Supporting Information

Designed synthesis of unique $ZnS@CdS@Cd_{0.5}Zn_{0.5}S-MoS_2$ hollow nano-spheres for efficient visible-light-driven H_2 evolution

Bowen Sun,[a] Hui Wang,[a] Jiakun Wu,[a] Yanling Geng,[a] Jixiang Xu,[a] Yaowei Wang,[b] Yanyan Li,*[a] Haifeng Lin*[a] and Lei Wang[a]

[a]*Key Laboratory of Eco-Chemical Engineering, Taishan Scholar Advantage and Characteristic Discipline Team of Eco-Chemical Process and Technology, Key Laboratory of Rubber-Plastics of Ministry of Education, Shandong Provincial Key Laboratory of Rubber-Plastics, College of Chemistry and Molecular Engineering, School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China*

[b]*Shandong Jingbo Petrochemical Co., Ltd., Binzhou 256500*

* Corresponding author. E-mail address: liyanyan6771@163.com (Y. Li), hflin20088@126.com (H. Lin).

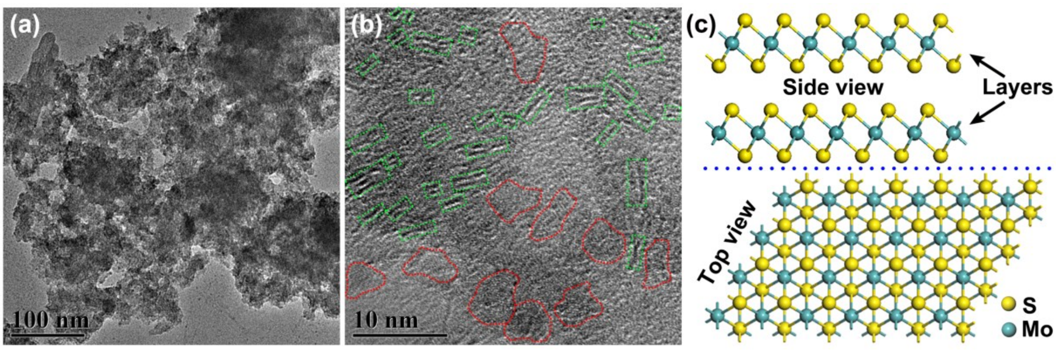

Fig. S1. (a) TEM and (b) HRTEM graphs of the prepared MoS_2 nanosheets. (c) The schematic atomic structures of MoS_2.

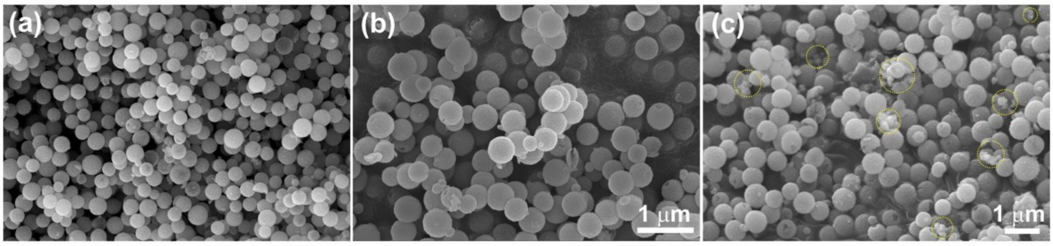

Fig. S2. SEM images of the ZnS@CdS nano-spheres coated with (a) 40 wt%, (b) 50 wt%, and (c) 60 wt% CdS.

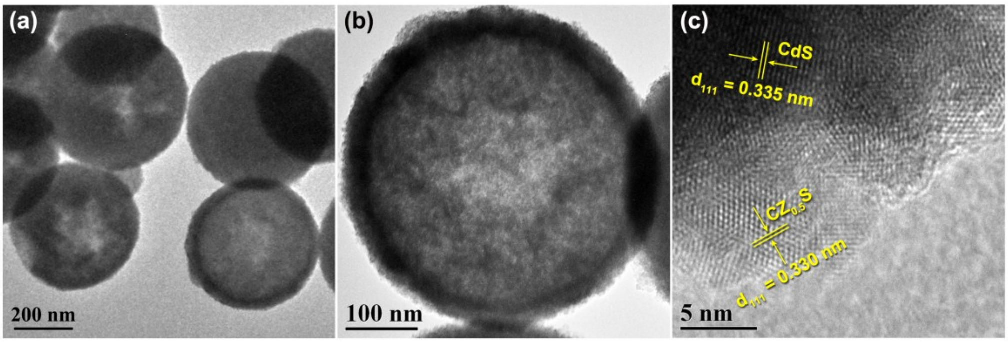

Fig. S3. (a, b) TEM and (c) HRTEM images of $ZS@50CS@30CZ_{0.5}S$ hollow nano-spheres.

