# Supporting Information

# $Ag_2ZnSnS_4$/Mo-mesh photoelectrode prepared by electroplating for efficient photoelectrochemical hydrogen generation

Xizhuang Liang [a], Peng Wang [a,*], Baibiao Huang [a], Qianqian Zhang [a], Zeyan Wang [a], Yuanyuan Liu [a], Zhaoke Zheng [a], Xiaoyan Qin [a], Xiaoyang Zhang [a], Ying Dai [b]

[a] State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

[b] School of Physics, Shandong University, Jinan 250100, China

*Corresponding author-mail address: pengwangicm@sdu.edu.cn (P. Wang)

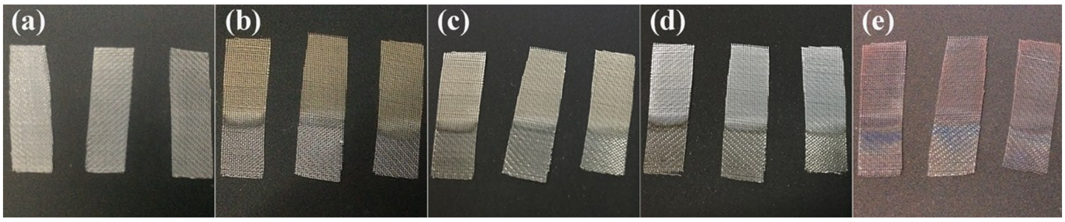


**Fig. S1**. The colour of (a) pure Mo-mesh, (b) Ag/Mo layers, (c) Sn/Ag/Mo layers, (d) Zn/Sn/Ag/Mo layers before sulfurization treatment and (e) as-prepared AZTS photoanode after sulfurization treatment.

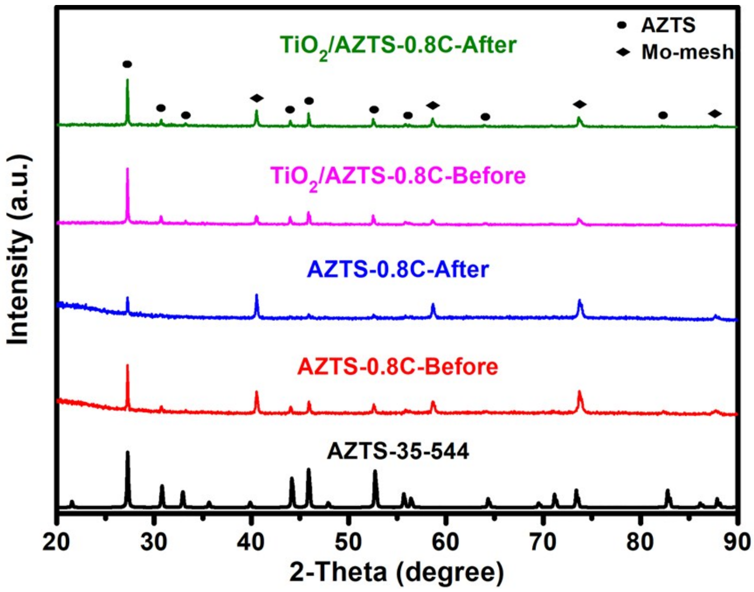


**Fig. S2**. XRD patterns of as-prepared AZTS-0.8C photoanode and $TiO_2$/AZTS-0.8C photoanode before and after photocurrent density-time (J-t) durability test.

