Supporting Information

Porous direct Z-scheme heterostructures of S-deficient CoS/CdS hexagonal nanoplates for robust photocatalytic H_2 generation

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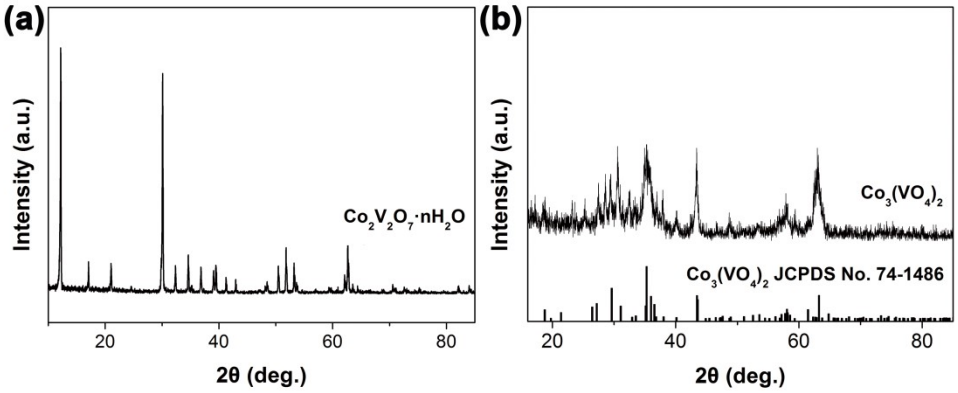

Fig. S1. XRD patterns of (a) $Co_2V_2O_7 \cdot nH_2O$ and (b) $Co_3(VO_4)_2$ HNPs.

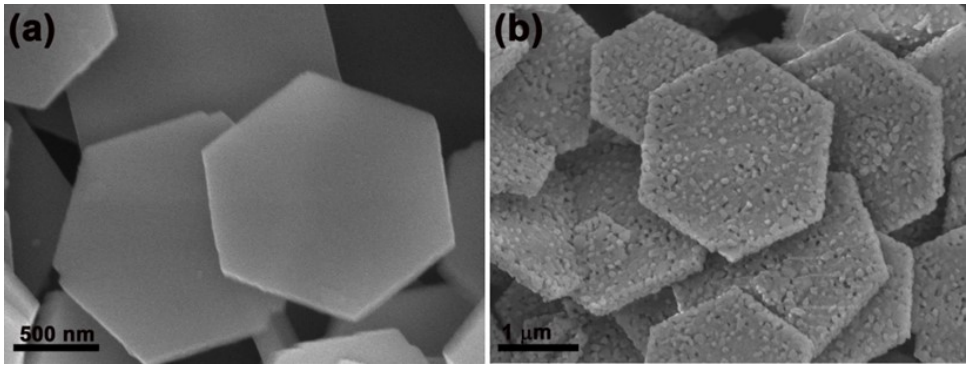

Fig. S2. SEM images of (a) $Co_2V_2O_7 \cdot nH_2O$ and (b) $Co_3(VO_4)_2$ HNPs.

