Supporting Information

ZnS and $Ag_2Mo_2O_7$ regulate interface engineering by constructing S-scheme heterojunctions to facilitate photocatalytic hydrogen production

Zhenlu Liu[1], Jing Xu*[1,3,4], Jiandong Wu[2], Ye Liu[1], Lijun Ma[1], Linying Hu[1]

1 School of Chemistry and Chemical Engineering, North Minzu University, Yinchuan 750021, PR China

2 School of Materials Science and Engineering, North Minzu University, Yinchuan 750021, PR China

3 Ningxia Key Laboratory of Solar Chemical Conversion Technology, North Minzu University, Yinchuan 750021, PR China

4 Key Laboratory for Chemical Engineering and Technology, State Ethnic Affairs Commission, North Minzu University, Yinchuan 750021, PR China

Email: wgyxj2000@163.com

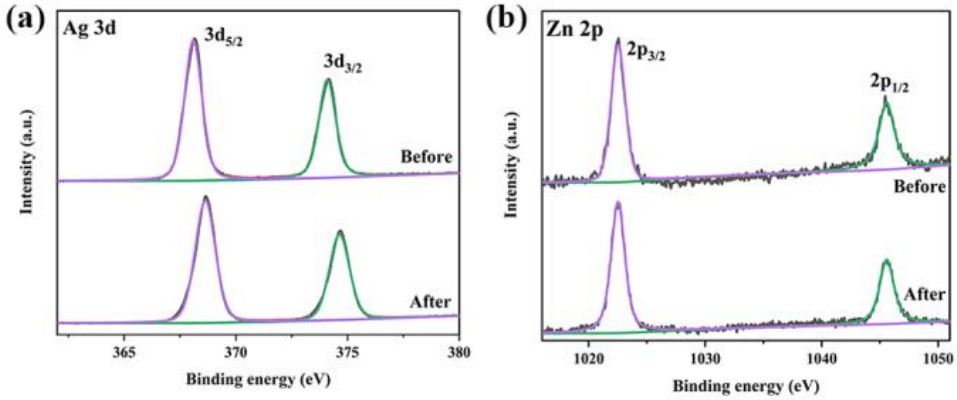

Figure S1 XPS comparison of Zn and Ag before and after reaction.

Table 1 Comparison with other reported ZnS performance.

Material	Sacrificial agent	Hydrogen evolution	Light	
$CuGaS_2$/ZnS	Na_2S/Na_2SO_3	137 μmol·g^{-1} h^{-1}	300 W Xe	[1]
ZnO/ZnS	/	247 μmol·g^{-1} h^{-1}	300 W Xe	[2]
CeO_2/ZnS	Na_2S/Na_2SO_3	417 μmol·g^{-1} h^{-1}	300 W Xe	[3]
ZIF-8/ZnS	TEOA	741.8 μmol·g^{-1} h^{-1}	300 W Xe	[4]
ZnO/ZnS	Methanol	757 μmol·g^{-1} h^{-1}	/	[5]
$NiCo_2O_4$/ZnS	Na_2S/Na_2SO_3	880 μmol·g^{-1} h^{-1}	300 W Xe	[6]
ZnO/ZnS	Na_2S/Na_2SO_3	2.4 mmol g^{-1} h^{-1}	300 W Xe	[7]
Pt/SnO_2/ZnS	TEOA	2.17 mmol g^{-1} h^{-1}	300 W Xe	[8]
ZrO_2/SnS_2/ZnS	Na_2S/Na_2SO_3	928.1 μmol·g^{-1} h^{-1}	300 W Xe	[9]
Bi_2S_3/ZnS	Na_2S/Na_2SO_3	176.2 μmol·h^{-1}	300 W Xe	[10]
g-C_3N_4/ZnS	Na_2S/Na_2SO_3	713.7 μmol·g^{-1} h^{-1}	300 W Xe	[11]
ZnO/ZnS	Na_2S	494.8 μmol·g^{-1} h^{-1}	150 W Xe	[12]
Cu_3P/ZnS	Na_2S/Na_2SO_3	792 μmol·g^{-1} h^{-1}	300 W Xe	[13]
Pt/ZnO/ZnS	H_2O	87.6 μmol·g^{-1} h^{-1}	300 W Xe	[14]
ZnO/ZnS	Na_2S/Na_2SO_3	15.7 μmol·g^{-1} h^{-1}	350 W Xe	[15]
Cu_3P/ZnS	Na_2S/Na_2SO_3	14937 μmol·g^{-1} h^{-1}	250 W QTH	[16]
$AgIn_5S_8$/ZnS	Na_2S/Na_2SO_3	932.8 μmol·g^{-1} h^{-1}	300 W Xe	[17]
Ti_3C_2/ZnS	Lactic acid	502.6 μmol·g^{-1} h^{-1}	300 W Xe	[18]
MoS_2/ZnS	Methanol	606 μmol·g^{-1} h^{-1}	Hg-pen	[19]
NiS_2/g-C_3N_4/ZnS	TEOA	348.5 μmol·g^{-1} h^{-1}	300 W Xe	[20]
rGO/ZnS	Methanol	108.8 μmol·g^{-1} h^{-1}	500 W Xe	[21]
$Ag_2Mo_2O_7$/ZnS	**TEOA**	**871.9 μmol·g^{-1} h^{-1}**	**5 W Xe**	**This work**

