First fabrication of Ni_3N/Ni_4N heterojunction to boost the H_2 evolution efficiency of $Zn_{0.5}Cd_{0.5}S$

Zhanbin Jin,[a] Tingting Wei,[a] Fengyan Li,[a] Qiu Zhang,[a] and Lin Xu*[a]*

Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P. R. cChina

Material characterizations

The composition and phase composition of the samples were studied by powder X-ray diffraction (D ≤ Max200PC, Japanese; Cu K α = 1.5404). The scanning range of 2 theta is 10 °~ 80 °, and the scanning rate is 10 °min^{-1}. The microstructure, size and EDX-mapping of the samples were studied by scanning electron microscope (Hitachi SU-8000 FE-SEM). The transmission electron microscope (TEM) was carried out on JEM-2100-F microscope with acceleration voltage of 200 kV. The sample powder was uniformly dispersed in ethanol by ultrasonic treatment and the very thin suspension droplets were placed on the copper plate and then dry in the oven. Using monochromatic Al K α radiation as excitation source, X-ray photoelectron spectroscopy (XPS), has been carried out on USWHA 150 photoelectron spectrometer. The binding energy of XPS is related to the C1 peak at 284.8 eV of uncertain carbon on the surface. The specific surface area of Brunauer Emmett Teller (BET) of the product powder was determined by using the nitrogen adsorption/desorption isotherm obtained by a Micromerics ASAP 2020 nitrogen adsorption/desorption apparatus. Photoluminescence (PL) was measured on F-7000 fluorescence spectrophotometer. The UV-vis diffuse reflection spectrum (DRS) of the sample was detected by varian cary 700 spectrophotometer from 200-800 nm and $BaSO_4$ was used as the reflectance standard. All the photocurrent measurements such as electrochemical impedance spectra (EIS) and Transient photocurren were measured in 0.5 M Na_2SO_4 solution electrolyte on an Ivium workstation (Ivium Stat.h, Ivium Holland, Inc.).

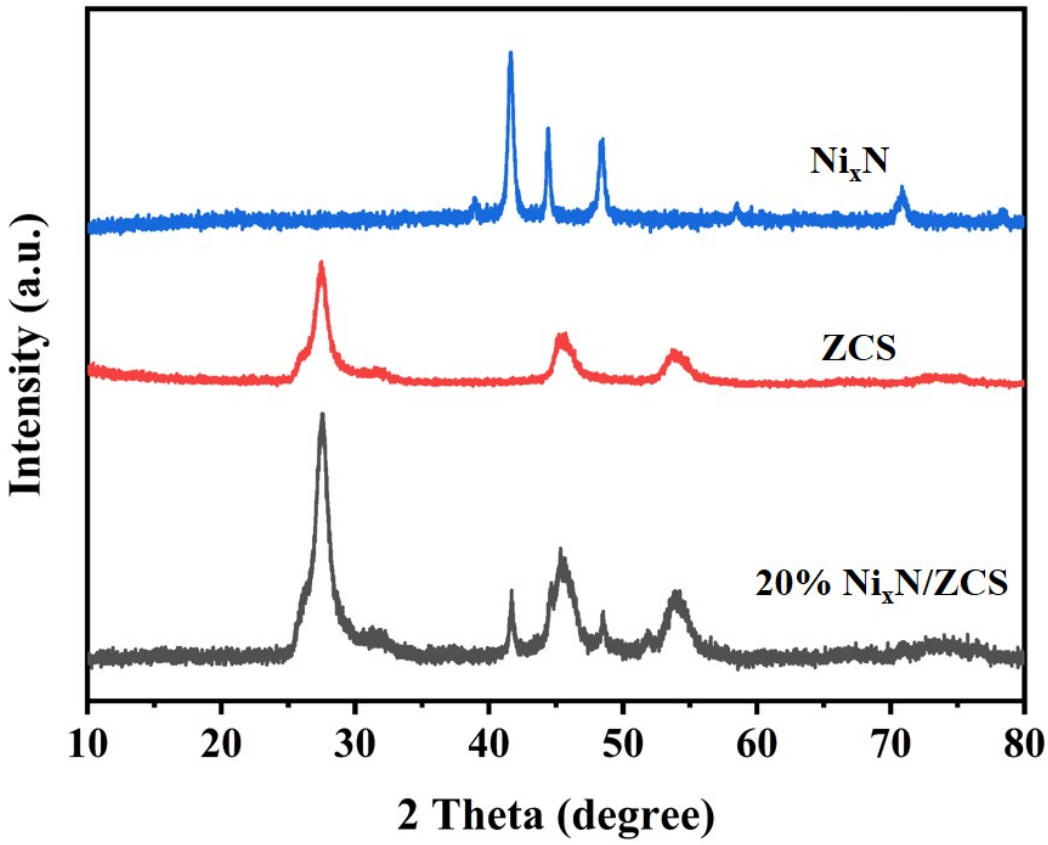


Fig. S1. The XRD of ZCS, Ni_xN and 20% Ni_xN/ZCS samples.

