Electronic Supplementary Information (ESI) for

$ZnIn_2S_4$@ReS_2/$AgInS_2$-based photoelectrochemical aptasensor for the ultrasensitive detection of Kanamycin

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S1 Experimental Section

S1.1 Materials

Sodium chloride (NaCl) was obtained from Damao Chemical Reagent Factory (Tianjin, China). Disodium phosphate (Na_2HPO_4) , L-ascorbic acid (AA), potassium ferricyanide ($K_3Fe(CN)_6$), potassium chloride (KCl), indium chloride tetrahydrate ($InCl_3·4H_2O$), indium nitrate ($In(NO_3)_3$), 3-mercaptopropionic acid (MPA),thiourea and ethylene glycol (EG) were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Potassium ferrocyanide trihydrate ($K_4Fe(CN)_6·3H_2O$) was ordered from Guangfu Fine Chemical Research Institute (Tianjin, China). Sodium dihydrogen phosphate dihydrate ($NaH_2PO_4·2H_2O$), Zinc acetate dihydrate ($Zn(CH_3COO)_2·2H_2O$), thioacetamide (TAA), silver nitrate ($AgNO_3$) and sodium sulfite were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Rhenium acid ammonium (H_4NO_4Re) was purchased in Wengjiang Chemical Reagent Co., Ltd. (Guangdong). 6-Mercaptohexanol (MCH) was acquired from Energy Chemical Reagent Co., Ltd. (Shanghai, China). All of the chemicals were analytical grade and directly used without further purification. The DNA oligonucleotides were obtained from Sangon Biotechnology Co. Ltd. (Shanghai, China).

The nucleic acids sequences used in this work are shown below:

Name	Sequences (5′ to 3′)
H-DNA	SH-TTTTTTTCGGCTTGGGGGTTGAGGCTAAGCCGA-NH_2
DNA_2	TCGGCTTAGCCTCAACCCCCA

S1.2 Instrumentations

The PEC measurement and electrochemical impedence spectroscopy (EIS) were carried out on the CHI 660D electrochemical workstation (CH Instruments, China). The working system is a traditional three-electrode system, the modified FTO electrode was used as the working electrode, Ag/AgCl (saturated KCl) electrode is the reference electrode and the platinum wire electrode is the counter electrode. A full-

band xenon lamp (Nanjing Yan'an Special Lighting Factory, China) was used as the light source. The applied voltage is 0.0 V and the switching time interval is 20 s. Scanning electron microscope (SEM) images were carried out with S-4800 scanning electron microscope (Hitachi Ltd., Japan). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were carried out with JEM-2100 transmission electron microcopy (JEOL Ltd., Japan). X-ray photoelectron spectroscopy (XPS) was performed with an ES-CALAB 250 X-ray photoelectron spectroscopy (Thermo Ltd, USA). The ultraviolet-visible (UV-vis) absorption spectrum was recorded in the UV-3600 UV spectroscopy (Shimadzu Co., Ltd., Japan)

S1.3 Synthesis of $ZnIn_2S_4$, ReS_2 and $ZnIn_2S_4/ReS_2$ heterojunction

Briefly, 0.2195 g $Zn(CH_3COO)_2 \cdot 2H_2O$ and 0.5863 g $InCl_3 \cdot 4H_2O$ were dissolved in 60 mL ultrapure water, and then 0.4508 g TAA was added into the solution. After stirring for 30 min, the mixture was transferred into a 100 mL teflon-lined autoclave and maintained at 160°C for 12 h. The product was collected by centrifugation and then washed several times with ultrapure water and ethanol, and dried at 60°C for 12 h.

ReS_2 was synthesized by a simple one-step hydrothermal process. 0.1475 g H_4NO_4Re and 0.1890 g CH_4N_2S were added to 35 mL ultrapure water and magnetic stirred until dissolved completely. Subsequently, the above solution was then transferred into a 50 mL teflon-lined autoclaveand and heated at 200℃ for 24 h.

The obtained $ZnIn_2S_4$ and ReS_2 were dissolved in ultrapure water respectively for further use. Then, $ZnIn_2S_4$ and ReS_2 were mixed at a ratio of 10:1. The obtained mixture was sonicated for 30 min and stirred overnight.

