

Supplementary Information

Spatially ordered NiOOH-ZnS/CdS heterostructures with efficient photo-carriers transmission channel for markedly-improved H₂ production

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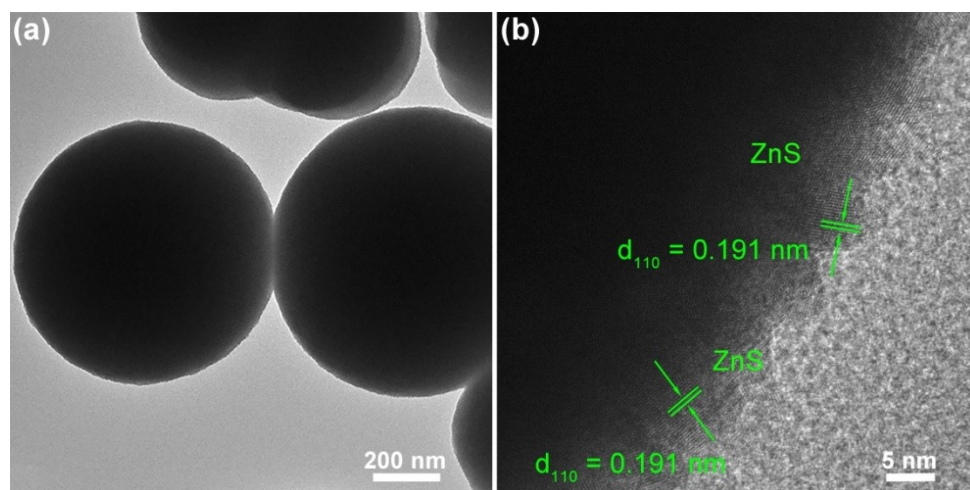


Fig. S1. (a) TEM and (b) HRTEM images of ZnS sample.

