

Supporting Information

High performance Vo-ZnO/ZnS benefiting nanoarchitectonics from the synergism between defect engineering and surface engineering for photoelectrochemical glucose sensor

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Reagents and apparatus

FTO glasses were purchased from Outhwaite New Energy Company. Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), urea (Ur), cetyltrimethylammonium bromide (CTAB), ascorbic acid (AA), sodium chloride (NaCl) were obtained from Sinopharm Chemical Reagent Co., Ltd. Glucose (Glu), uric acid (UA), dopamine (DA), fructose (Fru), lactose (Lac), cysteine (Cys), glycine (Gly), glucose oxidase (GOx) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. trisodium citrate dihydrate (TCD), sucrose (Suc), disodium hydrogen phosphate dodecahydrate (Na₂HPO₄·12H₂O), sodium dihydrogen phosphate dihydrate (NaH₂PO₄·2H₂O), ethanol obtained from Shanghai Pharmaceuticals.

Scanning electron microscopy (SEM, Hitachi S-3000 4800) and transmission electron microscopy (TEM) using a JEOL-2100F microscope equipped with energy-dispersive spectroscopy (EDS) are used to investigate the microscopic morphology and structure of samples. X-ray diffraction spectroscopy (XRD) using a D8 Tools XRD instrument at a voltage of 40 kV and a current of 30 mA with Cu-K α radiation ($k = 1.5406 \text{ \AA}$) is employed to examine the crystalline structure of samples. X-ray photoelectron spectroscopy (XPS) data of synthetic materials are measured by K-Alpha 1063 XPS to investigate the surface chemical elemental state of the material, Electron paramagnetic resonance (EPR) is used to analyze defects in materials by performing measurements at room temperature with a Bruker X/Q-band E580 FT/CW ELEXSYS spectrometer at room temperature in the X-band (9.86 GHz). The ultraviolet-visible (UV-vis) diffuse reflectance spectra used to investigate the light absorption of the materials were measured with a UV-2550 spectrophotometer. Photoluminescence (PL) experiments for analyzing the carrier complexation of materials are performed using a fluorescence spectrophotometer (Hitachi F7000).

Photoelectrochemical and glucose sensing testing

The photoelectrochemical properties of the materials were measured using a three-electrode system with an electrochemical workstation (CHI Instruments, Chenhua CHI 660, Shanghai, China), for which the sample was used as the working electrode, Ag/AgCl was the reference electrode, and a platinum sheet was the counter electrode. The electrochemical tests were performed in 0.1 M PBS (pH=7.4). Photocurrent-time test at 0.2V, open-circuit voltage (OCP) test, Mott-Schottky (MS) test and photoelectrochemical impedance spectra (PEIS) for all photoelectrodes test at 10⁶ Hz to 0.1 Hz light and open-circuit voltage were performed in the above system. The detection performance of glucose was investigated using 0.1 M PBS containing 2 mM AA.

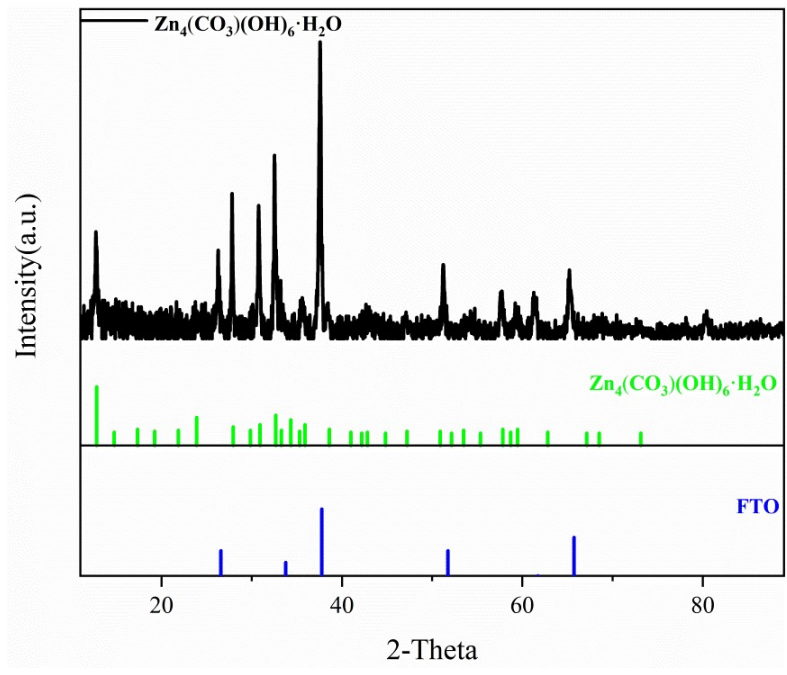


Figure S1 XRD spectra of $Zn_4(CO_3)(OH)_6 \cdot H_2O$.

