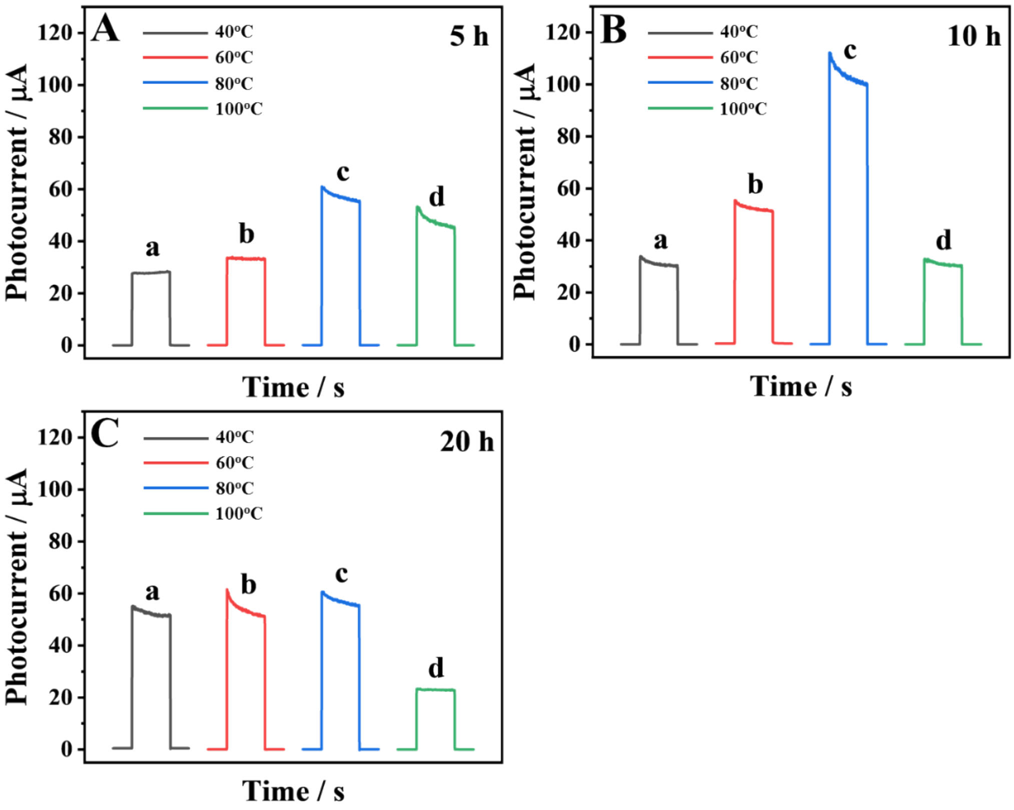

Fig. S1 Photocurrent of DES treated ZnO electrode at different reaction temperatures for different reaction times measured in 0.1 M PBS solution.