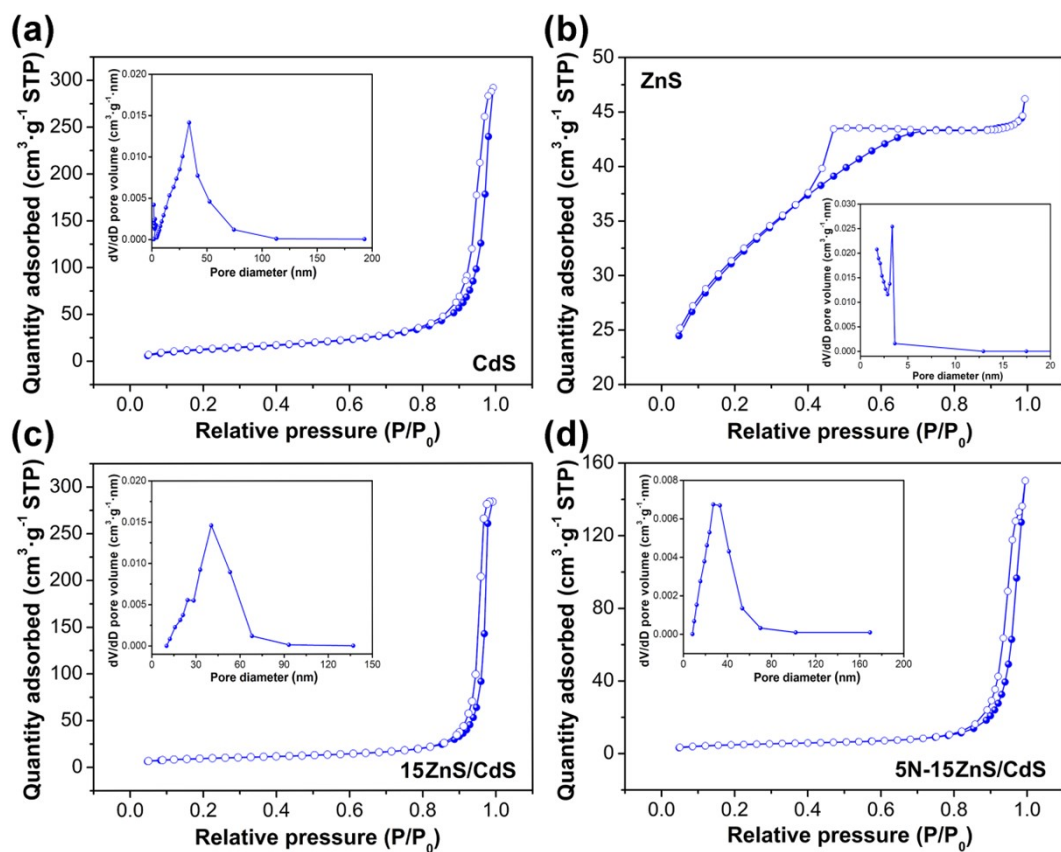


Fig. S2. N_2 adsorption-desorption isotherms and pore-size distributions of (a) CdS, (b) ZnS, (c) 15ZnS/CdS, and (d) 5N-15ZnS/CdS.

Table S1. Specific surface areas of different samples.

Sample	CdS	ZnS	15ZnS/CdS	5N-15ZnS/CdS
S_{BET} ($m^2 \cdot g^{-1}$)	48.3	106.0	32.3	17.1

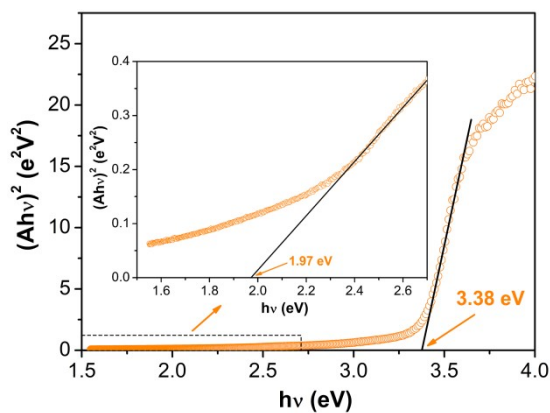


Fig. S3. Tauc plot of ZnS. Inset displays the bandgap relevant to zinc vacancies.

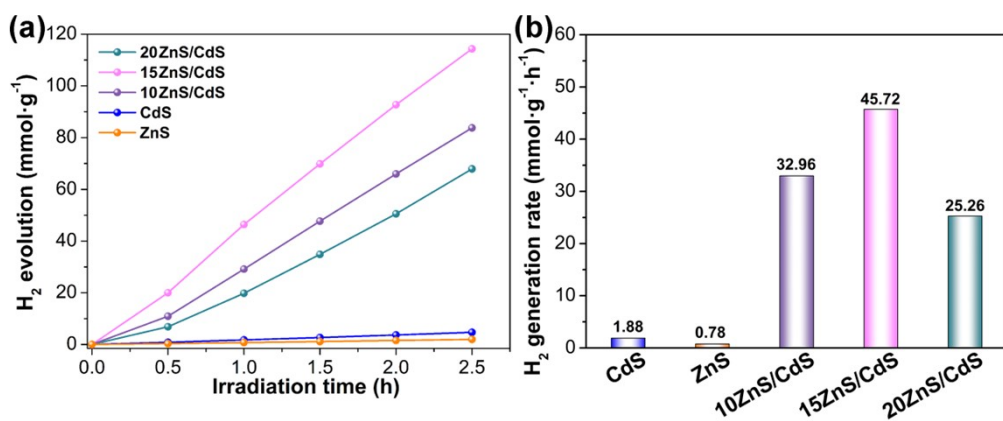


Fig. S4. (a) Photocatalytic H₂ generation activities and (b) average rates of different samples.

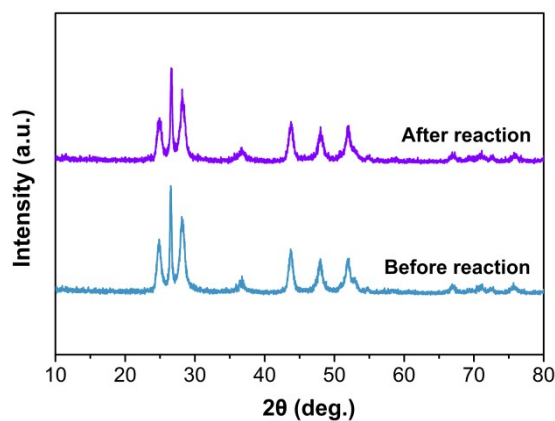


Fig. S5. XRD patterns of 5N-15ZnS/CdS before and after cyclic HER test.

