

A novel “turn-off” photoelectrochemical aptasensing platform for selective detection of tobramycin based on $\text{Ti}_3\text{C}_2\text{-MoS}_2/\text{BiOI}$ heterojunction

Xuejun Qi^{a,*}, Xing Zhao^a

^a School of Architecture and Civil Engineering, Xihua University, Chengdu 610039, PR China

* Corresponding author. E-mail address: xuejunqi@hotmail.com (Xuejun Qi).

Experimental

Materials and reagents

All reagents were of analytical grade and used without further purification. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_{24} \cdot 4\text{H}_2\text{O}$ and $\text{SC}(\text{NH}_2)_2$, KI, ethanol, ethylene glycol (EG) were purchased from Sinopharm Chemical Reagent Co., Ltd (www.sinoreagent.com). TOB aptamer probes were ordered from Shanghai Sangon Biotech Co., Ltd. (Shanghai, China). The sequence of the TOB aptamer is 5'-GGG ACT TGG TTT AGG TAA TGA GTCCC-3'. Phosphate buffered solution (PBS, 0.1 M) were prepared by mixing stock standard solutions of NaH_2PO_4 and Na_2HPO_4 . Ultra-pure water ($18.25 \text{ M}\Omega \cdot \text{cm}$) is utilized through all the experiments.

Apparatus

Bruker D8 Advance diffractometer was used to conduct the X-ray diffraction (XRD) under the $\text{Cu K}\alpha$ irradiation. And the ESCALAB 250Xi was used to conduct the X-ray photoelectron spectroscopy (XPS). UV-visible (UV-vis) spectrophotometer, an instrument for collecting the materials' Diffuse reflection spectra (DRS), was operated with the help of BaSO_4 as reference. And finally, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are two methods for characterizing the form of different specimens.

Preparation of materials

Preparation of Ti_3C_2 : 2 g of as-purchased Ti_3AlC_2 powders were slowly immersed in 40 mL HF and stirred for 48 h to remove Al layer for obtaining Ti_3C_2 . The mixture was centrifuged and washed with deionized water several times until the $\text{pH} \geq 6$, then dried at $80 \text{ }^\circ\text{C}$. Then, pristine Ti_3C_2 was intercalated by 30 mL dimethyl sulfoxide (DMSO). The mixture was continuously agitated for 18 h. Thereafter, the mixture underwent sonication for 1 h, and then centrifuged and dried at $80 \text{ }^\circ\text{C}$.

Preparation of MoS₂: (NH₄)₆Mo₂₄·4H₂O and SC(NH₂)₂ were dissolved in deionized water under stirring. Then, they were transferred to a 100 mL Teflon-lined stainless steel autoclave, and heated at 200 °C for 24 h.

Preparation of Ti₃C₂-MoS₂/BiOI heterojunction: Appropriate KI is dissolved in H₂O solution. Then, an appropriate Bi(NO₃)₃·5H₂O and the synthesized MoS₂, Ti₃C₂ are slowly added to the suspension obtained above and continuously stirred for half an hour. The mixed solution was heated at 180 °C for 24 h in 100 mL Teflon-lined autoclave. Finally, the product is continually washed three times together with deionized water and ethanol, and then dried at 60 °C for 12 h. MoS₂/BiOI-6% was prepared without adding the Ti₃C₂ by the above process.

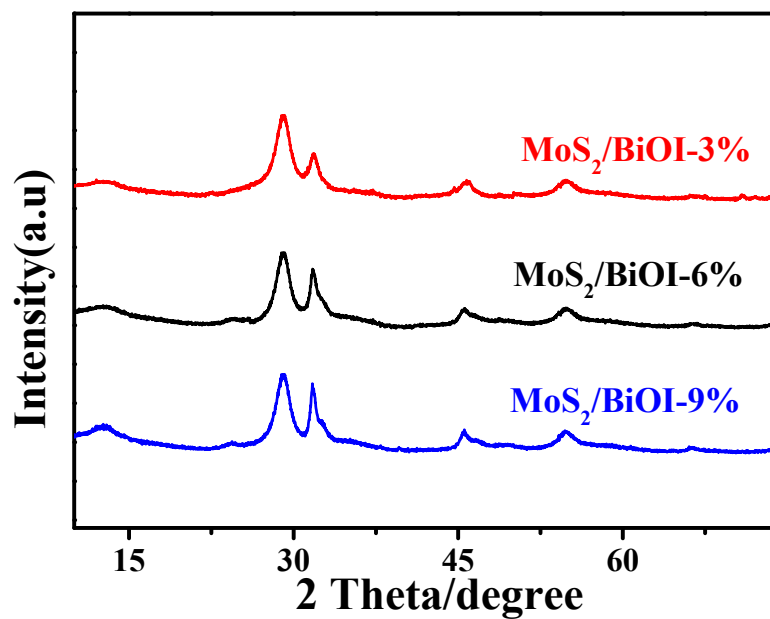


Figure S1. XRD spectrum of MoS₂/BiOI-3%, MoS₂/BiOI-6% and MoS₂/BiOI-9% composites.