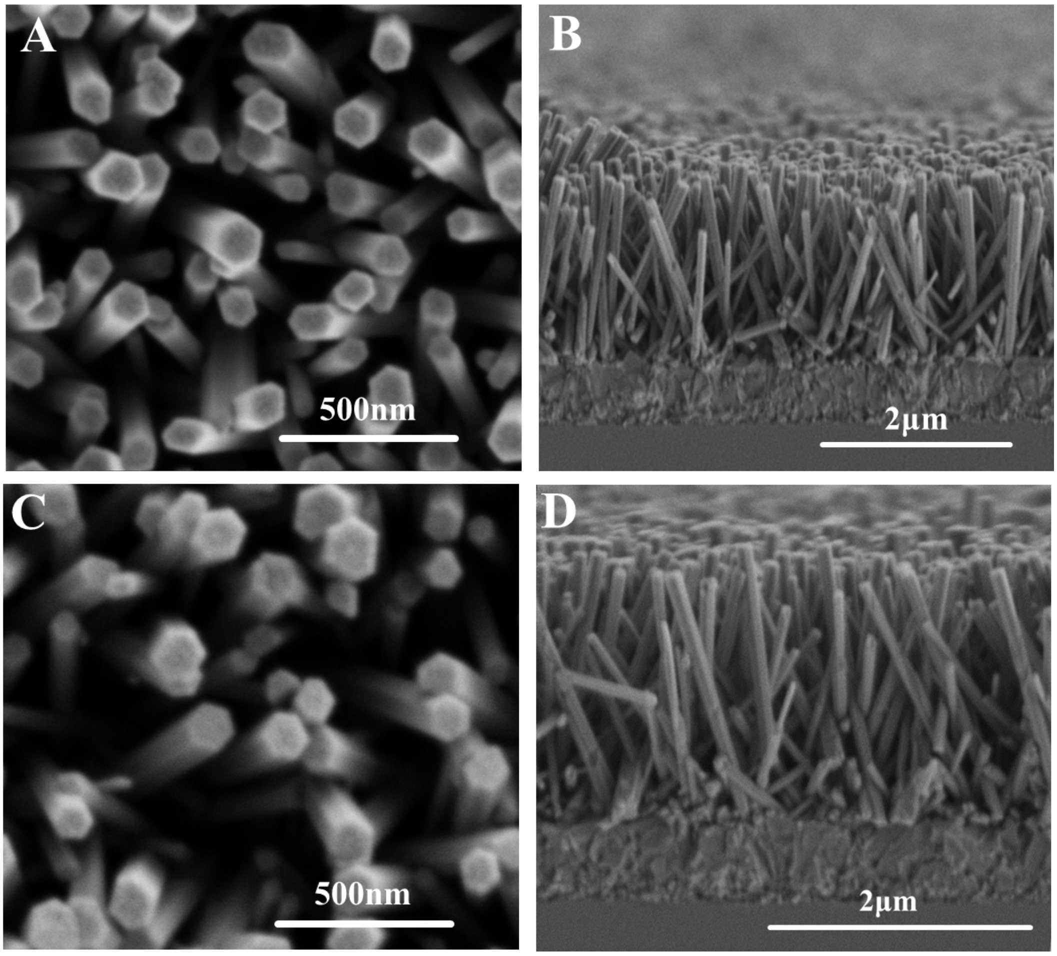

Fig. S2 SEM image of (A) top-view and (B) cross-sectional ZnO in different scales. SEM image of (C) top-view and (D) cross-sectional $Zn_{1-x}O$ in different scales.

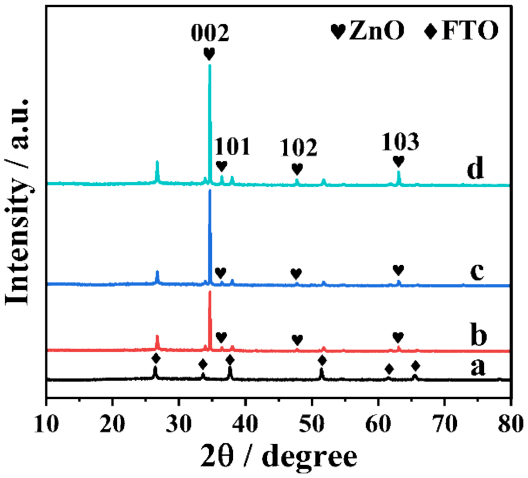

Fig. S3 XRD of FTO (a), ZnO (b) ZnO-450 °C (c) and $Zn_{1-x}O$ (d).

The crystallinity and phase purity of the as-prepared samples are analyzed by X-ray diffraction (XRD). The peaks of FTO substrate are shown in Fig. S3 (a). In addition, the diffraction peaks appearing at 2θ of 34.4° (002), 36.3° (101), 47.5° (10), 62.9° (103), and 72.6° (004) are well-matched with peaks of the hexagonal structure of ZnO (JCPDS no. 74-0534) (Fig. S3 b, c, d). After calcination and DES treatment, the crystallinity of the ZnO has been improved. The enhanced relative intensity of the (002) peak clearly reveals a highly preferred (002) orientation in the nanorod.