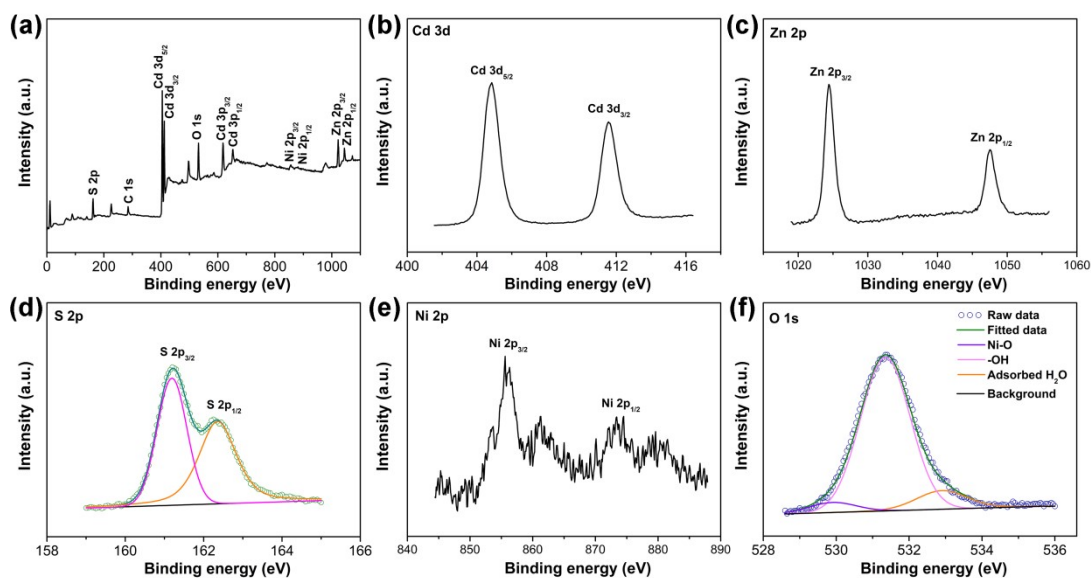


Fig. S6. (a) XPS survey and high-resolution (b) Cd 3d, (c) Zn 2p, (d) S 2p, (e) Ni 2p, and (f) O 1s XPS spectra of 5N-15ZnS/CdS after cyclic photocatalytic reaction.

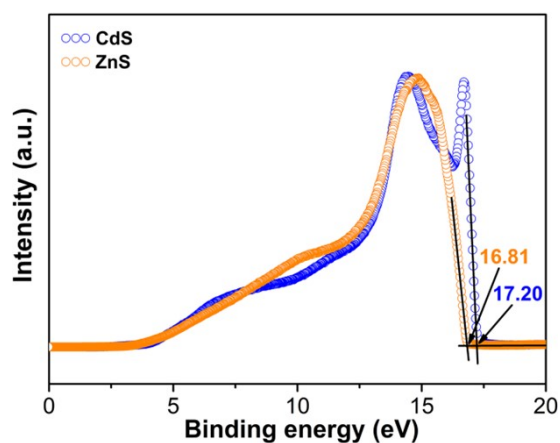


Fig. S7. UPS spectra of CdS and ZnS.