Reference

[1] M. Zhao, F. Huang, H. Lin, J. Zhou, J. Xu, Q. Wu, Y. Wang, CuGaS2-ZnS p-n nanoheterostructures: a promising visible light photo-catalyst for water-splitting hydrogen production, Nanoscale, 8 (2016) 16670-16676.

[2] Y. Piña-Pérez, O. Aguilar-Martínez, P. Acevedo-Peña, C.E. Santolalla-Vargas, S. Oros-Ruíz, F.

Galindo-Hernández, R. Gómez, F. Tzompantzi, Novel ZnS-ZnO composite synthesized by the solvothermal method through the partial sulfidation of ZnO for H2 production without sacrificial agent, Applied Catalysis B: Environmental, 230 (2018) 125-134.
[3] C. Xia, C. Xue, W. Bian, Y. Wei, J. Zhang, Morphology controlling strategy of ZnS/CeO2 catalysts to enhance the photocatalytic performance for hydrogen production, JCIS Open, 4 (2021).
[4] J. Zhou, J. Zhao, R. Liu, Defect engineering of zeolite imidazole framework derived ZnS nanosheets towards enhanced visible light driven photocatalytic hydrogen production, Applied Catalysis B: Environmental, 278 (2020).
[5] X. Yang, H. Liu, T. Li, B. Huang, W. Hu, Z. Jiang, J. Chen, Q. Niu, Preparation of flower-like ZnO@ZnS core-shell structure enhances photocatalytic hydrogen production, International Journal of Hydrogen Energy, 45 (2020) 26967-26978.
[6] C.-J. Chang, Z. Lee, M. Wei, C.-C. Chang, K.-W. Chu, Photocatalytic hydrogen production by magnetically separable Fe 3 O 4 @ZnS and NiCo 2 O 4 @ZnS core–shell nanoparticles, International Journal of Hydrogen Energy, 40 (2015) 11436-11443.
[7] H. Ren, K. Ye, H. Chen, F. Wang, Y. Hu, Q. Shi, H. Yu, R. Lv, M. Chen, ZnO@ZnS core–shell nanorods with homologous heterogeneous interface to enhance photocatalytic hydrogen production, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 652 (2022).
[8] X. Ji, H. Xu, S. Liang, L. Gan, R. Zhang, X. Wang, 3D ordered macroporous Pt/ZnS@ZnO core-shell heterostructure for highly effective photocatalytic hydrogen evolution, International Journal of Hydrogen Energy, 47 (2022) 17640-17649.
[9] Y. Tian, X. Yang, L. Li, Y. Zhu, Q. Wu, Y. Li, F. Ma, Y. Yu, A direct dual Z-scheme 3DOM SnS2-ZnS/ZrO2 composite with excellent photocatalytic degradation and hydrogen production performance, Chemosphere, 279 (2021) 130882.
[10] M. Nawaz, Morphology-controlled preparation of Bi2S3-ZnS chloroplast-like structures, formation mechanism and photocatalytic activity for hydrogen production, Journal of Photochemistry and Photobiology A: Chemistry, 332 (2017) 326-330.