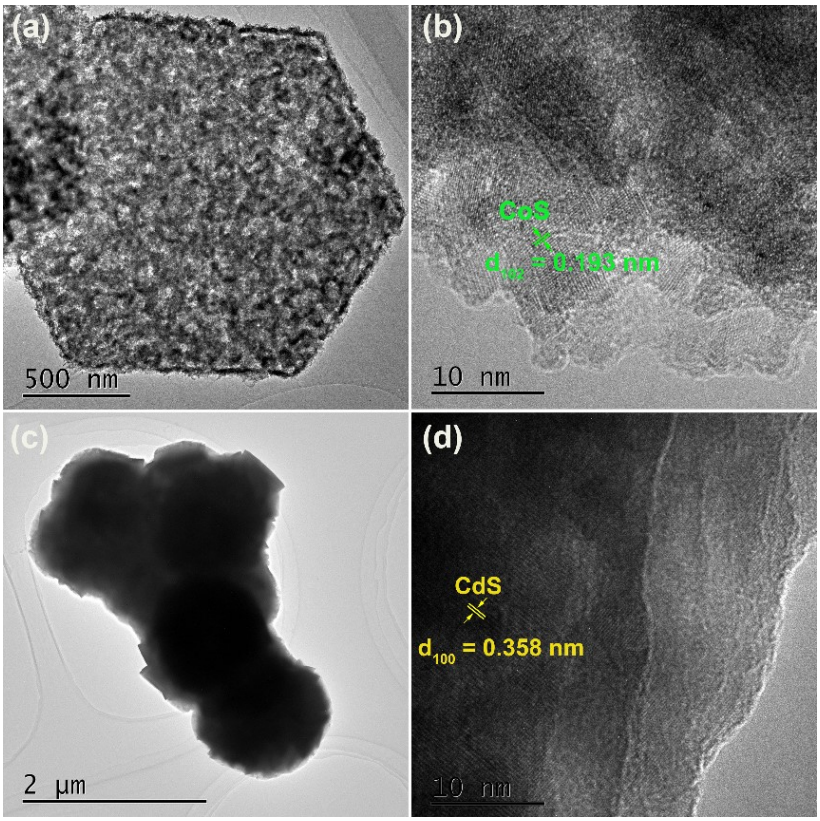

Fig. S3. (a, c) TEM and (b, d) HRTEM images of (a, b) CoS HNPs and (c, d) CdS nanocrystals.

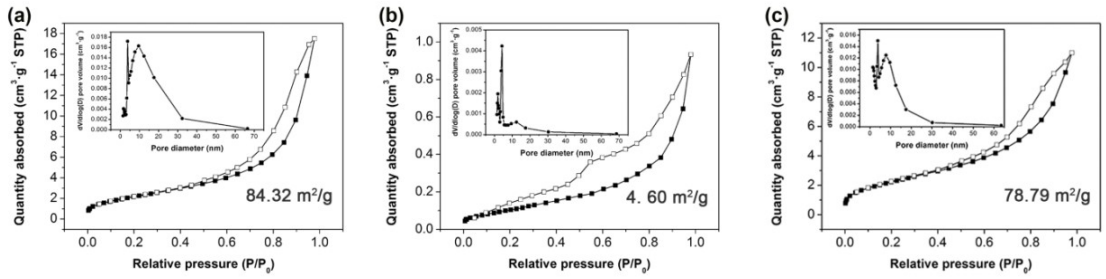

Fig. S4. N_2 adsorption-desorption isotherms and corresponding pore-size distributions of (a) CoS HNPs, (b) CdS nanocrystals, and (c) CoS/40% CdS hybrid HNPs.

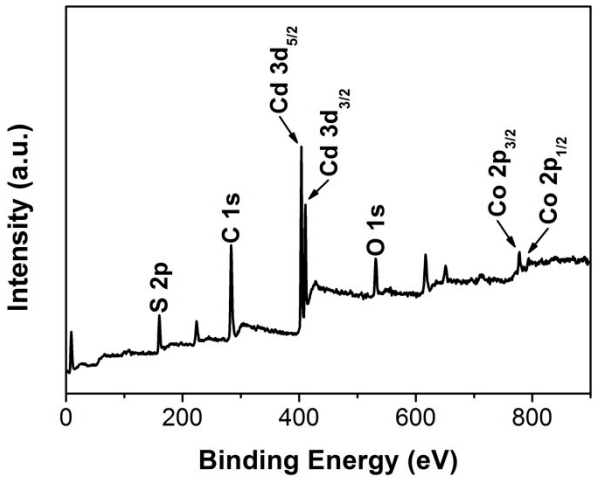

Fig. S5. XPS survey spectrum of the CoS/40% CdS hybrid HNPs.