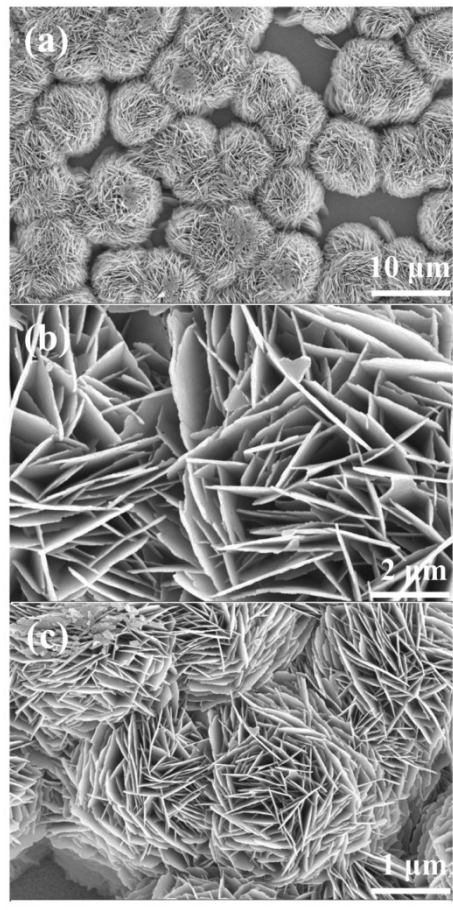


Figure S2 SEM images of $Zn_4(CO_3)(OH)_6 \cdot H_2O$ (a-c).

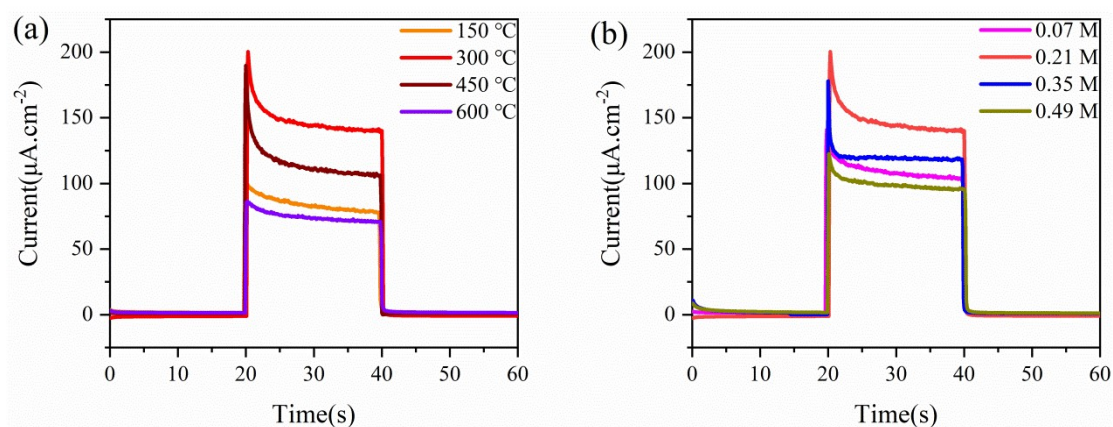


Figure S3 Effect of temperature (a) and sodium sulfide concentration (b) on the photoelectric response of Vo-ZnO/ZnS.

Table S1 Comparison of analytical performances of glucose sensors.

Materials	Sensor type	Liner range (mM)	Detection limit (μ M)	Sensitivity (μ A·mM ⁻¹ ·cm ⁻²)	Reference
Nafion/GOx/PtNDs/ZnONRs/ITO	EC	0.005-1	30	98.34	1
GR/PANI:rGO/GOx	EC	0.5-50	89	2.8 (μ A mM ⁻¹)	2
graphene	EC	0.4-2	124.19	16.16	3
BiVO ₄ /FTO	PEC	5-35	-	17.38	4
Fe ₂ O ₃ films	PEC	0.05-6	0.05	17.23	5
ITO/MTiO ₂ -Au NPs-MoS ₂ -GOx	PEC	0.004-1.75	1.2	4.42	6
Vo-ZnO/ZnS	PEC	0.2-1.4	15.9	49.43	This work
		1.4-3	-	17.64	

