Supplementary Information

A novel dual-model photoelectrochemical/electrochemical sensor for kanamycin detection based on Z-scheme TiO_2 disk/methylene blue

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1. Reagents and apparatus

ITO electrode was purchased from Zhuhai Kaivo Electronic Components Co., Ltd (China). Methyl alcohol, p-Phthalic acid, titanium tetraisopropanolate and methylene blue (MB) were provided from Shanghai Aladdin Industrial Co. Ltd, China. Bovine serum albumin (BSA) was obtained from Sigma Aldrich (USA). Ascorbic acid (AA), anhydrous methanol (MeOH) and N, N-dimethylformamide (DMF) were all offered by Sinopharm Chemical Reagent Co. Ltd. (China). Other chemicals were of analytical grade and used as received. All aqueous solutions were prepared with ultrapure water from a Milli-Q filtration system (Millipore Corp, USA). DNA oligonucleotides were acquired from Sangon Biotechnology Co., Ltd. and the sequences were listed in Table S1, and the Kana-aptamer sequence referred to the published literature[1].

Table S1. Oligonucleotide sequences used in experiments.

Oligos	5′-Sequences-3′
Apt	NH_2-$(CH_2)_6$-TGG GGG TTG AGG CTA AGC CGA
cDNA	TCG GCT TAG CCT CAA CCC CCA

Transmission electron microscopy (TEM) image was characterized by JEM-2100F microscope (JEM-2100F, Japan). X-ray diffraction (XRD) experiment was carried out on an X-ray diffractometer (D/MAX-RA, Japan). The UV-vis spectrum was obtained using a DS5 UV-vis spectrophotometer (DS5, England). A Xe lamp (PLSSXE300) fitted with a 420 nm filter was used as light source. PEC and electrochemical impedance spectroscopic (EIS) measurements were accomplished by a CHI 660E electrochemical workstation with an ITO electrode (diameter, 5.6 mm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the counter electrode. A xenon lamp with a wavelength greater

than 420 nm was used as the excitation light source. EIS measurements were performed in 0.1 M KCl + 5 mM (1:1) $[Fe(CN)_6]^{3-/4-}$ solution in the frequency range from 0.1 Hz to 100 kHz with 5 mV as the amplitude.

2. Photocurrent responses

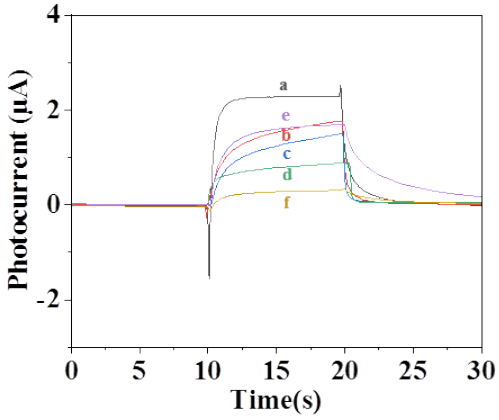

Fig. S1. PEC investigation: (a) TiO_2/ITO; (b) CS/TiO_2/ITO; (c) dsDNA/CS/TiO_2/ITO; (d) BSA/dsDNA/CS/TiO_2/ITO; (e) MB/BSA/dsDNA/CS/TiO_2/ITO; (f) Kana/MB/BSA/dsDNA/CS/TiO_2/ITO.

3. Reproducibility of the sensor

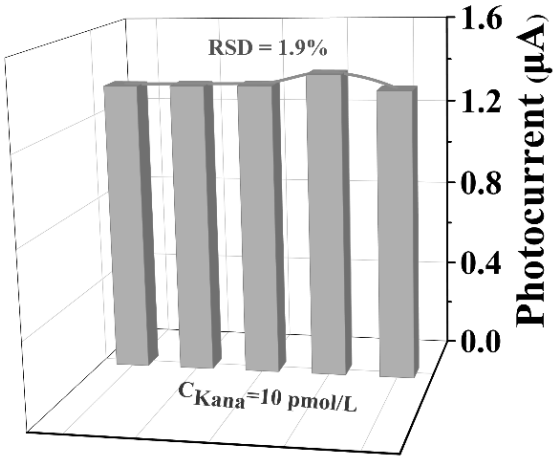

Fig. S2. Reproducibility of the sensor

4. Comparison of various methods for Kana detection

Table S2. Comparison of various methods for Kana detection.

Method	System	LOD	References
FL	CDs@Chol	7.2 μM	[2]
PEC/EC	Z-scheme AgBr/AgI-Ag-CNTs	0.4 pM/5 pM	[3]
FL	AuNCs-MnO_2	1.2 pM	[4]
ECL	6,6′-(1,4-phenylene)bis(1,3,5-triazine-2,4-diamine)	0.28 nM	[5]
MCE	AuMPs and PCR	2.5 pM	[6]
PEC	rGO-Bi_2WO_6-Au	0.78 pM	[7]
EC	VS_2/AuNPs	0.5 pM	[8]
FL	$CuWO_4$ nanomaterials	3.5 pM	[9]
SERS	MIL-101@AuNP nanohybrids	1 pg/mL	[10]
ECL	Ru@MOF	13.7 pM	[11]
EC	Ti_3C_2TX/MoS_2/MWCNT@rGONR	135 pM	[12]
PEC	Z-scheme Zn-defective CdS/ZnS	1.86 pg/mL	[13]
PEC	**Z-scheme TiO_2/MB**	**0.17 pM**	**This work**
EC		**1.8 pM**	

MCE: microchip electrophoresis. ECL: Electrochemiluminescence. FL: fluorescence. EC: electrochemical. PEC: photoelectrochemical. SERS: surface-enhanced Raman spectroscopy.

5. References

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