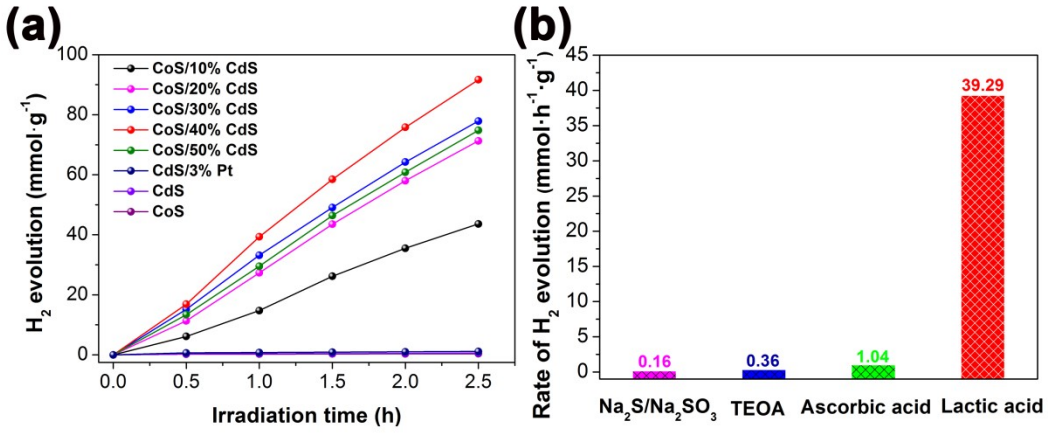

Fig. S6. (a) Photocatalytic H_2 evolution activities of different samples. (b) Average HER rates of CoS/40% CdS measured with different sacrificial agents.

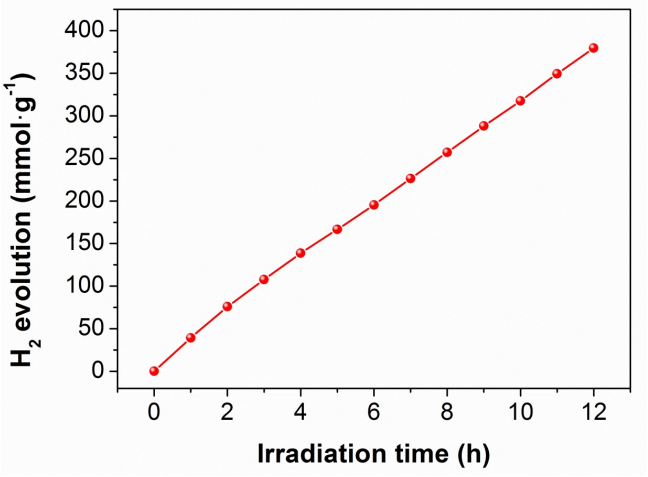

Fig. S7. Photocatalytic HER activity of CoS/40% CdS measured for 12 hours.

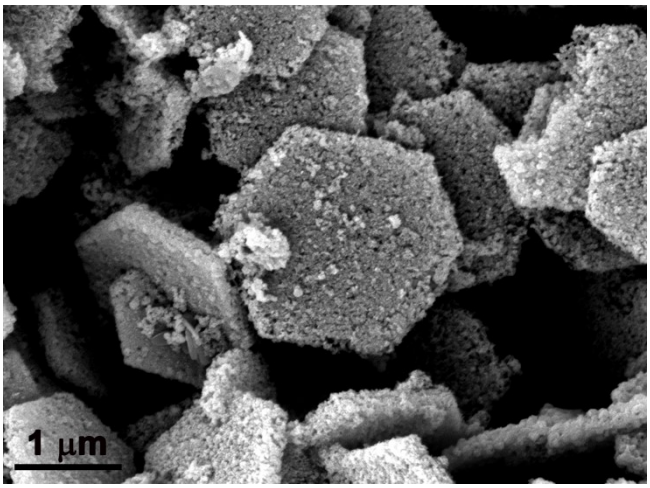

Fig. S8. SEM graph of the CoS/40% CdS composite after photocatalytic reaction.

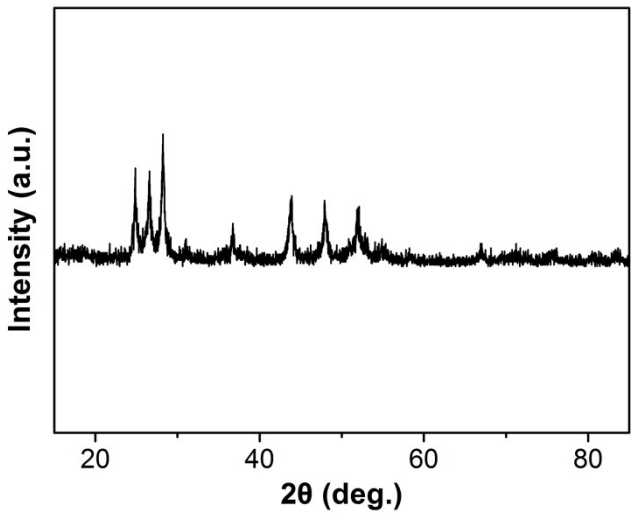

Fig. S9. XRD pattern of the CoS/40% CdS hybrid after photocatalytic test.