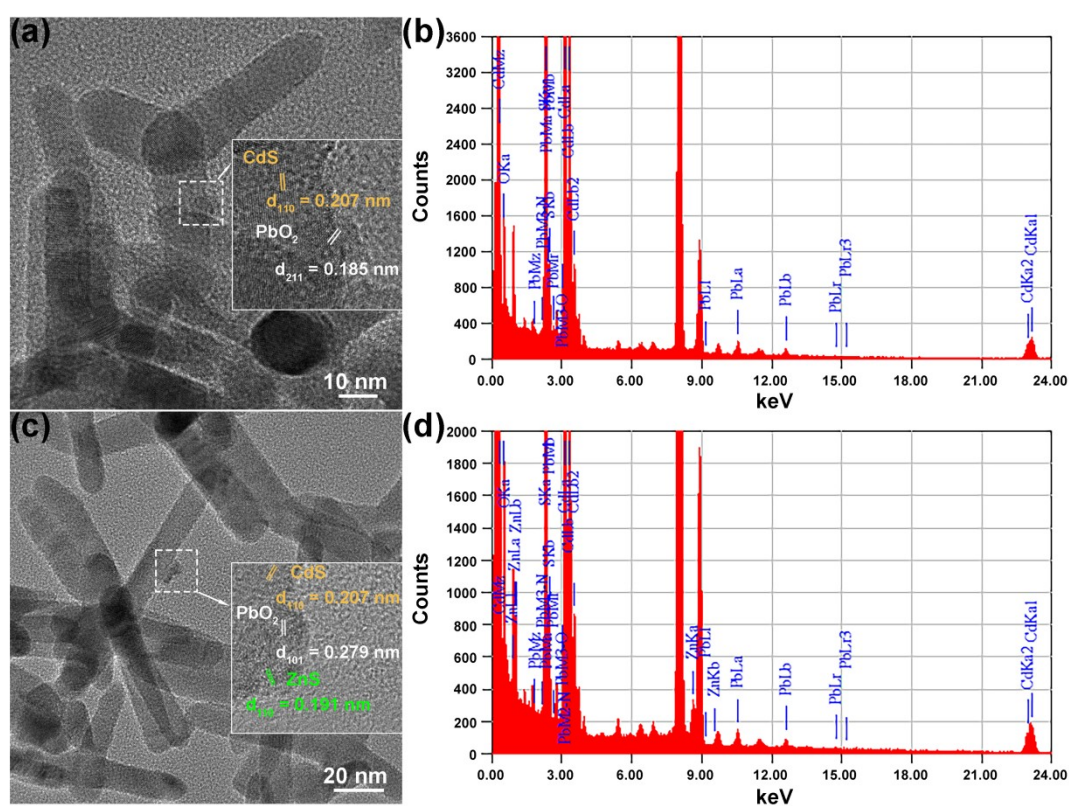


Fig. S8. (a, c) TEM, HRTEM (insets) and (b, d) EDX results of (a, b) CdS and (c, d) 15ZnS/CdS.

Table S2. Comparison on the HER activities of CdS-based photocatalysts.

Photocatalyst	Hole scavenger (aqueous solution)	Light source (Xe lamp)	Maximum rate (mmol·h ⁻¹ ·g ⁻¹)	AQY (420 nm)	Reference
5N-15ZnS/CdS	Na ₂ S/Na ₂ SO ₃	λ > 420 nm	152.20	40.9% 32.2% (400 nm)	This work
CdS/MoS ₂ /Mo	Na ₂ S/Na ₂ SO ₃	λ > 420 nm	4.54	11.03%	1
Ag ₂ S@CdS/ZnS	Na ₂ S/Na ₂ SO ₃	λ > 420 nm	3.76	6.83% (365 nm)	2
Co ₃ O ₄ /CdS	TEOA	λ > 420 nm	16.32	32.21%	3