S1.4 Synthesis of $AgInS_2$ QDs

0.1 mmol $AgNO_3$, 0.4 mmol $In(NO_3)_3$ and 50 mL ultrapure water were added into a clean three-neck flask successively. After stirring, 0.1 mmol of mercaptopropionic acid (MPA) was added into the mixture. The pH of the solution was adjusted to 9 with 1 M NaOH solution, the obtained solution was stirred under N_2 protection for 30 min. Finally, 0.6 mmol Na_2S was added and reacted at 100℃ for 2 h.

S1.5 Fabrication of PEC aptasensor

Before construction of the PEC aptasensor, bare FTO electrode (0.45 cm^2) was washed thoroughly with ethanol and ultrapure water several times. After drying at 60℃, 30 μL of $ZnIn_2S_4/ReS_2$ heterojunction was dropped and dried at room temperature. In the meantime, the H-DNA was annealed at 95°C for 5 min and cooling down to the room temperature. Then, the annealed H-DNA (300 μL, 1 μM) was activated with TCEP (3 μL, 1.2 mM) for 30 min before use. Whereafter, 30 μL of pretreated H-DNA (1 μM) was incubated on the electrode surface overnight to acquire H-DNA/$ZnIn_2S_4/ReS_2$/FTO. After that, MCH was modified to block the nonspecific binding sites. Afterwards, 30 μL of $AgInS_2$ preactived with EDC and NHS was modified on the terminal of H-DNA to form the sensitization structure. Whereafter, 30 μL of DNA_2 was incubated on the above electrode, the H-DNA changed into a double-stranded structure. Finally, Kana with different concentrations were incubated through specific recognition with H-DNA.

S1.6 Photoelectrochemical and EIS test

The photoelectrochemical test of this experiment was carried out in 0.1 M PBS buffer (pH 7.4) containing 0.1 M ascorbic acid (AA), in which AA was present as an electron donor. In the test, the light source was 250 W xenon lamp, the wavelength range was 280~1000 nm. The switching frequency of the light source was once every 20 s, and the applied voltage was 0.0 V. The photocurrent is generated when an external light source hits the electrode surface.

Electrochemical impedance spectroscopy (EIS) was carried out with CHI 660D electrochemical workstation (CH Instruments, China) using a traditional three-electrode system, the modified FTO electrode as the working electrode, Ag/AgCl (saturated KCl) electrode was the reference electrode and the platinum wire electrode was the counter electrode. The electrolyte was 0.01 M of PBS (pH 7.4) including 0.1 M of KCl and 2 mM of $K_3[Fe(CN)_6/K_4[Fe(CN)_6]$ (1:1), the frequency was ranged from 100 mHz to 100 KHz, and the amplitude was 5 mV. The working electrodes at different modified processes as follows:

(a) $ZnIn_2S_4/ReS_2$/FTO,

(b) H-DNA/$ZnIn_2S_4$/ReS_2/FTO,

(c) MCH/H-DNA/$ZnIn_2S_4$/ReS_2/FTO,

(d) $AgInS_2$/MCH/H-DNA/$ZnIn_2S_4$/ReS_2/FTO,

(e) DNA_2/$AgInS_2$/MCH/H-DNA/$ZnIn_2S_4$/ReS_2/FTO,

(f) Kana/$AgInS_2$//MCH/H-DNA/$ZnIn_2S_4$/ReS_2/FTO.

S2 Result and discussion

S2.1 The characterization of $ZnIn_2S_4$, ReS_2 and $ZnIn_2S_4$/ReS_2 and $AgInS_2$