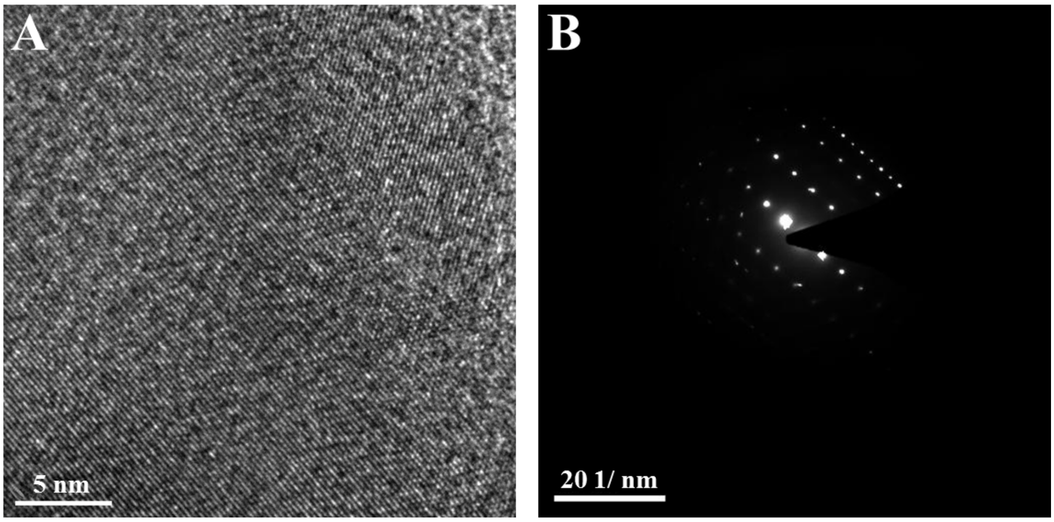

Fig. S4 HRTEM images (A) and SAED diffraction pattern (B) of $Zn_{1-x}O$.

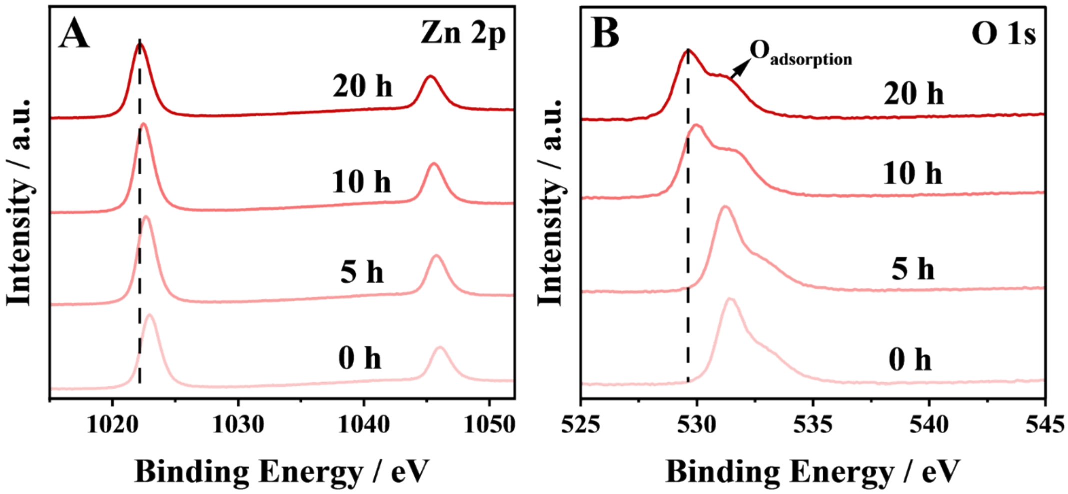

Fig. S5 XPS spectra of Zn 2p (A) and O 1s (B) for DES treated ZnO at 80 °C in different reaction times.