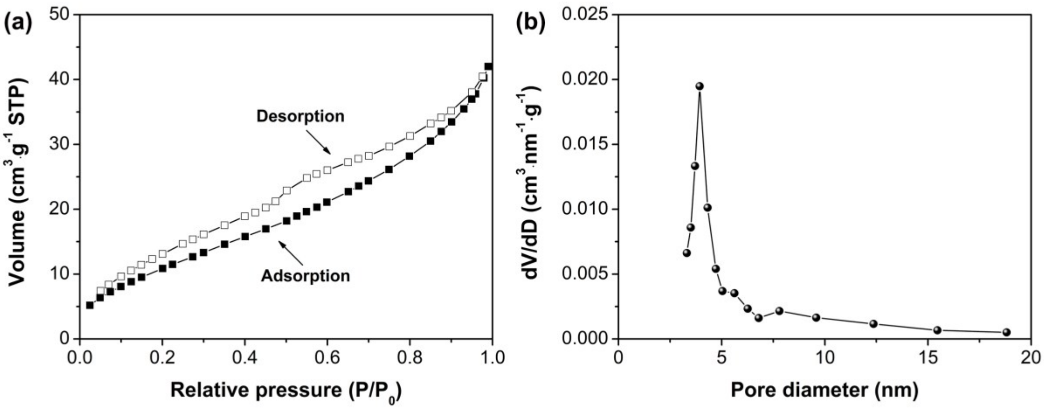

Fig. S4. (a) N_2 adsorption-desorption isotherm and (b) corresponding BJH pore-size distribution of the $ZS@50CS@30CZ_{0.5}S$-10M hybrid nano-spheres.

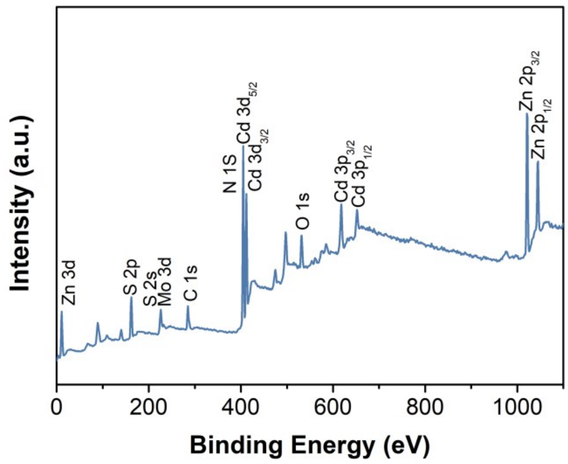

Fig. S5. XPS survey spectrum of the ZS@50CS@30$CZ_{0.5}$S-10M hybrid.

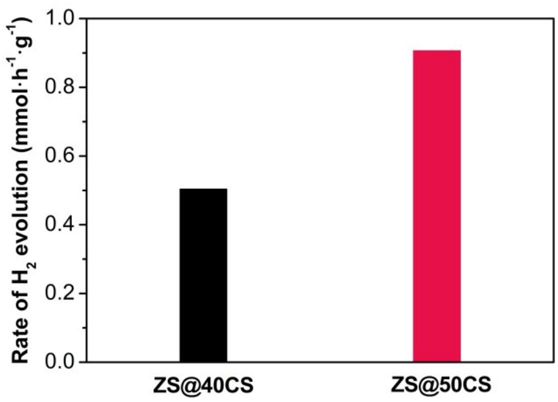

Fig. S6. H_2 evolution rates of the ZnS@CdS composites with different CdS loading amounts.

