Electronic Supplementary Material (ESI) for Materials Advances. This journal is © The Royal Society of Chemistry 2021

## Supplementary Information

Amorphous  $NiS_x$  film as a robust cocatalyst for boosting photocatalytic

hydrogen generation over ultrafine ZnCdS nanoparticles

Shenglong Gan, Min Deng, Dongfang Hou\*, Lei huang, Xiu-qing Qiao and Dong-sheng Li\* College of Materials and Chemical Engineering, Hubei Provincial Collaborative Innovation Center for New Energy Microgrid, Key laboratory of inorganic nonmetallic crystalline and energy conversion materials, China Three Gorges University, Yichang 443002, P. R. China



Fig. S1 SEM images: (a) ZCS, (b) ZCS-NS2, (c) CS-NS, and (d) ZS-NS nanocomposites.



Fig. S2 The XRD patterns of ZCS and ZCS-NSE.



Fig. S3 High-resolution XPS spectra of Ni 2p of (a) CdS and (b) ZnS.



Fig. S4 Nitrogen adsorption/desorption isotherms and the corresponding pore-size distribution curves of the CS-NS, ZS-NS, CdS and ZnS.

As shown in Fig. S4 and Table S1, the present synthetic method can be extended to synthesize CS-NS, ZS-NS, CdS and ZnS with large specific surface areas, which is benefit to improve the photocatalytic performance.

Sample	$\frac{S_{BET}}{(m^2g^{\text{-}1})}$	Mean pore diameter (nm)	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )
ZCS	102.23	11.75	0.30
ZCS-NS1	89.01	12.60	0.28
ZCS-NS2	96.30	11.90	0.29
ZCS-NS3	95.14	11.82	0.28
ZnS	70.66	13.77	0.247
ZS-NS	67.11	15.31	0.26
CdS	78.57	13.61	0.27
CS-NS	70.63	14.02	0.25

Table S1 The corresponding textural properties of prepared samples.

Table S2 Comparison of some nickel sulfide cocatalysts for photocatalytic hydrogen evolution.

Photocatalyst	Light source	Sacrificial agent	Activity	Ref.
			mmol h <sup>-1</sup> g <sup>-1</sup>	. 1
NiS/CdS	300 W Xe-lamp	$Na_2S, Na_2SO_3$	1.131	11
NiS/Zn <sub>0.5</sub> Cd <sub>0.5</sub> S	λ>420 nm 300 W Xe-lamp	Na <sub>2</sub> S, Na <sub>2</sub> SO <sub>3</sub>	16.780	2 <sup>2</sup>
	λ>420 nm			
NiS/Zn <sub>0.5</sub> Cd <sub>0.5</sub> S/ RGO	solar simulator	Na <sub>2</sub> S, Na <sub>2</sub> SO <sub>3</sub>	7.514	3 <sup>3</sup>
NiS/Cd <sub>0.4</sub> Zn <sub>0.6</sub> S	AM 1.5, 100 mW cm <sup>-2</sup> 300 W Xe-lamp	Na <sub>2</sub> S, Na <sub>2</sub> SO <sub>3</sub>	1.2	4 <sup>4</sup>
	λ>420 nm			
CdS/NiS/RGO	300 W Xe-lamp	lactic acid	14.960	55
	λ>420 nm			
NiS/ZnIn <sub>2</sub> S <sub>4</sub>	320 W Xe-lamp	lactic acid	3.333	66
2 .	$\lambda > 420 \text{ nm}$			
C2N4- Zno 5Cdo 5S -NiS	300 W Xe-lamp	Na S. Na SO	53 19	77
	$\lambda > 120 \text{ nm}$	11020, 1102003	00.17	,
7n Cd S/Mas2/Nis	200  W  Ya lamp	No S. No SO	41.20	<b>Q</b> 8
ZII <sub>0.2</sub> Cu <sub>0.8</sub> 5/10052/1015		$11a_25, 11a_250_3$	41.29	0
	solar light irradiation	11	<b>7</b> 0 4	00
$N_1Sx/Cd_{0.8}Zn_{0.2}S/rGO$	300 W Xe-lamp	lactic acid	7.84	99
	λ>420 nm			
Cd <sub>0.5</sub> Zn <sub>0.5</sub> S(en)/NiS	300 W Xe-lamp	$Na_2S$ , $Na_2SO_3$	38.187	$10^{10}$
	λ>420 nm			
CdS/La2Ti2O7/NiS2	300 W Xe-lamp	lactic acid	12.77	$11^{11}$
	λ>400 nm			
NiS/g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp	triethanolamine	16.4	1212
	an AM 15G filter			
NiS/CdS	300 W Xe-lamp	lactic acid	30.1	1313
1110/040	1>120 nm	nuclio uciu	50.1	15
NiSy/Cd7n9	$\frac{1}{200}$ W Vo lown	lactic soid	67 75	This
INISX/CULIIS		lactic acid	07.73	11115
	λ>420 nm			Work