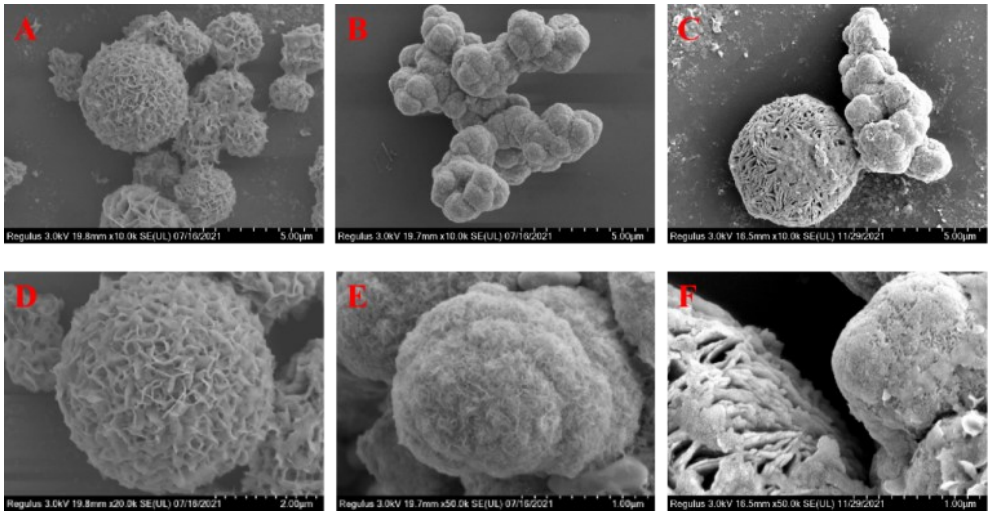

Fig. S1 SEM images of $ZnIn_2S_4$ (A) and (D); ReS_2 (B) and (E); $ZnIn_2S_4$/ReS_2 (C) and (F).

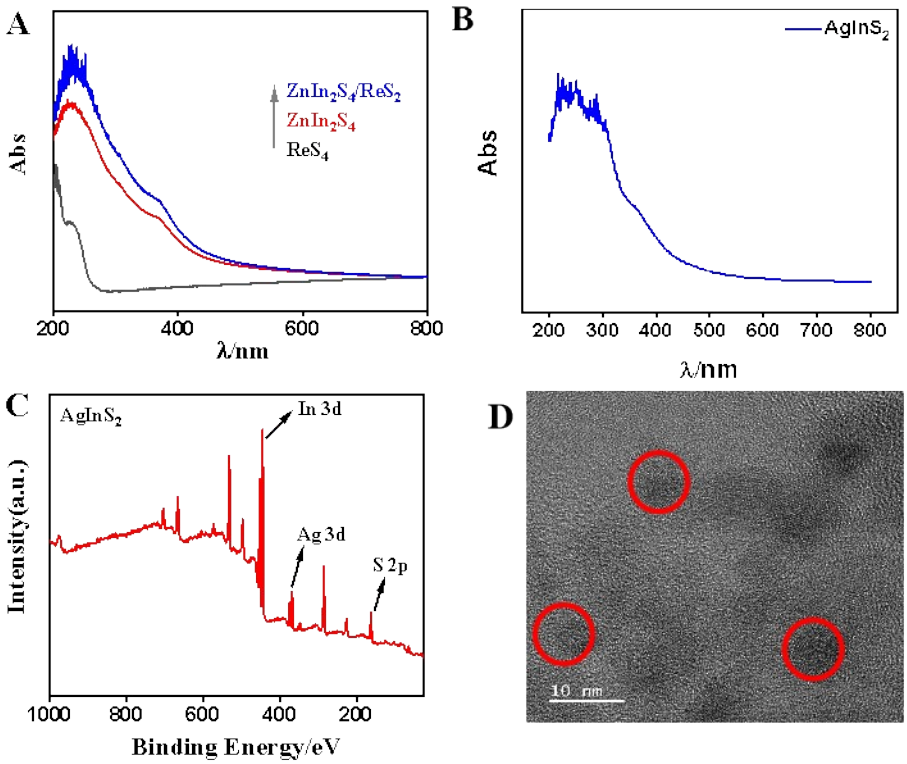

Fig. S2 UV-vis absorbance spectrum of (A) $ZnIn_2S_4$, ReS_2 and $ZnIn_2S_4/ReS_2$, UV-vis absorbance spectrum (B), XPS survey spectrum (C) and HR-TEM image (D) of $AgInS_2$.