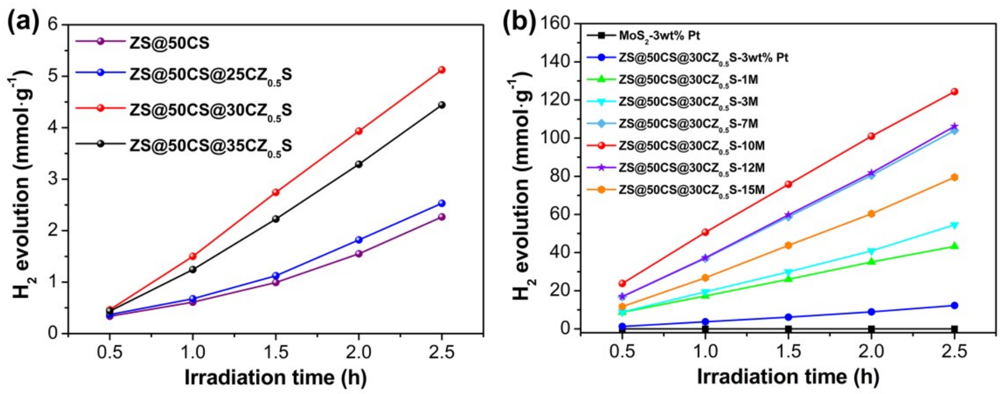

Fig. S7. (a) Photocatalytic HER activities of ZS@50CS, ZS@50CS@25CZS, ZS@50CS@30CZS, and ZS@50CS@35CZS. (b) Time-dependent photocatalytic H_2 evolution of different photocatalysts.

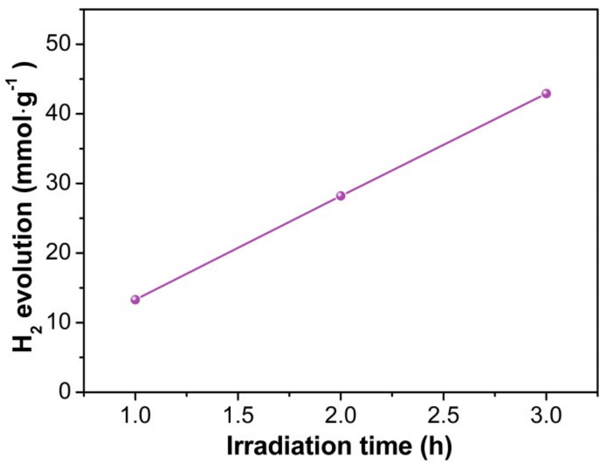

Fig. S8. H_2-evolving curve for calculating the apparent quantum yield of ZS@50CS@30CZ$_{0.5}$S-10M.

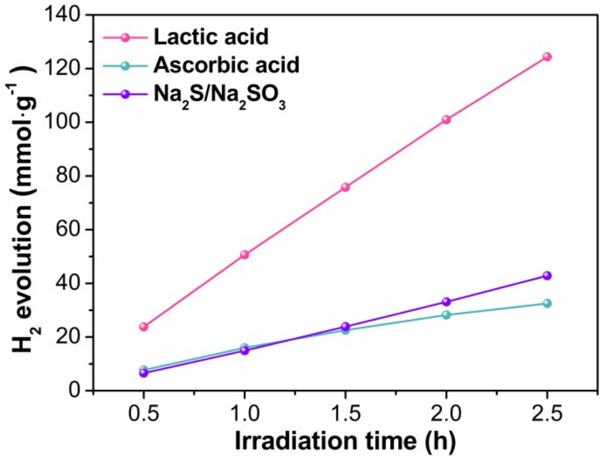

Fig. S9. Photocatalytic HER activities of ZS@50CS@30CZ$_{0.5}$S-10M in different sacrificial agent solutions.