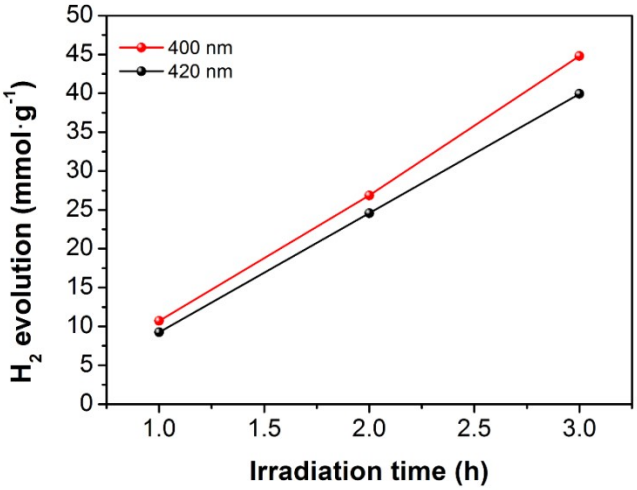

Fig. S10. HER activities of CoS/40% CdS tested under 400-nm and 420-nm monochromatic-light irradiation.

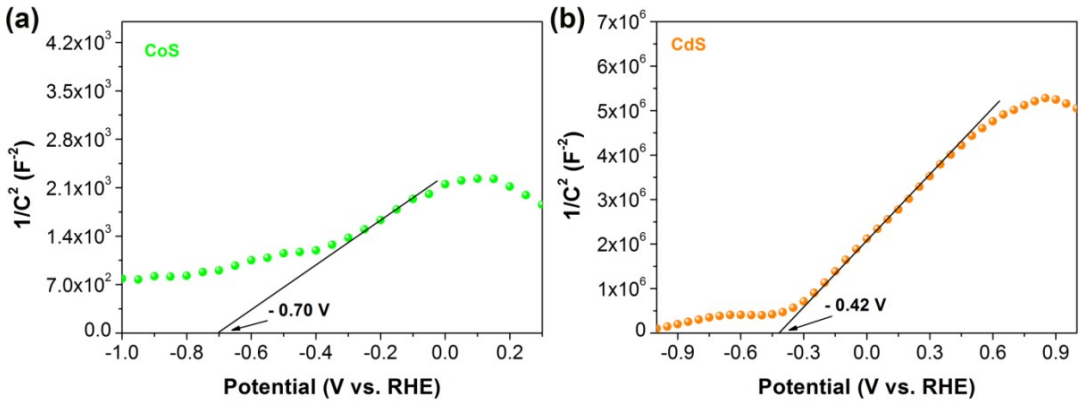

Fig. S11. Mott-Schottky curves of (a) CoS HNPs and (b) CdS nanocrystals.

Table S1. Visible-light-induced HER activities of CdS- and CoS-based composite photocatalysts.

Photocatalyst	Hole scavenger (aqueous solution)	Light source (Xe lamp)	Maximum rate ($mmol \cdot h^{-1} \cdot g^{-1}$)	AQY (420 nm)	Reference
CoS/CdS	Lactic acid	λ > 400 nm	39.29	12.5% 14.5% (400 nm)	This work
CdS/Co_3S_4	Lactic acid	λ > 420 nm	1.08	-	[1]
CdS/CoS_x	Lactic acid	λ > 420 nm	9.47	-	[2]
CdS/Co_9S_8	Lactic acid	λ > 420 nm	11.60	-	[3]
CoS_x/$Mn_{0.5}Cd_{0.5}S$	Na_2S/Na_2SO_3	λ > 420 nm	8.60	4.7%	[4]
CdS/Co_9S_8	Na_2S/Na_2SO_3	λ > 420 nm	1.06	-	[5]
CdS/Co_9S_8-RGO	Na_2S/Na_2SO_3	λ > 420 nm	4.82	-	[6]
Co_3S_4/Co-CdS	Na_2S/Na_2SO_3	λ > 420 nm	15.17	-	[7]