S2.2 Optimization of experimental conditions

In order to acquire better PEC performances, the ratio of $ZnIn_2S_4$ and CdSe, the incubation time of H-DNA and $AgInS_2$, DNA_2 and H-DNA, Kana and H-DNA were optimized. As shown in Fig. 5A, the optimal ratio of ReS_2 was 10%, and the photocurrent response was 40 μA. After the aptasensor electrode was modified with H-DNA and MCH, the photocurrent decreased significantly. For the purpose of improving the detection sensitivity, $AgInS_2$ was introduced to amplify the signal response. The incubation time of $AgInS_2$ was a significant factor affecting the amplification effect. As shown in Fig. 5B, the photocurrent response under different incubation time of $AgInS_2$ was distinct and the optimal incubation time was 1 h. After DNA_2 was modified, the photocurrent decreased and finally stabilized at 20 min because of the saturation of DNA_2 (Fig. 5C). Finally, because of the conformational change of H-DNA resulted from the specific recognition between H-DNA and Kana, $AgInS_2$ was closer to the electrode surface, an increased photocurrent response

obtained. Therefore, the optimal incubation time of H-DNA and Kana (1×10^{-7} M) were 30 min (Fig. 5D).

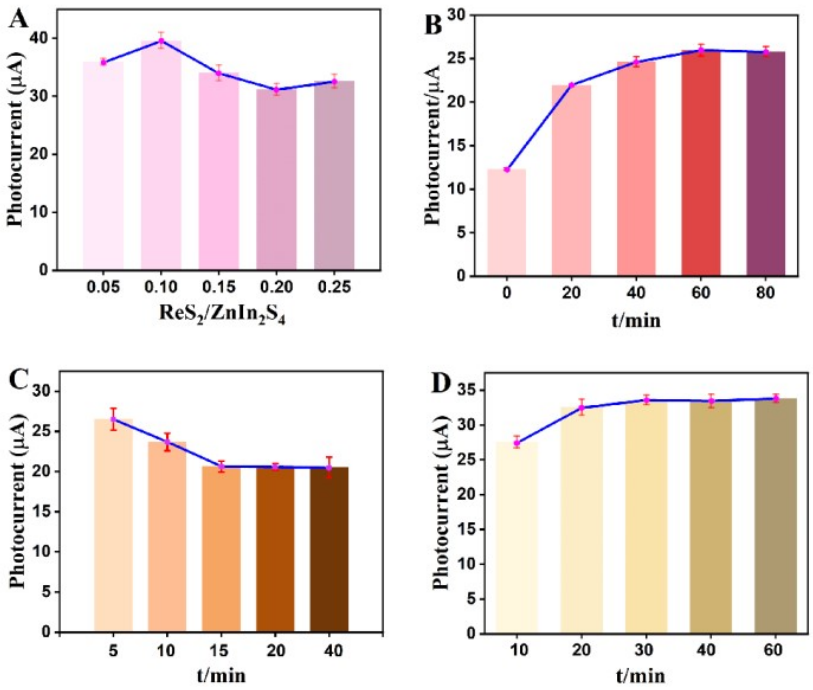

Fig. S3 (A) Optimization of ReS_2 proportion; Optimization of reaction time of (B) $AgInS_2$ and aptamer DNA, (C) DNA_2 with aptamer DNA, (D) kana with aptamer DNA.

S2.3 The calculation of LOD.

The LOD was calculated according to 3σ/S, where σ was the standard deviation of three independently blank samples response and the S was the slope of the analytical curve.

S2.4 Comparison with other detection methods.

Table S1. Comparison with other detection methods.

Detection method	Detection range (μM)	Minimum detection line (μM)	Reference
Fluorescence	4×10^{-3}-8×10^{-2}	5.2×10^{-4}	[1]
Fluorescence	2×10^{-2}-1	1.46×10^{-2}	[2]
Colorimetric	2.5×10^{-2}-0.8	2.058×10^{-2}	[3]
Colorimetric	1×10^{-5}-5×10^{-2}	0.9×10^{-5}	[4]

Electrochemiluminescence	1.0×10^{-3}-100	7.98×10^{-4}	[5]
Electrochemiluminescence	1×10^{-3}-10	2.8×10^{-4}	[6]
Microbial acoustic	/	4	[7]
Photoelectrochemical	1-1×10^{-3}	1.27×10^{-4}	[8]
Photoelectrochemical	1.0×10^{-5}-0.1	0.708×10^{-5}	This working

S2.5 Detection of Kana in actual sample.

Table S2. Detection of Kana in milk samples.

Sample	Added (10^{-10} M)	Found (10^{-10} M)	Recovery (%)	RSD (%, n=3)
Milk1	5	5.257	105.14	1.77
Milk2	50	46.881	93.76	0.19
Milk3	500	457.09	91.42	1.42

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