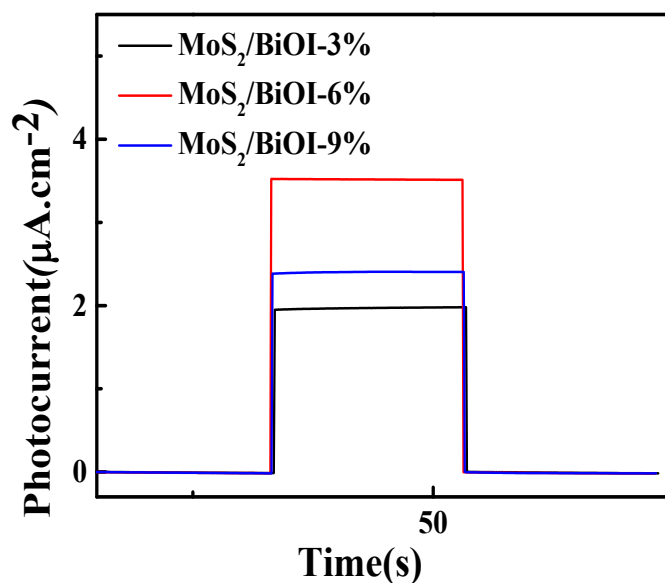


Figure S2 Photocurrent responses of the MoS₂/BiOI-X composites in 0.1 M PBS.

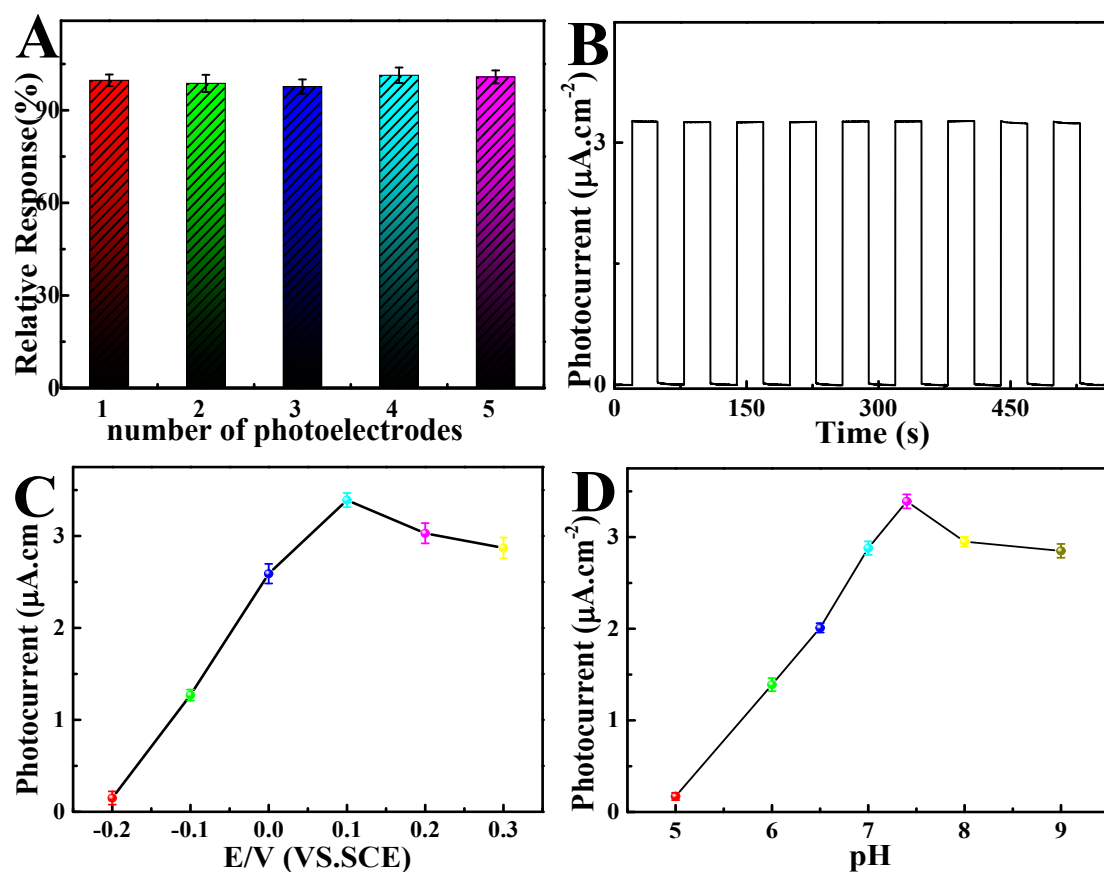


Figure S3. (C) repeatability and (D) stability of the PEC aptasensor based on aptamer/ $\text{Ti}_3\text{C}_2\text{-MoS}_2/\text{BiOI-6\%}$ for TOB detection; Influence of different reaction parameters on the photocurrent response of the electrode. (C) the bias potentials, (D) different pH values in 0.1 M PBS containing 0.1 M AA.