It can be clearly observed that all the core level peaks Zn 2p and O 1s of the DES treated ZnO are consistently shifted towards low binding energies as a function of treatment time. This is because the binding energy of the core level electrons is measured against the Fermi level of the sample holder[2], which is equilibrated with the Fermi level of the sample, and the presence of Zn_{vac} causes the changes of Fermi levels (Fig.2 C).

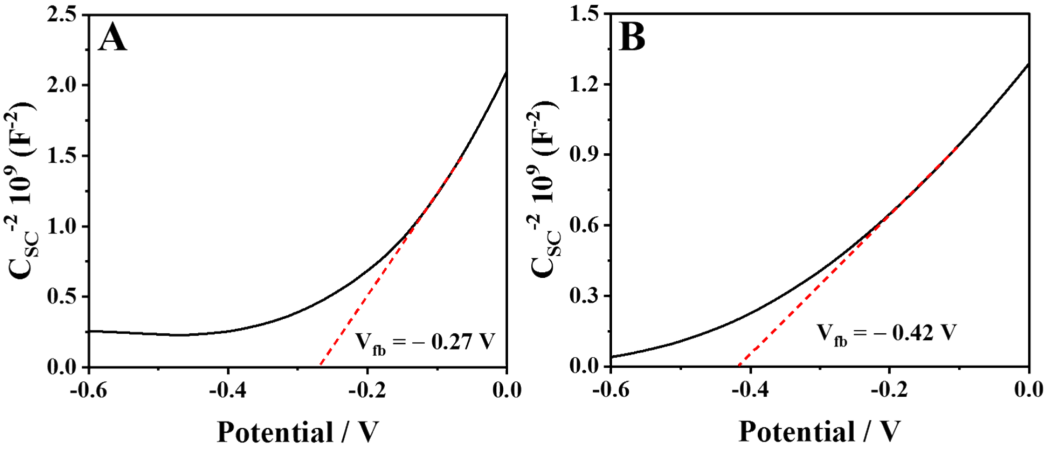

Fig. S6 Mott−Schottky plots of ZnO (A) and $Zn_{1-x}O$ (B) measured in 0.5 M Na_2SO_4 solution at a measuring frequency of 100 Hz.

The V_{fb} of the electrodes can be calculated by making the intersection of the extension line of the Mott−Schottky diagram and the horizontal axis.[3] According to Fig. S6 A and B, the V_{fb} of ZnO and $Zn_{1-x}O$ were -0.27 V vs. SCE (0.38 V vs. RHE) and -0.42 V vs. SCE (0.23 V vs. RHE). Thus, the E_{CB} of ZnO and $Zn_{1-x}O$ is 0.18 and 0.03 V, which is 0.2 V more negative than that of the V_{fb}.[4] Based on the formula $E_g = E_{VB} + E_{CB}$, the energy band positions of ZnO and $Zn_{1-x}O$ can be schematically drawn in Fig. 2C.