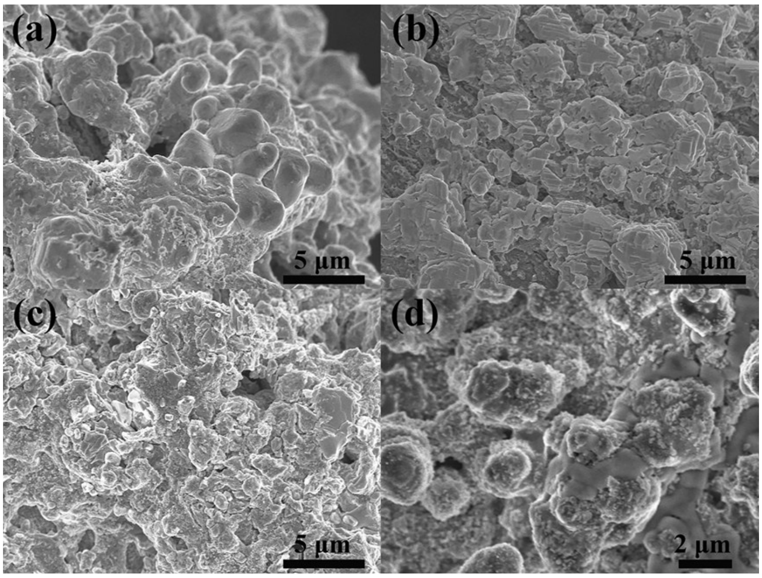


**Fig. S3**. SEM images of AZTS photoanode surface with the different deposition charge quantities: (a) AZTS-0.4C, (c) AZTS-1.2C, and SEM images of AZTS-0.8C photoanode surface (b) before and (d) after photocurrent density-time (J-t) durability test shown in Fig. 6c of the main text.

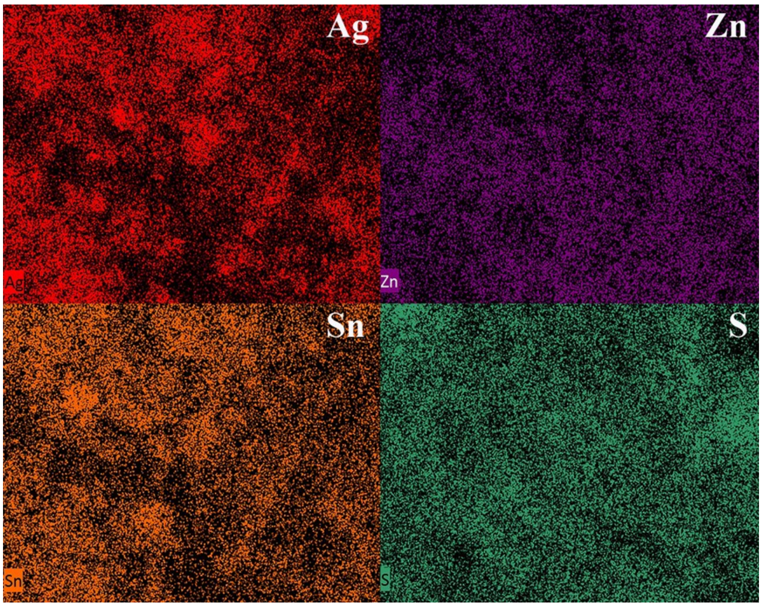


**Fig. S4**. EDS element mapping results of (a) Ag (red points), (b) Zn (purple points), (c) Sn (orange points) and (d) S (green points) in AZTS-0.8C photoanode.

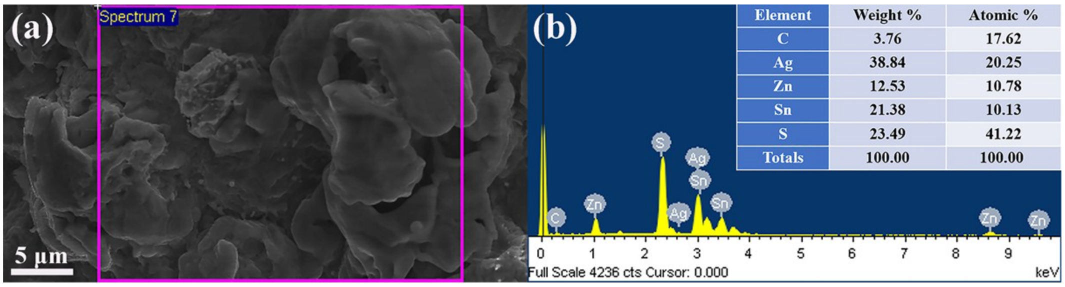


**Fig. S5**. Energy Dispersive Spectrometer (EDS) spectrum (a) and the detailed information about the composition of AZTS-0.8C photoanode (b).

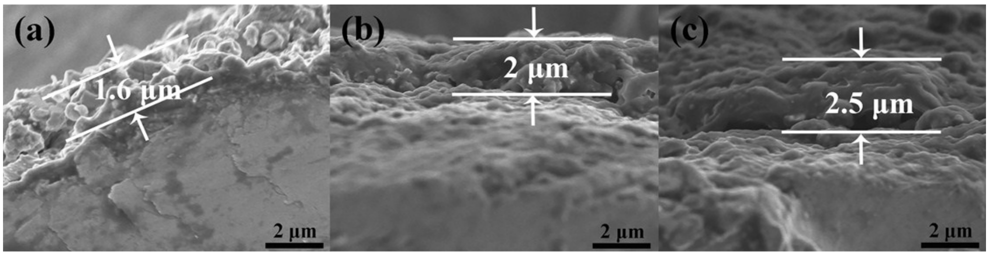


**Fig. S6**. Side-view SEM images of AZTS photoanode with the different deposition charge quantities: (a) AZTS-0.4C, (b) AZTS -0.8C and (c) AZTS-1.2C.