MoSe₂/CdS-CdSe	Lactic acid	$\lambda > 420$ nm	24.34	28.5% (500 nm)	4
ZnIn₂S₄/CdS	Na ₂ S/Na ₂ SO ₃	$\lambda > 420$ nm	7.4	12.6%	5
TP/TAP/CdS	Ascorbic acid	$\lambda > 420$ nm	47.6	25.23%	6
CdS/Nb₂C	Na ₂ S/Na ₂ SO ₃	$\lambda > 420$ nm	2.53	3.69%	7
CdS@NiB	TEOA	$\lambda > 420$ nm	28.11	16.45%	8
CdS/PT	Lactic acid	$\lambda > 420$ nm	9.28	24.3%	9
NiO/CdS	Na ₂ S/Na ₂ SO ₃	$\lambda > 420$ nm	15.6	16%	10
WN/CdS	Lactic acid	$\lambda > 420$ nm	24.13	18.59%	11
MoSe₂/CdS	Lactic acid	$\lambda > 420$ nm	4.7	15.6% (450 nm)	12
CdS/Cu₇S₄/g-C₃N₄	Na ₂ S/Na ₂ SO ₃	$\lambda > 420$ nm	3.57	4.4%	13
CeO_{2-x}S_x@CdS	Na ₂ S/Na ₂ SO ₃	$\lambda > 420$ nm	1.15	-	14
CdS/MoO₂/MoS₂	Lactic acid	400–800 nm	1.25	11.3%	15
CdS@Au/MXene	Lactic acid	$\lambda > 420$ nm	5.37	16.7%	16
B-g-C₃N_x/Bi₂S₃/CdS	Methanol	$\lambda > 420$ nm	4.78	-	17
CdS@TPPA	Sodium ascorbate	$\lambda > 420$ nm	24.3	4.29%	18
CdS–NiFeS	Na ₂ S/Na ₂ SO ₃	320–780 nm	62.67	22.1% (380 nm)	19
MOF/CdS	Benzyl alcohol	$\lambda > 350$ nm	0.63	1.45%	20
SAO/CdS	Na ₂ S/Na ₂ SO ₃	$\lambda > 420$ nm	1.21	30.1%	21
CdS/VC	Lactic acid	$\lambda > 420$ nm	14.2	8.7%	22
CdS-CTF-1	Lactic acid	$\lambda > 420$ nm	11.43	16.3%	23
CdS/MoC	Lactic acid	$\lambda > 420$ nm	56.13	7.6%	24
Zr-MOF/CdS	Lactic acid	$\lambda > 420$ nm	1.86	-	25
Ca-modified CoP_x@CdS	Na ₂ S/Na ₂ SO ₃	$\lambda > 420$ nm	24.42	35.4%	26
P-CdS/Ni-MOL	Lactic acid	$\lambda > 420$ nm	29.81	4.78% (450 nm)	27
CdS/Cu₇S₄	Na ₂ S/Na ₂ SO ₃	$\lambda > 420$ nm	27.8	14.7%	28
MnO₂@CdS	Na ₂ S/Na ₂ SO ₃	$\lambda > 420$ nm	3.94	16.9% (450 nm)	29
CdS/ZnS	Na ₂ S/Na ₂ SO ₃	$\lambda > 400$ nm	14.02	2.76% (400 nm)	30

Table S3. Fitting parameters for the TRPL spectra of different samples.

Sample	τ_1 (ns)	Ref ₁ (%)	τ_2 (ns)	Ref ₂ (%)	τ_{avg} (ns)
CdS	0.63	37.3	4.19	62.7	1.92
ZnS	4.18	38.4	9.33	61.6	7.35