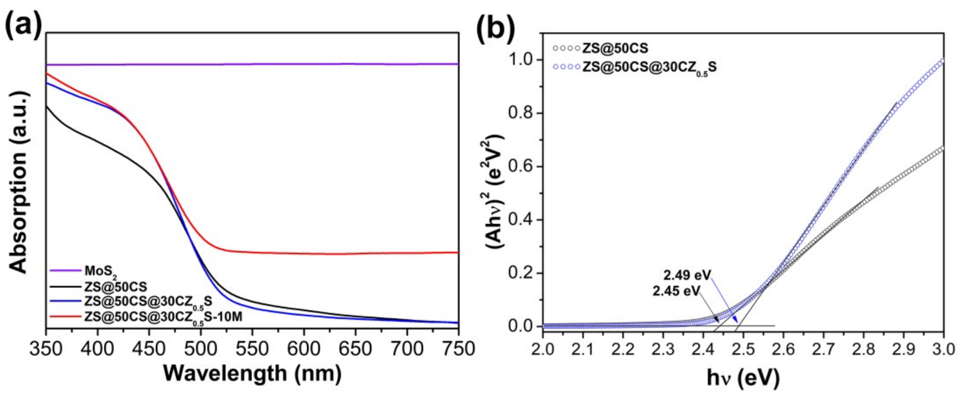

Fig. S10. (a) UV-vis absorption spectra and (b) corresponding bandgaps of different samples.

Table S1. HER activities of different photocatalysts.

Photocatalyst	Hole scavenger (aqueous solution)	Light source (Xe lamp)	Maximum rate ($mmol·h^{-1}·g^{-1}$)	Reference
$ZnS@CdS@Cd_{0.5}Zn_{0.5}S-MoS_2$	Lactic acid	λ > 420 nm	50.65	This work
MoS_2/CdS	Lactic acid	λ > 420 nm	5.40	[1]
$CdS@MoS_2$	Lactic acid	λ > 420 nm	26.14	[2]
CdS/MoS_2	TEOA	λ > 420 nm	1.79	[3]
CdS/MoS_2	S^{2-}/SO_3^{2-}	λ > 420 nm	0.38	[4]
MoS_2/CdS	Lactic acid	λ > 420 nm	10.85	[5]
MoS_2/CdS	Lactic acid	λ > 420 nm	49.80	[6]
MoS_2 QDs/CdS	Lactic acid	λ > 420 nm	1.03	[7]
$CdS-MoS_2$-MXene	Na_2S/Na_2SO_3	λ > 420 nm	9.68	[8]
$CdS@MoS_2$	Na_2S/Na_2SO_3	λ > 420 nm	17.20	[9]
CdS NP/Cd NSs/Pt	Na_2S/Na_2SO_3	λ > 420 nm	1.68	[10]
Graphene-CdS-MoS_2	Lactic acid	λ > 420 nm	12.83	[11]
CdS/Graphene Nanoribbon	Lactic acid	λ > 420 nm	1.89	[12]
$MoS_2-Mn_{0.2}Cd_{0.8}S/MnS$	Na_2S/Na_2SO_3	λ > 420 nm	19.90	[13]
MoS_2/CdS	Lactic acid	λ > 420 nm	15.26	[14]
WS_2/CdS	Lactic acid	λ > 420 nm	4.20	[15]
CdS/ZnS	Na_2S/Na_2SO_3	λ > 420 nm	11.62	[16]
Pt/CdS	Lactic acid	λ > 420 nm	1.49	[17]
Pt-PdS/CdS	Na_2S/Na_2SO_3	λ > 420 nm	8.77	[18]
$Ni_2P@CdS$	-	λ > 420 nm	2.54	[19]
$Cu_{1.94}S-Zn_xCd_{1-x}S$	Na_2S/Na_2SO_3	λ > 420 nm	7.74	[20]
CdS/WS_2	Lactic acid	350-1800 nm	14.10	[21]
$Co(OH)_2/CdS$	TEOA	λ > 420 nm	14.43	[22]
$MnO_x@CdS/CoP$	Na_2S/Na_2SO_3	UV and vis	23.84	[23]
CdS/Co_9S_8	Na_2S/Na_2SO_3	λ > 420 nm	5.15	[24]
MoS_2-NiS/CdS	Lactic acid	λ > 420 nm	2.53	[25]
$NiCo_2S_4/CdS$	Lactic acid	λ > 420 nm	20.0	[26]

References:

[1] X. Zong, H. J. Yan, G. P. Wu, G. J. Ma, F. Y. Wen, L. Wang and C. Li, Enhancement of photocatalytic H_2 evolution on CdS by loading MoS_2 as cocatalyst under visible light irradiation, *J. Am. Chem. Soc.*, 2008, **130**, 7176–7177.