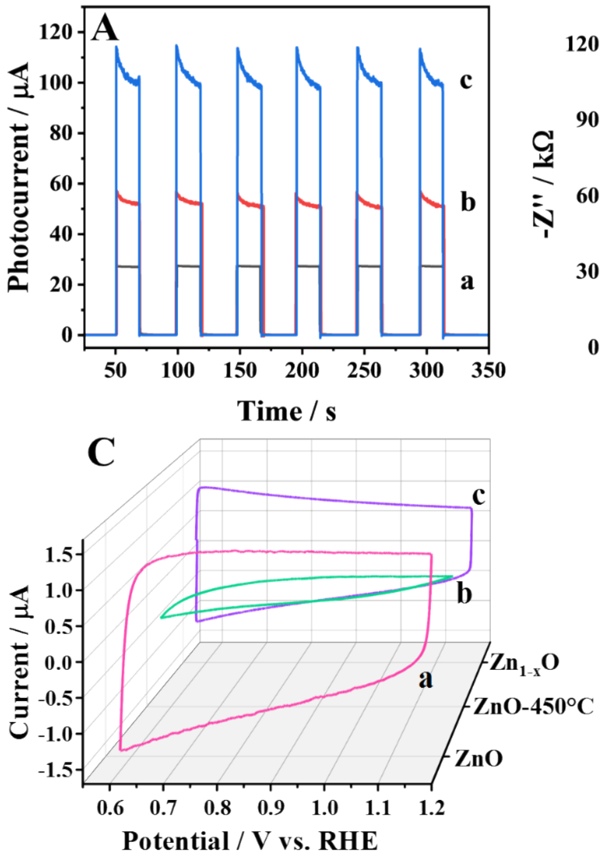

Fig. S7 (A) Photocurrent of the ZnO (a), ZnO-450°C (b) and $Zn_{1-x}O$ (c) electrodes in several repeated light on/off cycles in PEC system. (B) EIS Nyquist plots of ZnO (a), ZnO-450°C (b) and $Zn_{1-x}O$ (c). (C) CV of the ZnO (a), ZnO-450°C (b) and $Zn_{1-x}O$ (c) at a scan rate of 50 mV/s.

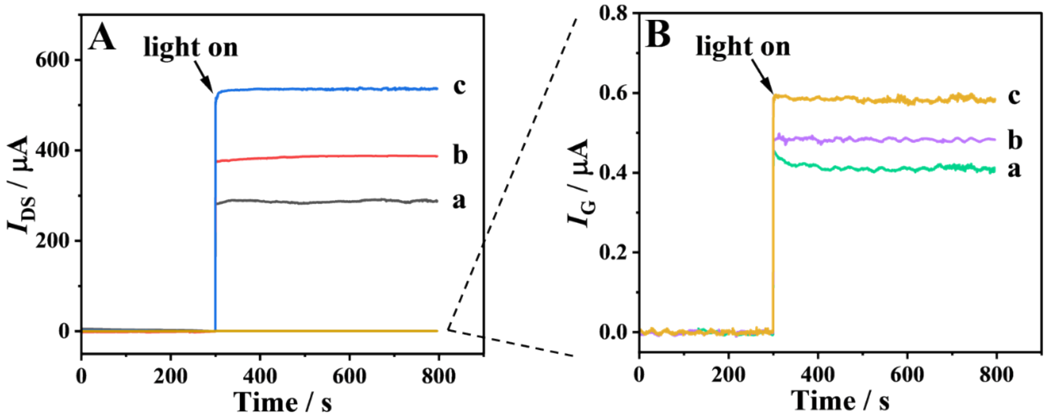

Fig. S8 (A) I_{DS} of ZnO (a), ZnO-450°C (b) and $Zn_{1-x}O$ (c) gate electrodes; and (B) I_G of the ZnO (a), ZnO-450°C (b) and $Zn_{1-x}O$ (c) gate electrodes of the OPECT device under illumination (I-time, $V_G = 0$ V, $V_{DS} = -0.2$ V)