15ZnS/CdS	0.38	46.5	2.25	53.5	1.08
5N-15ZnS/CdS	0.29	52.8	1.50	47.2	0.86

References

- 1 L. Zhao, J. Jia, Z. Yang, J. Yu, A. Wang, Y. Sang, W. Zhou and H. Liu, *Appl. Catal. B-Environ.*, 2017, **210**, 290-296.
- 2 F. Zhao, Y. L. Law, N. Zhang, X. Wang, W. Wu, Z. Luo and Y. Wang, *Small*, 2023, **19**, 2208266.
- 3 C. Zhang, B. Liu, W. Li, X. Liu, K. Wang, Y. Deng, Z. Guo and Z. Lv, *J. Mater. Chem. A*, 2021, **9**, 11665-11673.
- 4 Y. Liu, Y. Li, Y. Lin, S. Yang, Q. Zhang and F. Peng, *Chem. Eng. J.*, 2020, **383**, 123133.
- 5 C. Q. Li, X. Du, S. Jiang, Y. Liu, Z. L. Niu, Z. Y. Liu, S. S. Yi and X. Z. Yue, *Adv. Sci.*, 2022, **9**, 2201773.
- 6 R. Gao, J. Bai, R. Shen, L. Hao, C. Huang, L. Wang, G. Liang, P. Zhang and X. Li, *J. Mater. Sci. Technol.*, 2023, **137**, 223-231.
- 7 M. Tayyab, U. E. Kulsoom, Y. Liu, S. Mansoor, M. Khan, Z. Akmal, A. Mushtaq, M. Arif, U. Shamriaz, L. Zhou, J. Lei and J. Zhang, *Int. J. Hydrogen Energy*, 2024, **51**, 1400-1413.
- 8 Z. Lv, Y. Wang, Y. Liu, J. Wang, G. Qin, Z. Guo and C. Zhang, *J. Phys. Chem. C*, 2022, **126**, 9041-9050.
- 9 C. Cheng, B. He, J. Fan, B. Cheng, S. Cao and J. Yu, *Adv. Mater.*, 2021, **33**, 13877-13889.
- 10 P. Wang, X. Huang, T. Dong, Y. Ren and J. Hu, *Appl. Surf. Sci.*, 2022, **606**, 154940.
- 11 H. Liu, J. Chen, W. Guo, Q. Xu and Y. Min, *J. Colloid Interface Sci.*, 2022, **613**, 652-660.
- 12 X. Yang, W. Liu, C. Han, C. Zhao, H. Tang, Q. Liu and J. Xu, *Mater. Today Phys.*, 2020, **15**, 100261.
- 13 J. Chu, X. Han, Z. Yu, Y. Du, B. Song and P. Xu, *ACS Appl. Mater. Interfaces*, 2018, **10**, 20404-20411.
- 14 N.-C. Zheng, T. Ouyang, Y. Chen, Z. Wang, D.-Y. Chen and Z.-Q. Liu, *Catal. Sci. Technol.*, 2019, **9**, 1357-1364.
- 15 C. Bie, B. Zhu, L. Wang, H. Yu, C. Jiang, T. Chen and J. Yu, *Angew. Chem. Int. Ed.*, 2022, **61**, 2212045.
- 16 Z. Li, W. Huang, J. Liu, K. Lv and Q. Li, *ACS Catal.*, 2021, **11**, 8510-8520.
- 17 Y. Xiao, M. Li, H. Li, Z. Wang and Y. Wang, *Nano Energy*, 2024, **120**, 109164.
- 18 Y. Chen, D. Yang, Y. Gao, R. Li, K. An, W. Wang, Z. Zhao, X. Xin, H. Ren and Z. Jiang, *Research*, 2021, **2021**, 9798564.
- 19 G. Sun, Z. Tai, F. Li, Q. Ye, T. Wang, Z. Fang, X. Hou, L. Jia and H. Wang, *ACS Sustain. Chem. Eng.*, 2023, **11**, 4009-4019.
- 20 B. Liu, J. Cai, J. Zhang, H. Tan, B. Cheng and J. Xu, *Chin. J. Catal.*, 2023, **51**, 204-215.
- 21 T. Wang, L. Xu, J. Cui, J. Wu, Z. Li, Y. Wu, B. Tian and Y. Tian, *Nano Lett.*, 2022, **22**, 6664-6670.
- 22 L. Tian, S. Min and F. Wang, *Appl. Catal. B-Environ.*, 2019, **259**, 118029.
- 23 D. Wang, H. Zeng, X. Xiong, M.-F. Wu, M. Xia, M. Xie, J.-P. Zou and S.-L. Luo, *Sci. Bull.*, 2020, **65**, 113-122.
- 24 Y. Lei, X. Wu, S. Li, J. Huang, K. H. Ng and Y. Lai, *J. Clean. Prod.*, 2021, **322**, 129018.
- 25 H. Hu, K. Zhang, G. Yan, L. Shi, B. Jia, H. Huang, Y. Zhang, X. Sun and T. Ma, *Chin. J. Catal.*,

2022, **43**, 2332-2341.

- 26 X. Ren, F. Liu, Q. Wang, H. Song, S. Luo, S. Li, G. Yang, B. Deng, Z. Huang, X.-S. Wang, L. Shi and J. Ye, *Appl. Catal. B-Environ.*, 2022, **303**, 120887.
- 27 W. Yang, M. Xu, K. Y. Tao, J. H. Zhang, D. C. Zhong and T. B. Lu, *Small*, 2022, **18**, 2200332.
- 28 D. Ren, R. Shen, Z. Jiang, X. Lu, X. Li, *Chin. J. Catal.*, 2020, **41**, 31-40.
- 29 S. Zulfiqar, S. Liu, N. Rahman, H. Tang, S. Shah, X.-H. Yu and Q.-Q. Liu, *Rare Met.*, 2021, **40**, 2381-2391.
- 30 D. Zhang, J. Teng, H. Yang, Z. Fang, K. Song, L. Wang, H. Hou, X. Lu, C. R. Bowen and W. Yang, *Carbon Energy*, 2022, **5**, 2381-2391.