	420 nm		500 nm		520 nm	
Sample -	H <sub>2</sub> evolution (µmol g <sup>-1</sup> h <sup>-1</sup> )	AQE	$H_2$ evolution (µmol g <sup>-1</sup> h <sup>-1</sup> )	AQE	$H_2$ evolution (µmol g <sup>-1</sup> h <sup>-1</sup> )	AQE
ZCS	216.3	0.155%	23.7	0.015%	5.7	0.003%
ZCS-NS2	23991.0	17.073%	3286.8	1.965%	92.3	0.053%

Table S3 The photocatalytic hydrogen evolution rates under single-wavelength light and the corresponding AQE of ZCS and ZCS-NS2.



Fig. S5 The XRD patterns of the fresh and used ZCS-NS2 photocatalyst



Fig. S6 Time-resolved PL decay under the excitation of 420 nm for ZCS and ZCS-NS2 samples.

Table S4 The radiative fluorescence lifetimes and relative percentages of the photoinduced charge carriers in the ZCS and ZCS-NS2

Sample	$\tau_1(ns)$	Rel. (%)	$\tau_2(ns)$	Rel. (%)	τ(ns)

ZCS	1.02	43.27	4.82	56.73	3.18
ZCS-NS2	1.42	57.54	8.06	42.46	4.24

## References

- 1 J. Zhang, S. Z. Qiao, L. Qi and J. Yu, *Phys. Chem. Chem. Phys.*, 2013, **15**, 12088-12094.
- 2 X. Zhao, J. Feng, J. Liu, W. Shi, G. Yang, G.-C. Wang and P. Cheng, *Angew. Chem. Int. Ed.*, 2018, **57**, 9790-9794.
- 3 J. Zhang, L. Qi, J. Ran, J. Yu and S. Z. Qiao, Adv. Energy Mater., 2014, 4, 1301925.
- 4 J. Wang, B. Li, J. Chen, N. Li, J. Zheng, J. Zhao and Z. Zhu, *Appl. Surf. Sci.*, 2012, **259**, 118-123.
- 5 L. Li, J. Wu, B. Liu, X. Liu, C. Li, Y. Gong, Y. Huang and L. Pan, *Catal. Today*, 2018, **315**, 110-116.
- 6 A. Yan, X. Shi, F. Huang, M. Fujitsuka and T. Majima, *Appl. Catal., B*, 2019, **250**, 163-170.
- 7 G. Xu, X. Lin, Y. Tong, H. Du, L. Gu and Y. Yuan, *Mater. Lett.*, 2019, **255**, 126593.
- 8 C. An, J. Feng, J. Liu, G. Wei, J. Du, H. Wang, S. Jin and J. Zhang, *Inorg Chem Front*, 2017, **4**, 1042-1047.
- 9 C. Xue, H. Li, H. An, B. Yang, J. Wei and G. Yang, ACS Catal., 2018, 8, 1532-1545.
- 10 M. Chen, P. Wu, Y. Zhu, S. Yang, Y. Lu and Z. Lin, *Int. J. Hydrogen Energy*, 2018, **43**, 10938-10949.
- 11 J. Yue, J. Xu, J. Niu and M. Chen, Int. J. Hydrogen Energy, 2019, 44, 19603-19613.
- H. Zhao, H. Zhang, G. Cui, Y. Dong, G. Wang, P. Jiang, X. Wu and N. Zhao, *Appl. Catal., B*, 2018, 225, 284-290.
- 13 Y. Zhang, Z. Peng, S. Guan and X. Fu, *Appl. Catal., B*, 2018, **224**, 1000-1008.