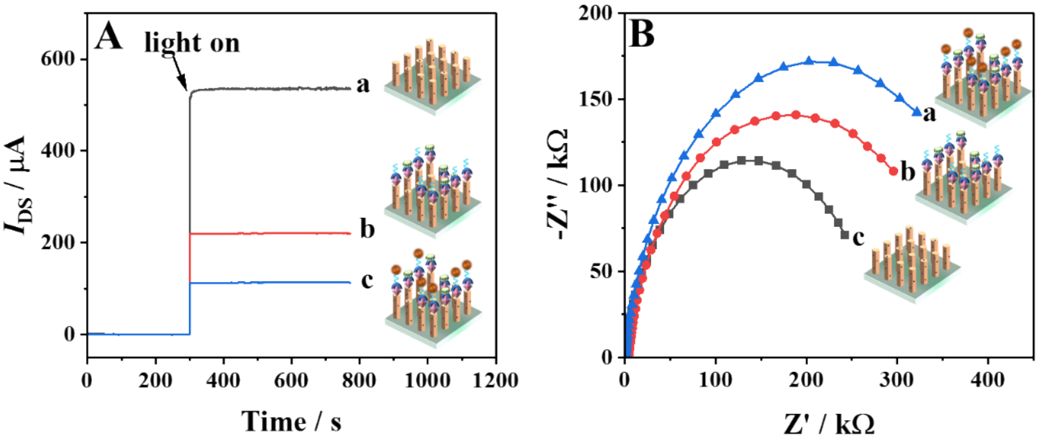

Fig. S9 (A) I_{DS} of $Zn_{1-x}O$ (a), Apt/$Zn_{1-x}O$ (b) and OTA/Apt/$Zn_{1-x}O$ (c) gate electrodes of the OPECT aptasensor. (B) EIS Nyquist plots of $Zn_{1-x}O$ (a), Apt/$Zn_{1-x}O$ (b) and OTA/Apt/$Zn_{1-x}O$ (c).

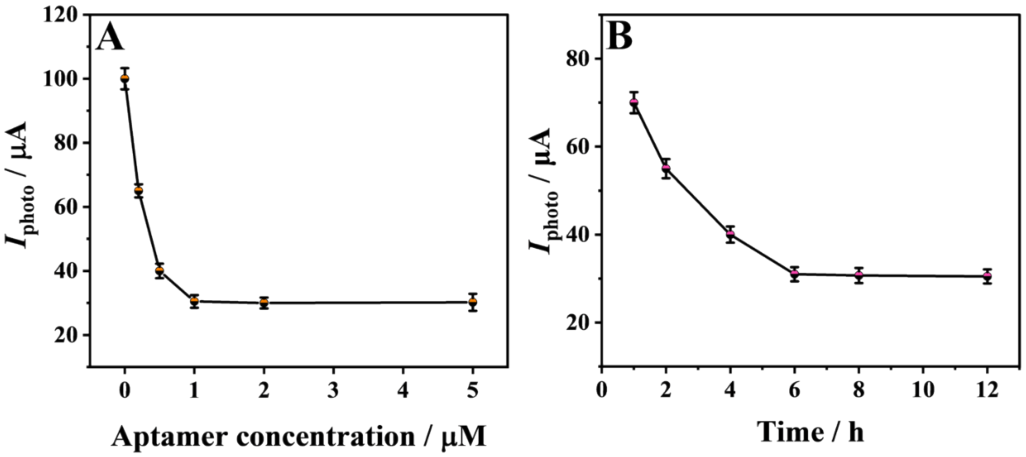

Fig. S10 (A) Effect of aptamer concentration on current of $Zn_{1-x}O$ electrode. (B) Effect of incubation time of aptamer on current of $Zn_{1-x}O$ electrode.

In addition, the concentration of the aptamer modified onto the gate electrode has an impact on the current for the device. To obtain the best OPECT response, the concentration of the aptamer was optimized. The effects of different concentrations of OTA aptamers on the photocurrent in PEC device are illustrated in Fig. S10 A. When the concentration of OTA aptamer increased to 1μM, the photocurrent intensity tended to be stable. Therefore, 1 μM was optioned as the optimal concentration to modify on the gate electrode. The incubation time of the aptamer was also optimized Fig. S10 B. 6 h was optioned as the optimal incubation time of the aptamer to modify on the gate electrode.