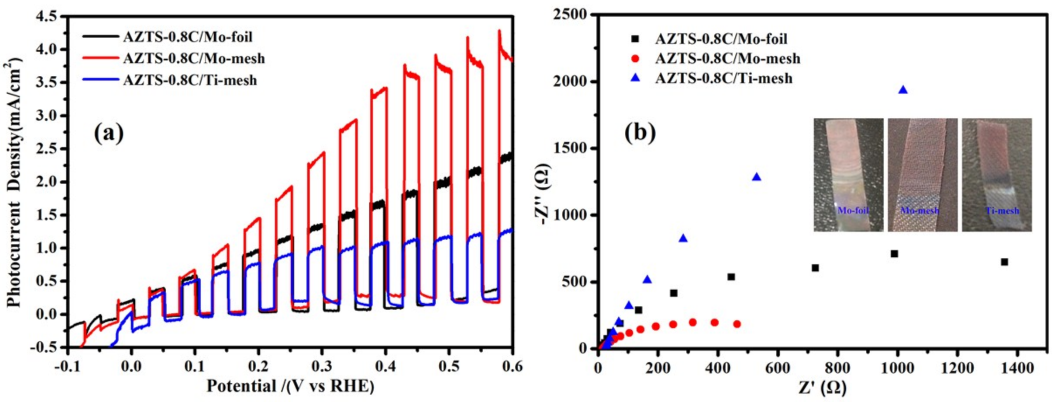


**Fig. S7**. (a) Photocurrent density-applied potential (*J*-*V*) curves and (b) electrochemical impedance spectra (EIS) plots of AZTS-0.8C/Mo-foil, AZTS-0.8C/Mo-mesh and

AZTS-0.8C/Ti-mesh photoanodes in $Na_2SO_4$ (0.1 M) electrolyte with sacrificial reagents (0.05 M $Na_2S$ + 0.05 M $Na_2SO_3$) under simulated sunlight radiation.