[2] Y. Yang, Y. Zhang, Z. B. Fang, L. L. Zhang, Z. Y. Zheng, Z. F. Wang, W. H. Feng, S. X. Weng, S. Y. Zhang and P. Liu, Simultaneous realization of enhanced photoactivity and promoted photostability by multilayered MoS_2 coating on CdS nanowire structure via compact coating methodology, *ACS Appl. Mater. Interfaces*, 2017, **9**, 6950–6958.

[3] W. Zhao, J. C. Liu, Z. X. Ding, J. H. Zhang and X. Y. Wang, Optimal synthesis of platinum-free 1D/2D CdS/MoS_2 (CM) heterojunctions with improved photocatalytic hydrogen production performance, *J. Alloys Compd*., 2020, **813**, 152234.

[4] J. H. Xiong, Y. H. Liu, D. K. Wang, S. J. Liang, W. M. Wu and L. Wu, An efficient cocatalyst of defect-decorated MoS_2 ultrathin nanoplates for the promotion of photocatalytic hydrogen evolution over CdS nanocrystal, *J. Mater. Chem. A*, 2015, **3**, 12631–12635.

[5] H. F. Lin, Y. Y. Li, H. Y. Li and X. Wang, Multi-node CdS hetero-nanowires grown with defect-rich oxygen-doped MoS_2 ultrathin nanosheets for efficient visible-light photocatalytic H_2 evolution, *Nano Res*., 2017, **10**, 1377–1392.

[6] X. L. Yin, L. L. Li, W. J. Jiang, Y. Zhang, X. Zhang, L. J. Wan and J. S. Hu, MoS_2/CdS Nanosheets-on-nanorod heterostructure for highly efficient photocatalytic H_2 generation under visible light irradiation, *ACS Appl. Mater. Interfaces*, 2016, **8**, 15258–15266.

[7] J. Sun, L. X. Duan, Q. Wu and W. F. Yao, Synthesis of MoS_2 quantum dots cocatalysts and their efficient photocatalytic performance for hydrogen evolution, *Chem. Eng. J.*, 2018, **332**, 449–455.

[8] R. Chen, P. F. Wang, J. Chen, C. Wang and Y. H. Ao, Synergetic effect of MoS_2 and MXene on the enhanced H_2 evolution performance of CdS under visible light irradiation, *Appl. Surf. Sci*., 2019, 473, 11–19.

[9] S. W. Zhang, H. C. Yang, H. H. Gao, R. Y. Cao, J. Z. Huang and X. J. Xu, One-pot synthesis of CdS irregular nanospheres hybridized with oxygen-incorporated defect-rich MoS_2 ultrathin nanosheets for efficient photocatalytic hydrogen evolution, *ACS Appl. Mater. Interfaces*, 2017, **9**, 23635–23646.

[10] L. Shang, B. Tong, H. J. Yu, G. I. N. Waterhouse, C. Zhou, Y. F. Zhao, T. Muhammad, L. Z. Wu, C. H. Tung and T. R. Zhang, CdS Nanoparticle-decorated Cd nanosheets for efficient visible light-driven photocatalytic hydrogen evolution, *Adv. Energy. Mater*., 2016, **6**, 1501241.

[11] M. Q. Yang, C. Han and Y. J. Xu, Insight into the effect of highly dispersed MoS_2 versus layer-structured MoS_2 on the photocorrosion and photoactivity of CdS in graphene-CdS-MoS_2 composites, *J. Phys. Chem. C*, 2015, **119**, 27234–27246.

[12] Y. Xia, B. Cheng, J. J. Fan, J. G. Yu and G. Liu, Unraveling photoexcited charge transfer pathway and process of CdS/graphene nanoribbon composites toward visible-light photocatalytic hydrogen evolution, *Small* 2019, **15**, 1902459.

[13] J. M. Wang, J. Luo, D. Liu, S. T. Chen and T. Y. Peng, One-pot solvothermal synthesis of MoS_2-modified $Mn_{0.2}Cd_{0.8}S$/MnS heterojunction photocatalysts for highly efficient visible-light-driven H_2 production, *Appl. Catal. B: Environ*., 2019, **241**, 130–140.