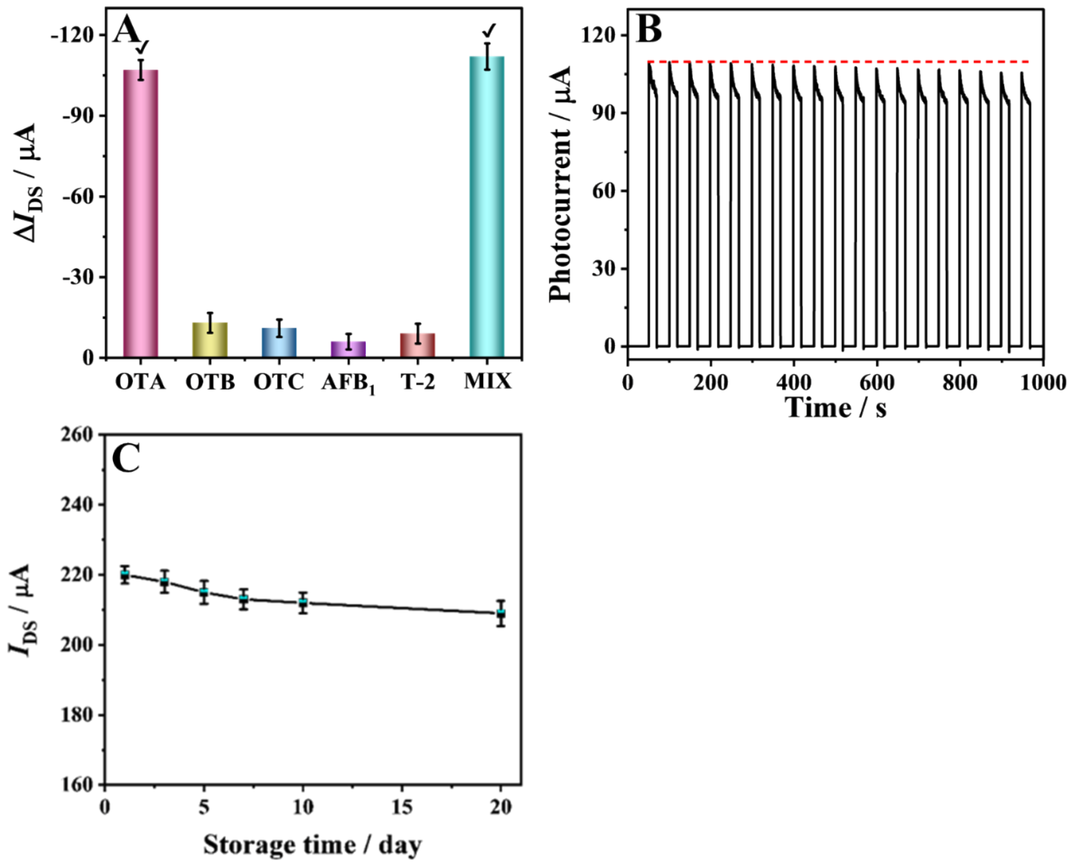

Fig. S11 (A) The selectivity of the photo-induced OECT aptasensor. (B) The stability evaluation of $Zn_{1-x}O$ electrode for 1000 s. (C) The long-term storage stability of the OPECT aptasensor.

Long-term storage stability (Fig. S11C): After the gate electrodes were modified with aptamers and stored them in the refrigerator (4°C) for 1, 3, 5, 7, 10 and 20 days. Then, the gate electrodes were taken out and conducted OPECT test.

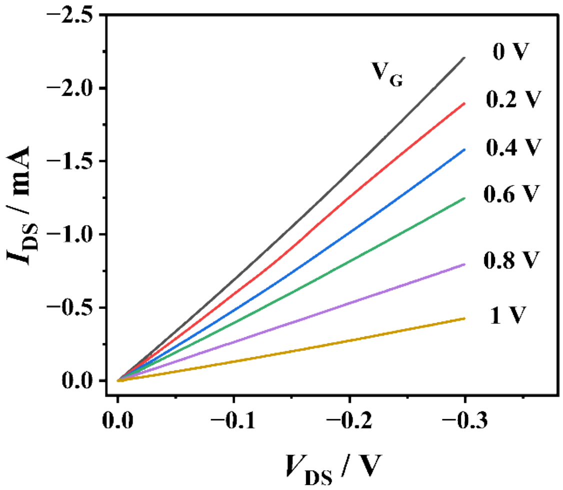

Fig. S12 The output characteristics (I_{DS}-V_{DS}) of the OPECT device with $Zn_{1-x}O$ gate electrode.