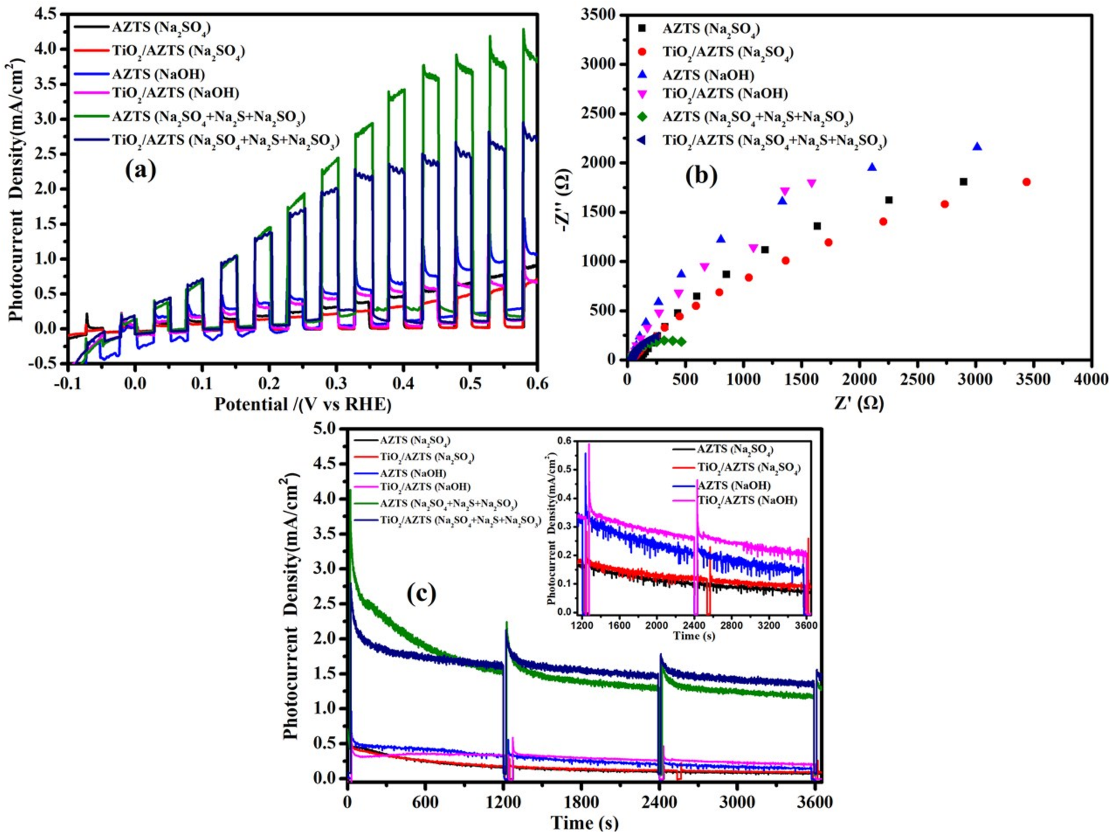


**Fig. S8**. (a) Photocurrent density-applied potential (J-V) curves, (b) electrochemical impedance spectra (EIS) plots and (c) PEC durability tests of AZTS-0.8C photoanode and $TiO_2$/AZTS-0.8C photoanode measured at 0.4 V vs RHE in neutral $Na_2SO_4$ (0.1 M) and NaOH (0.1 M) without sacrificial reagents and $Na_2SO_4$ (0.1 M) with sacrificial reagents (0.05 M $Na_2S$ + 0.05 M $Na_2SO_3$).

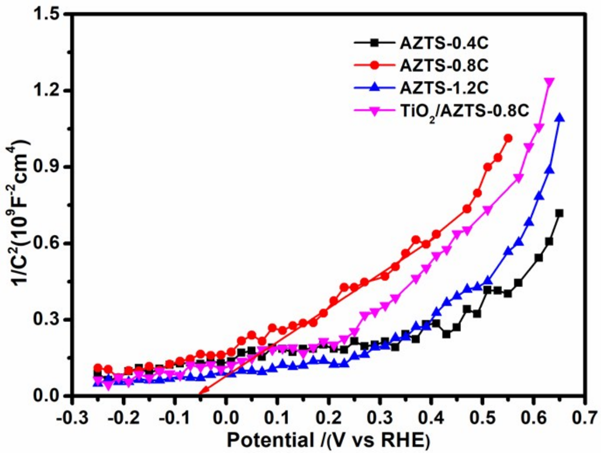


**Fig. S9**. Motte-Schottky plots of AZTS photoanode and $TiO_2$/AZTS-0.8C photoanode measured at a frequency of 1 kHz in dark.

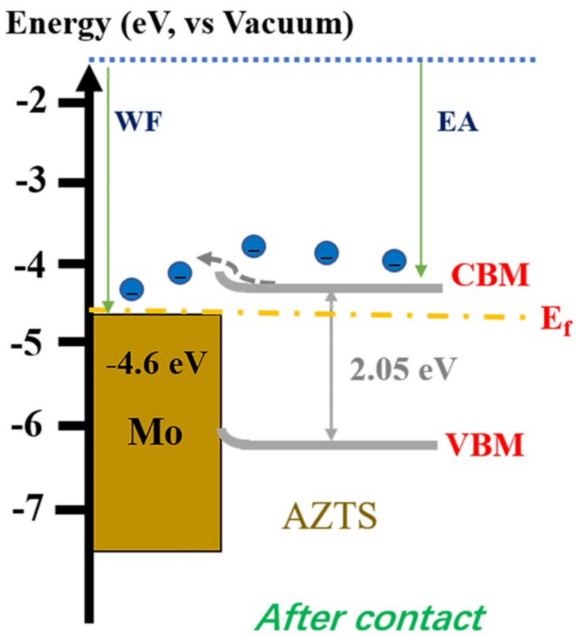


**Fig. S10**. Calculated band position diagram of AZTS/Mo mesh.

According to previous literatures,[S6-S9] the electron affinity (*EA*) of the compound could be given by the following *Eq.(1)* and *(2)*.