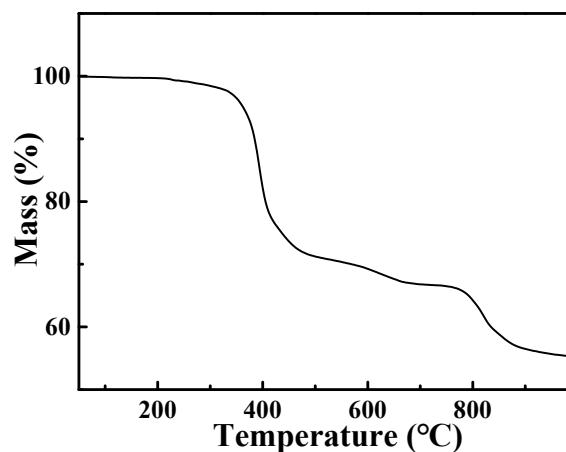


Figure S4 TGA of $\text{Ti}_3\text{C}_2\text{-MoS}_2/\text{BiOI-6\%}$.

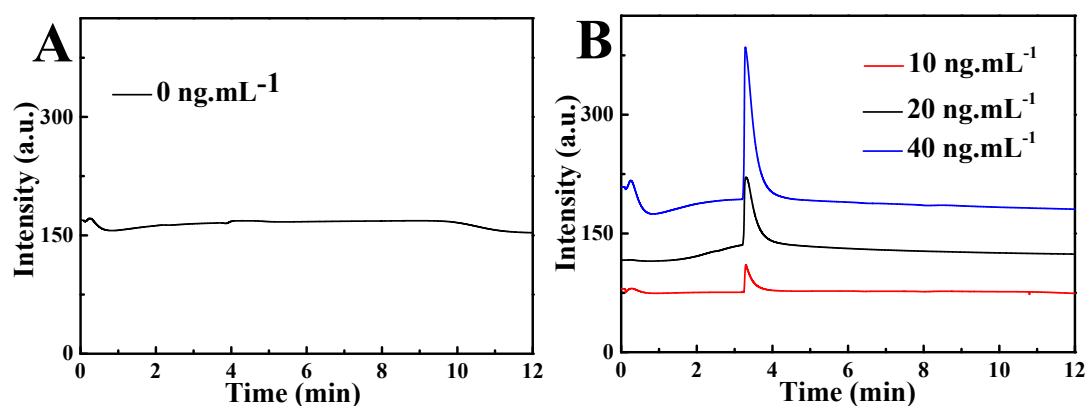


Figure S5 LC-MS for TOB.

Table S1 Comparison of different methods for detecting TOB. LOD: limit of detection.

Method	Linear Range (ng.mL^{-1})	LOD	Ref.
Electrochemical	0.01-5	6.79 pg.mL^{-1}	1
PEC aptasensor	0.005-5	2 pg.mL^{-1}	2
Quartz crystal microbalance	0.036-0.315	12 pg.mL^{-1}	3
PEC aptasensor	10.5-105	8.99 ng.mL^{-1}	4

PEC aptasensor

0.001-40

0.5 pg.mL^{-1}

This work

Reference

1. M. Wang, B. Hu, C. Yang, Z. Zhang, L. He and S. Fang, Electrochemical biosensing based on protein-directed carbon nanospheres embedded with SnO_x and TiO₂ nanocrystals for sensitive detection of tobramycin, *Biosens. Bioelectron.*, 2018, **99**, 176-185.
2. L. Qiao, Y. Zhu, T. J. Zeng, Y. Y. Zhang, M. J. Zhang, K. X. Song, N. Yin, Y. N. Tao, Y. Zhao, Y. Zhang and C. Zhang, "Turn-off" photoelectrochemical aptasensor based on g-C₃N₄/WC/WO₃ composites for tobramycin detection, *Food Chem.*, 2023, **403**, 134287.
3. M. L. Yola, L. Uzun, N. Ozaltin and A. Denizli, Development of molecular imprinted nanosensor for determination of tobramycin in pharmaceuticals and foods, *Talanta*, 2014, **120**, 318–324.
4. X. Liu, Y. Jiang, J. Luo, X. Guo, Y. Ying, Y. Wen and Y. Wu, A SnO₂/Bi₂S₃-based photoelectrochemical aptasensor for sensitive detection of tobramycin in milk, *Food Chem.*, 2021, **344**, 128716.