[11] X. Hao, J. Zhou, Z. Cui, Y. Wang, Y. Wang, Z. Zou, Zn-vacancy mediated electron-hole separation in ZnS/g-C3N4 heterojunction for efficient visible-light photocatalytic hydrogen production, Applied Catalysis B: Environmental, 229 (2018) 41-51.
[12] E. Hong, J.H. Kim, Oxide content optimized ZnS–ZnO heterostructures via facile thermal treatment process for enhanced photocatalytic hydrogen production, International Journal of Hydrogen Energy, 39 (2014) 9985-9993.
[13] W. Cai, F. Zhang, Y. Wang, D. Li, A novel I-type 0D/0D ZnS@Cu3P heterojunction for photocatalytic hydrogen evolution, Inorganic Chemistry Communications, 134 (2021).
[14] S. Sun, D. Ren, M. Yang, J. Cui, Q. Yang, S. Liang, In-situ construction of direct Z-scheme sea-urchin-like ZnS/SnO2 heterojunctions for boosted photocatalytic hydrogen production, International Journal of Hydrogen Energy, 47 (2022) 9201-9208.
[15] J. Jiang, G. Wang, Y. Shao, J. Wang, S. Zhou, Y. Su, Step-scheme ZnO@ZnS hollow microspheres for improved photocatalytic H2 production performance, Chinese Journal of Catalysis, 43 (2022) 329-338.
[16] R. Rameshbabu, P. Ravi, G. Pecchi, E.J. Delgado, R.V. Mangalaraja, M. Sathish, Black Trumpet Mushroom-like ZnS incorporated with Cu3P: Noble metal free photocatalyst for superior photocatalytic H2 production, J Colloid Interface Sci, 590 (2021) 82-93.
[17] S. Zhu, Y. Zhang, X. Qian, X. Wang, W. Su, Zn defect-mediated Z-scheme electron-hole

separation in AgIn5S8/ZnS heterojunction for enhanced visible-light photocatalytic hydrogen evolution, Applied Surface Science, 504 (2020).
[18] L. Tie, S. Yang, C. Yu, H. Chen, Y. Liu, S. Dong, J. Sun, J. Sun, In situ decoration of ZnS nanoparticles with Ti3C2 MXene nanosheets for efficient photocatalytic hydrogen evolution, J Colloid Interface Sci, 545 (2019) 63-70.
[19] J.E. Samaniego-Benitez, L. Lartundo-Rojas, A. García-García, H.A. Calderón, A. Mantilla, One-step synthesis and photocatalytic behavior for H2 production from water of ZnS/MoS2 composite material, Catalysis Today, 360 (2021) 99-105.
[20] D. Wei, Y. Liu, X. Shao, X. Zhao, S. Ghufran, L. Wang, R. Wu, J. Guo, C. Yang, Cooperative effects of zinc–nickel sulfides as a dual cocatalyst for the enhanced photocatalytic hydrogen evolution activity of g-C3N4, Journal of Environmental Chemical Engineering, 10 (2022).
[21] M. Sathishkumar, M. Saroja, M. Venkatachalam, P. Gowthaman, S. Kannan, A. Balamurugan, rGO encapsulated ZnS photocatalysts for enhanced hydrogen evolution, Materials Letters, 323 (2022).