$$\chi_{comp} = \sqrt[N]{\chi_1^r \chi_2^s \cdots \chi_{n-1}^{\ p} \chi_n^q} \qquad Eq.(1)$$

$$EA = \chi_{comp} - \frac{1}{2}E_g \qquad Eq.(2)$$

$E_g$ is the band gap of the semiconductor. $\chi_{comp}$ is the electronegativity of a compound which is given by the geometric mean of the electronegativities of the constituent atoms. $\chi_n$, $N$ and $n$ are the electronegativity of the constituent atom, the total number of atoms and the number of the species in the compound, respectively. The superscripts ($r$, $s$, ... $p$, $q$) refer to the numbers of every element in the molecule, respectively. The electronegativity values of Ag, Zn, Sn and S are 4.44, 4.45, 4.30, 6.22, respectively.[S10] From *Eq.(1)* and *(2)*, the electronegativity and electron affinity values of $Ag_2ZnSnS_4$ are estimated to be about 5.24 and 4.22 eV vs vacuum level. For n-type semi-conductors the electron affinities are almost equal to the work functions of the semiconductors, so the work function of $Ag_2ZnSnS_4$ is at approximately 4.22 eV. The work function of Mo is 4.6 eV. [S11] When the metal Mo and AZTS are in contact, the electrons can flow from the low work function (high Fermi level) into the metal (low Fermi level) until the Fermi level is balanced and form a Schottky contact, as shown in Fig. S10.

| Photoanode /Substrate | Synthetic method | Electrolyte | PEC performances | IPCE | Stability test | Ref. |
|---|---|---|---|---|---|---|
| AZTS/ZnS/FTO | Co-precipitation | $Na_2SO_4$ + triethanolamine | 0.3 mA/cm$^2$ at 0.7 V vs RHE | N/A | 1000s | S1 |
| AZTS/ITO | Dip-coating | $LiClO_4$ + triethanolamine | 0.03 mA/cm$^2$ at 0 V vs Ag/AgCl | ~0.1% | N/A | S2 |
| Ag–Zn–Sn–S/ITO | Chemical bath deposition | $Na_2S$ + $K_2SO_3$ | 0.65 mA/cm$^2$ at 1 V vs Ag/AgCl | N/A | N/A | S3 |
| AZTS/FTO | Sulfurization of sputtering metal precursors | NaCl | 0.23 mA/cm$^2$ at 0.7 V vs RHE | N/A | N/A | S4 |
| Au@AZTS/FTO | Spin-coating | $Na_2S$ + $Na_2SO_3$ | 2.75 mA/cm$^2$ at 0 V vs Ag/AgCl | ~8% | 600s | S5 |
| AZTS/Mo-mesh | Electrodeposition | $Na_2SO_4$ + $Na_2S$ + $Na_2SO_3$ | 4.0 mA/cm$^2$ at 0.6 V vs RHE | ~25% | 3600s | This work |
| $TiO_2$/AZTS/Mo-mesh | Electrodeposition and ALD | $Na_2SO_4$ + $Na_2S$ + $Na_2SO_3$ | 3.0 mA/cm$^2$ at 0.6 V vs RHE | ~20% | 3600s | This work |

**Table S1.** Comparisons of preparation methods and PEC performance of AZTS/Mo-mesh and $TiO_2$/AZTS/Mo-mesh.

## References


[S1] S. Ikeda, T. Nakamura, T. Harada and M. Matsumura, *Phys. Chem. Chem. Phys.*, 2010, **12**, 13943-13949.

[S2] T. Sasamura, T. Osaki, T. Kameyama, T. Shibayama, A. Kudo, S. Kuwabata and T. Torimoto, *Chem. Lett.*, 2012, **41**, 1009-1011.

[S3] L.-Y. Yeh and K.-W. Cheng, *Thin Solid Films*, 2014, **558**, 289-293.

[S4] K.-W. Cheng and S.-W. Hong, *ACS Appl. Mater. Interfaces*, 2018, **10**, 22130-22142.

[S5] X. Cheng, J. Liu, J. Feng, E. Zhang, H. Wang, X. Liu, J. Liu, H. Rong, X. Meng and J. Zhang, *J. Mater. Chem. A*, 2018, **6**, 11898-11908.

[S6] M. A. Butler and D. S. Ginley, *J. Electrochem. Soc.*, 1978, **125**, 228-232.

[S7] Y. Xu and M. A. A. Schoonen, *Am. Mineral*, 2000, **85**, 543-556.

[S8] J. Lu, H. Jin, Y. Dai, K. Yang and B. Huang, *International Journal of Photoenergy*, 2012, **2012**. 928503.

[S9] Z. Lou, B. Huang, Z. Wang, X. Ma, R. Zhang, X. Zhang, X, Qin, Y. Dai and M.-H. Whangbo, *Chem. Mater.*, 2014**, 26**, 3873-3875.

[S10] D. Yu, Z.-D. Chen, F. Wang and S.-Z. Li, *Acta Phys. Chim. Sin*., 2001, **17**, 15-22.

[S11] H. B. Michaelson, *J. Appl. Phys.*, 1977, **48**, 4729-4733.