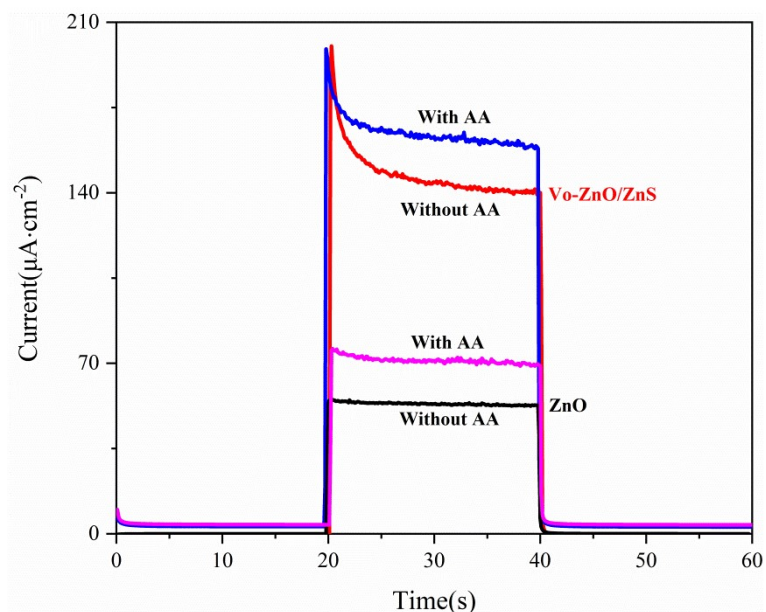


Figure S4 Photoelectric response of ZnO and Vo-ZnO/ZnS with and without AA.

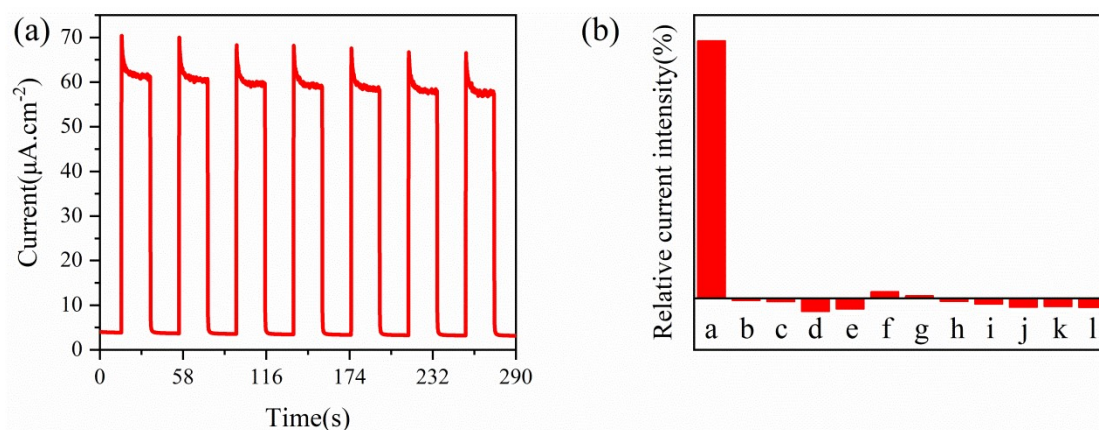


Figure S5 Stability test of Vo-ZnO/ZnS under absence of 3 mM glucose condition (a); Influence of interferences on the photoelectric response (b).

Notes and references

1. N. S. Ridhuan, N. Mohamad Nor, K. Abdul Razak, Z. Lockman and N. D. Zakaria, *Journal of Solid State Electrochemistry*, 2021, 25, 1065-1072.
2. A. Popov, R. Aukstakojyte, J. Gaidukevic, V. Lisyte, A. Kausaite-Minkstimiene, J. Barkauskas and A. Ramanaviciene, *Sensors (Basel)*, 2021, 21.
3. S. Wei, Y. Hao, Z. Ying, C. Xu, Q. Wei, S. Xue, H.-M. Cheng, W. Ren, L.-P. Ma and Y. Zeng, *Journal of Materials Science & Technology*, 2020, 37, 71-76.
4. L. He, Z. Yang, C. Gong, H. Liu, F. Zhong, F. Hu, Y. Zhang, G. Wang and B. Zhang, *Journal of Electroanalytical Chemistry*, 2021, 882, 114912.
5. F. Liu, P. Wang, Q. Zhang, Z. Wang, Y. Liu, Z. Zheng, X. Qin, X. Zhang, Y. Dai and B. Huang, *Electroanalysis*, 2019, 31, 1809-1814.
6. B. Çakıroğlu and M. Özacar, *Electroanalysis*, 2020, 32, 166-177.