CdS/CoS_2	Ascorbic acid	λ > 420 nm	5.54	10.2%	[8]
Co_9S_8/CdS	Na_2S/Na_2SO_3	λ > 420 nm	14.96	-	[9]
Co_xS/SCN	Triethanolamine	λ > 420 nm	0.57	-	[10]
CdS/CoO_X	Na_2S/Na_2SO_3	λ > 420 nm	3.50	-	[11]
$CdS/Co\text{-}MoS_x$	Lactic acid	λ > 420 nm	13.50	23.5%	[12]
$CdS/CoMoS_4$	Lactic acid	λ > 420 nm	2.68	-	[13]
$a\text{-}CoMoS_x/CdS$	Lactic acid	λ > 420 nm	3.57	-	[14]
$Cd_{0.5}Zn_{0.5}S/CoO$	Na_2S/Na_2SO_3	λ > 420 nm	1.78	-	[15]
$Co_3S_4/CNNS$	Triethanolamine	λ > 420 nm	20.54	7.9%	[16]
CdS/CoO	Lactic acid	λ > 420 nm	6.45	-	[17]
WO_3/CoS_2	Triethanolamine	λ ≥ 420 nm	4.42	-	[18]
$Co_9S_8/Zn_{0.5}Cd_{0.5}S$	Na_2S/Na_2SO_3	λ > 400 nm	10.90	-	[19]
$CoS_2/g\text{-}C_3N_4$	Triethanolamine	λ > 420 nm	0.58	1.1%	[20]

References:

[1] F. Zhang, H.Q. Zhuang, J. Song, Y.L. Men, Y.X. Pan, S.H. Yu, Coupling cobalt sulfide nanosheets with cadmium sulfide nanoparticles for highly efficient visible-light-driven photocatalysis, *Appl. Catal. B: Environ*., 2018, **226**, 103–110.

[2] W. B. Li, K. Fang, Y. G. Zhang, Z. W. Chen, L. Wang and Y. Y. Bu, Fabrication of 1D/2D CdS/CoS_x direct Z-scheme photocatalyst with enhanced photocatalytic hydrogen evolution performance, *Int. J. Hydrogen Energy*, 2021, **46**, 9351-9359.

[3] C. Feng, Z. Y. Chen, J. P. Jing, M. M. Sun, J. Han, K. Fang and W. B. Li, Synergistic effect of hierarchical structure and Z-scheme heterojunction constructed by CdS nanoparticles and nanoflower-structured Co_9S_8 with significantly enhanced photocatalytic hydrogen production performance, *J. Photochem. Photobiol. A: Chem.*, 2021, **409**, 113160.

[4] M. D. Wang, Q. W. Liu, N. Xu, N. X. Su, X. X. Wang and W. Y. Su, An amorphous CoS_x modified $Mn_{0.5}Cd_{0.5}S$ solid solution with enhanced visible-light photocatalytic H_2-production activity, *Catal. Sci. Technol*., 2018, **8**, 4122-4128.

[5] B. Qiu, Q. Zhu, M. Du, L. Fan, M. Xing and J. Zhang, Efficient Solar Light Harvesting CdS/Co_9S_8 Hollow Cubes for Z-Scheme Photocatalytic Water Splitting, *Angew. Chem. Int. Ed*., 2017, **56**, 2684-2688.

[6] S. S. Kai, B. J. Xi, H. B. Li and S. L. Xiong, Z-scheme CdS/Co_9S_8-RGO for photocatalytic hydrogen production, *Inorg. Chem. Front*., 2020, **7**, 2692-2701.

[7] Y. P. Liu, B. X. Wang, Q. Zhang, S. Y. Yang, Y. H. Li, J. L. Zuo, H. J. Wang and F. Peng, A novel bicomponent Co_3S_4/Co@C cocatalyst on CdS, accelerating charge separation for highly efficient photocatalytic hydrogen evolution, *Green Chem*., 2020, **22**, 238-247.

[8] P. F. Wang, Y. S. Mao, L. N. Li, Z. R. Shen, X. Luo, K. F. Wu, P. F. An, H. T. Wang, L. N. Su, Y. Li and S. H. Zhan, Unraveling the Interfacial Charge Migration Pathway at the Atomic Level in a Highly Efficient Z-Scheme Photocatalyst, *Angew. Chem. Int. Ed*., 2019, **58**, 11329-11334.