[14] X. H. Qian, J. Y. Zhang, Z. Guo, S. Z. Liu, J. X. Liu and J. Lin, Facile ultrasound-driven formation and deposition of few-layered MoS_2 nanosheets on CdS for highly enhanced photocatalytic hydrogen evolution, *Appl. Surf. Sci*., 2019, **481**, 795–801.

[15] X. Zong, J. F. Han, G. J. Ma, H. J. Yan, G. P. Wu and C. Li, Photocatalytic H_2 evolution on CdS loaded with WS_2 as cocatalyst under visible light irradiation, *J. Phys. Chem. C*, 2011, **115**, 12202–12208.

[16] X. Q. Hao, Z. W. Cui, J. Z. Zhou, Y. C. Wang, Y. Hu, Y. Wang and Z. G. Zou, Architecture of high efficient zinc vacancy mediated Z-scheme photocatalyst from metal-organic frameworks, *Nano Energy*., 2018, **52**, 105–116.

[17] J. Jin, J. G. Yu, G. Liu and P. K. Wong, Single crystal CdS nanowires with high visible-light photocatalytic H_2-production performance, *J. Mater. Chem. A*, 2013, **1**, 10927–10934.

[18] H. J. Yan, J. H. Yang, G. J. Ma, G. P. Wu, X. Zong, Z. B. Lei, J. Y. Shi and C. Li, Visible-light-driven hydrogen production with extremely high quantum efficiency on Pt-PdS/CdS photocatalyst, *J. Catal.,* 2009, **266**, 165–168.

[19] W. L. Zhen, X. F. Ning, B. J. Yang, Y. Q. Wu, Z. Li and G. X. Lu, The enhancement of CdS photocatalytic activity for water splitting via anti-photocorrosion by coating Ni_2P shell and removing nascent formed oxygen with artificial gill, *Appl. Catal. B: Environ*., 2018, **221**, 243–257.

[20] Y. G. Chen, S. Zhao, X. Wang, Q. Peng, R. Lin, Y. Wang, R. A. Shen, X. Cao, L. B. Zhang, G. Zhou, J. Li, A. D. Xia and Y. D. Li. Synergetic integration of $Cu_{1.94}S$-$Zn_xCd_{1-x}S$ heteronanorods for enhanced visible-light-driven photocatalytic hydrogen production, *J. Am. Chem. Soc*., 2016, **138**, 4286–4289.

[21] K. Zhang, M. Fujitsuka, Y. K. Du and T. Majima, 2D/2D Heterostructured CdS/WS_2 with efficient charge separation improving H_2 evolution under visible light irradiation, *ACS Appl. Mater. Interfaces*, 2018, **10**, 20458–20466.

[22] X. Zhou, J. Jin, X. J. Zhu, J. Huang, J. G. Yu, W. Y. Wong and W. K. Wong, New $Co(OH)_2$/CdS nanowires for efficient visible light photocatalytic hydrogen production, *J. Mater. Chem. A*, 2016, 5282–5287.

[23] M. Y. Xing, B. C. Qiu, M. M. Du, Q. H. Zhu, L. Z. Wang and J. L. Zhang, Spatially separated CdS shells exposed with reduction surfaces for enhancing photocatalytic hydrogen evolution, *Adv. Funct. Mater*., 2017, **27**, 1702624

[24] P. F. Tan, Y. Liu, A. Q. Zhu, W. X. Zeng, H. Cui and J. Pan, Rational design of Z-Scheme system based on 3D hierarchical CdS supported 0D Co_9S_8 nanoparticles for superior photocatalytic H_2 generation, *ACS Sustainable Chem. Eng*., 2018, **6**, 10385–10394.

[25] M. C. Yin, W. L. Zhang, F. F. Qiao, J. F. Sun, Y. T. Fan and Z. J. Li, Hydrothermal synthesis of MoS_2-NiS/CdS with enhanced photocatalytic hydrogen production activity and stability, *J. Solid State Chem.*, 2019, **270**, 531–538.

[26] C. H. Li, S. W. Du, H. M. Wang, S. B. Naghadeh, A. L. Allen, X. Lin, G. J. Li, Y. Liu, H. Xu, C. Q. He, J. Z. Zhang and P. F. Fang, Enhanced visible-light-driven photocatalytic hydrogen generation using $NiCo_2S_4$/CdS nanocomposites, *Chem. Eng. J.*, 2019, **378**, 122089.