The output characteristic (I_{DS}-V_{DS}) with different fixed V_G steps (from 0 to 1 V), showed V_G-dependent on/off states of the device and the trend was consistent with the transfer characteristic curves.

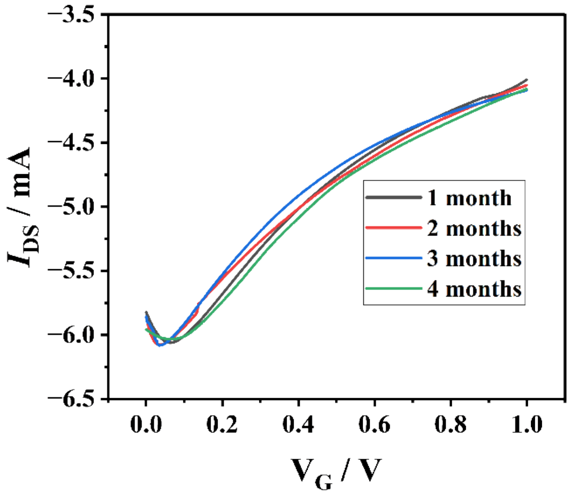

Fig. S13 The storage stability of the source and drain electrodes.

The storage stability of the source and drain electrodes for 1, 2, 3, 4 months has been tested showing excellent long-term storage stability. Up to now, the preparation time of the source and drain electrodes have been four months. We estimate that it can be stored for six months at least because the source and drain electrodes were sealed with polyethylene plastic film which separates PEDOT:PSS and air well.

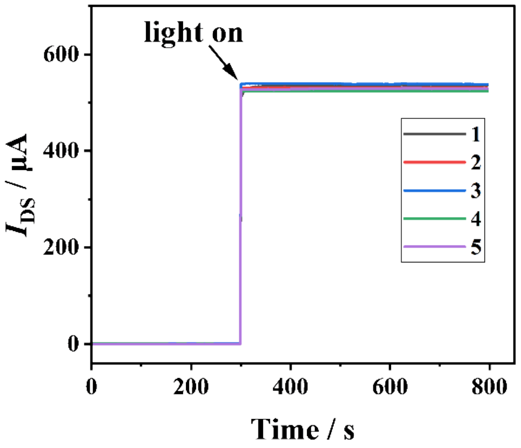

Fig. S14 The repeatability for gate electrodes and channel in OPECT device.

After 5 times tested, the I_{DS} signal did not change significantly showing good repeatability.

Table S1. Determination of OTA toxin in corn flour samples using the OPECT aptasensor (n = 3).

Sample	Added (ng/L)	Found (ng/L)	Recovery (%)	RSD (%)
1	0	0	--	--
2	0.01	0.0097	97.0	4.8
3	0.1	0.0957	95.7	6.3
4	5	5.01	100.2	3.6

Table S2. Comparison with other detection methods for detecting OTA toxin.

Methods	Liner range (μg/L)	Detection limit (ng/L)	Refs.
Multiplexed self-powered sensor	0.001-20	0.18	5
Electrochemiluminescence Aptasensor	0.5-4	170	6
Electrochemiluminescence biosensing platform	0.00001-0.1	0.0047	7
Photoelectrochromic Sensor	1-100	330	8
Photoelectrochemical sensor	0.000005-10	0.00173	9
Organic photo-electrochemical transistor aptasensor	0.000005-50	0.00167	This work

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