[9] C. Xia, C. Y. Xue, W. X. Bian, J. Liu, J. J. Wang, Y. J. Wei and J. B. Zhang, Hollow Co_9S_8/CdS Nanocages as Efficient Photocatalysts for Hydrogen Evolution, *ACS Appl. Nano Mater*., 2021, **4**,

2743-2751.

[10] Q. H. Shen, R. H. Bibi, L. F. Wei, D. D. Hao, N. X. Li and J. C. Zhou, Well-dispersed CoS_x nanoparticles modified tubular sulfur doped carbon nitride for enhanced photocatalytic H_2 production activity, *Int. J. Hydrogen Energy*, 2019, **44**, 14550-14560.

[11] Y. Liu, S. P. Ding, Y. Q. Shi, X. F. Liu, Z. Z. Wu, Q. Q. Jiang, T. F. Zhou, N. K. Liu and J. C. Hu, Construction of CdS/CoO_x core-shell nanorods for efficient photocatalytic H_2 evolution, *Appl. Catal. B: Environ*., 2018, **234**, 109–116.

[12] Y. G. Lei, J. H. Hou, F. Wang, X. H. Ma, Z. L. Jin, J. Xu and S. X. Min, Boosting the catalytic performance of MoS_x cocatalysts over CdS nanoparticles for photocatalytic H_2 evolution by Co doping via a facile photochemical route, *Appl. Surf. Sci*., 2017, **420**, 456–464.

[13] Q. H. Li, X. Q. Qiao, Y. L. Jia, D. F. Hou and D. S. Li, Amorphous $CoMoS_4$ Nanostructure for Photocatalytic H_2 Generation, Nitrophenol Reduction, and Methylene Blue Adsorption, *ACS Appl. Nano Mater*., 2020, **3**, 68-76.

[14] W. J. Liu, X. F. Wang, H. G. Yu and J. G. Yu, Direct Photoinduced Synthesis of Amorphous $CoMoS_x$ Cocatalyst and Its Improved Photocatalytic H_2-Evolution Activity of CdS, *ACS Sustainable Chem. Eng*., 2018, **6**, 12436–12445.

[15] H. T. Zhao, L. Y. Guo, C. W. Xing, H. Y. Liu and X. Y. Li, A homojunction–heterojunction–homojunction scaffold boosts photocatalytic H_2 evolution over $Cd_{0.5}Zn_{0.5}S$/CoO hybrids, *J. Mater. Chem. A*, 2020, **8**, 1955–1965.

[16] H. C. Yang, J. M. Yin, R. Y. Cao, P. X. Sun, S. W. Zhang and X. J. Xu, Constructing highly dispersed 0D Co_3S_4 quantum dots/2D g-C_3N_4 nanosheets nanocomposites for excellent photocatalytic performance, *Sci. Bull*., 2019, **64**, 1510-1517.

[17] J. Y. Chu, G. J. Sun, X. J. Han, X. Chen, J. J. Wang, W. Hu, I. Waluyo, A. Hunt, Y. C. Du, B. Song and P. Xu, Ultrafine CoO nanoparticles as an efficient cocatalyst for enhanced photocatalytic hydrogen evolution, *Nanoscale*, 2019, **11**, 15633-15640.

[18] L. J. Ma, J. Xu, L. J. Li, M. Mao and S. Zhao, Hydrothermal synthesis of WO_3/CoS_2 n–n heterojunction for Z-scheme photocatalytic H_2 evolution, *New J. Chem*., 2020, **44**, 18326-18336.

[19] X. L. Li, R. B. He, Y. J. Dai, S. S. Li, N. Xiao, A. X. Wang, Y. Q. Gao, N. Li, J. F. Gao, L. H. Zhang and L. Ge, Design and fabrication of $Co_9S_8/Zn_{0.5}Cd_{0.5}S$ hollow nanocages with significantly enhanced photocatalytic hydrogen production activity, *Chem. Eng. J*., 2020, **400**, 125474.

[20] Y. Z. Zhang, J. W. Shi, Z. X. Huang, X. J. Guan, S. C. Zong, C. Cheng, B. T. Zheng and L. J. Guo, Synchronous construction of CoS_2 in-situ loading and S doping for g-C_3N_4: Enhanced photocatalytic H_2-evolution activity and mechanism insight, *Chem. Eng. J*., 2020, **401**, 126135.