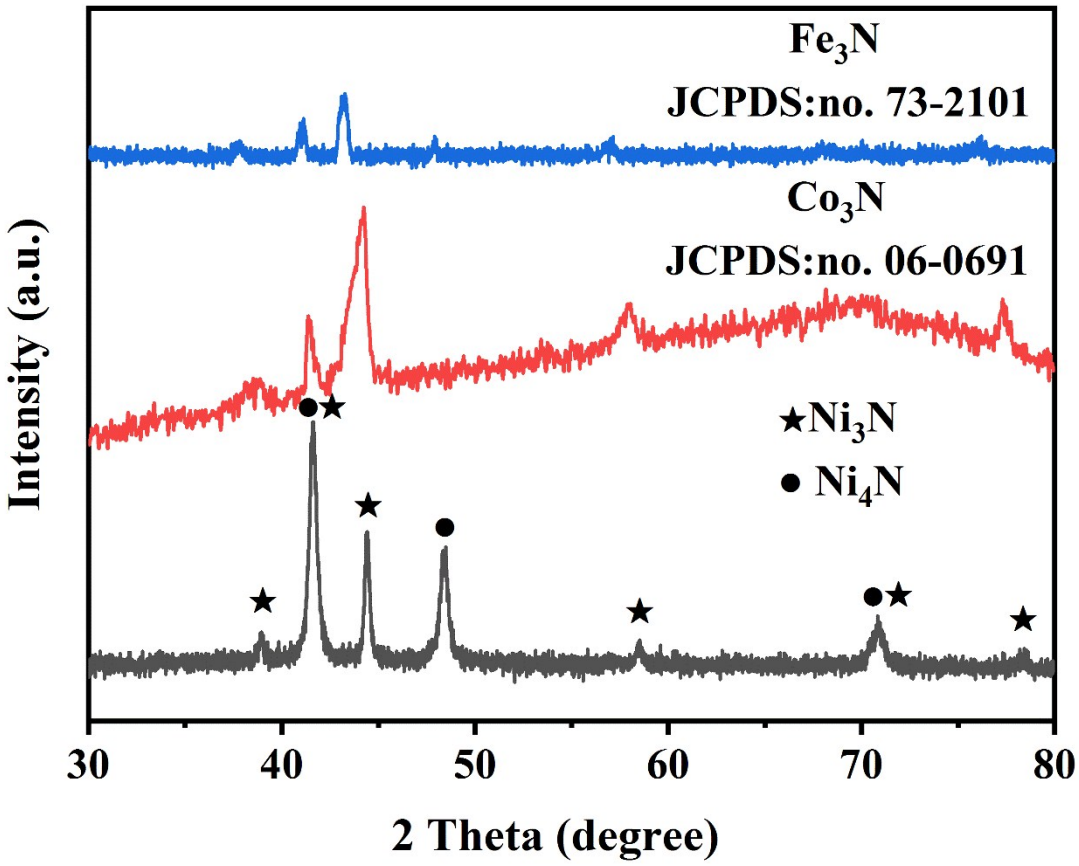


Fig. S2. The XRD of Fe_3N, NixN and Co_3N samples

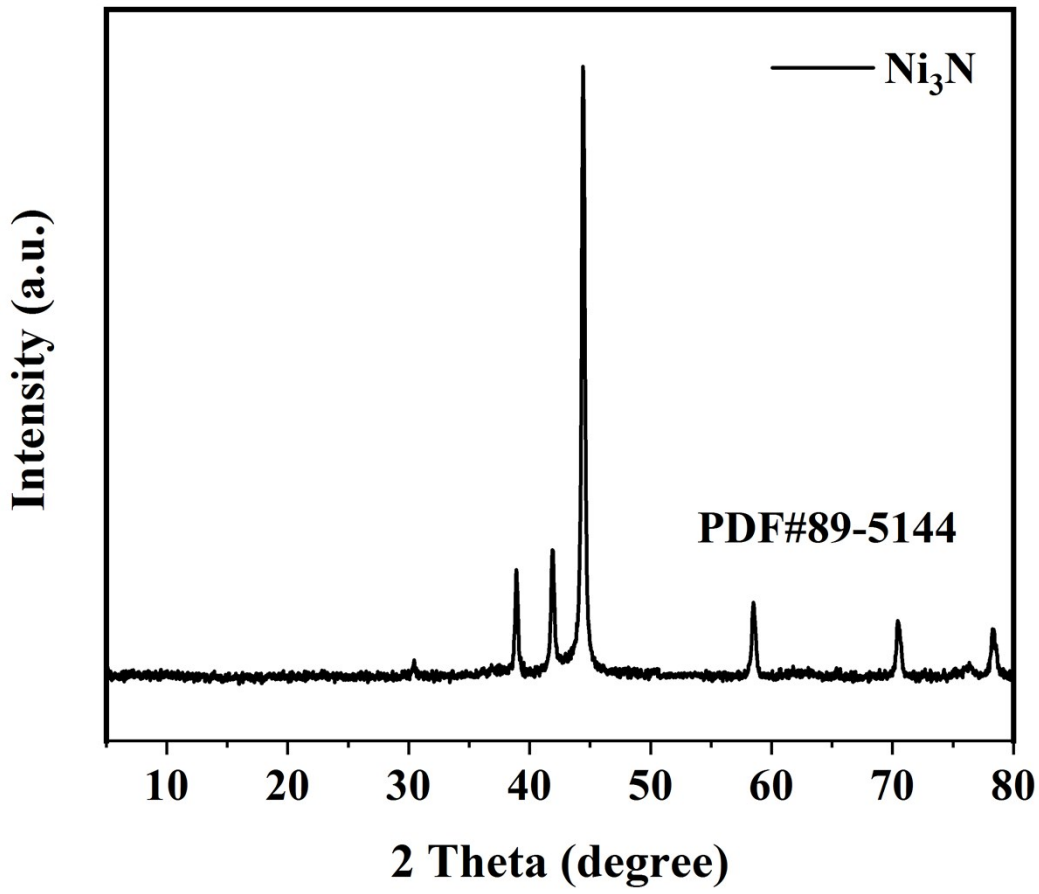
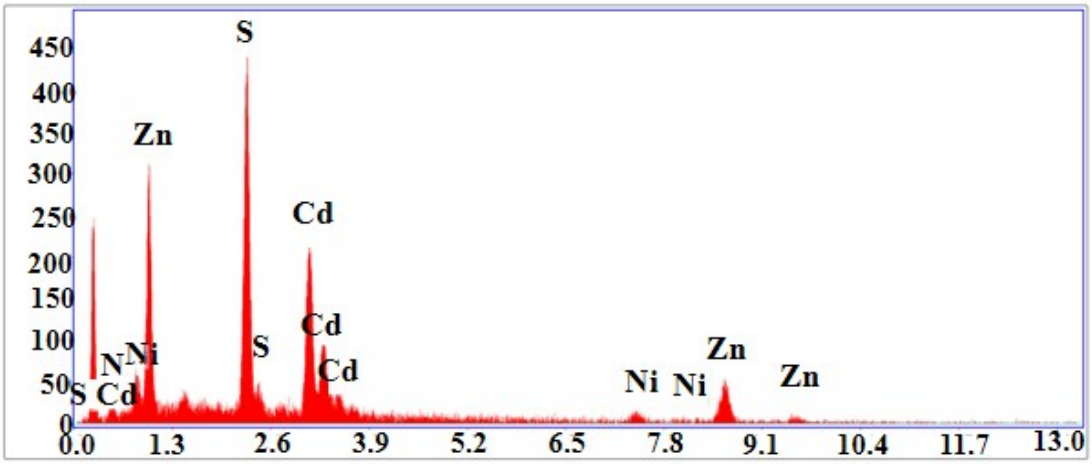


Fig. S3. The XRD of Ni_3N sample.



Elements	Weight%	Atom%	Intensity	Error %
N K	0.05	0.21	0.03	99.99
S K	30.57	54.51	325.18	5.69
CdL	42.56	21.65	187.17	6.35
NiK	1.64	1.60	5.95	58.71
ZnK	25.18	22.03	57.07	11.51

Fig. S4. EDX data of sample 2% Ni_xN/ZCS.

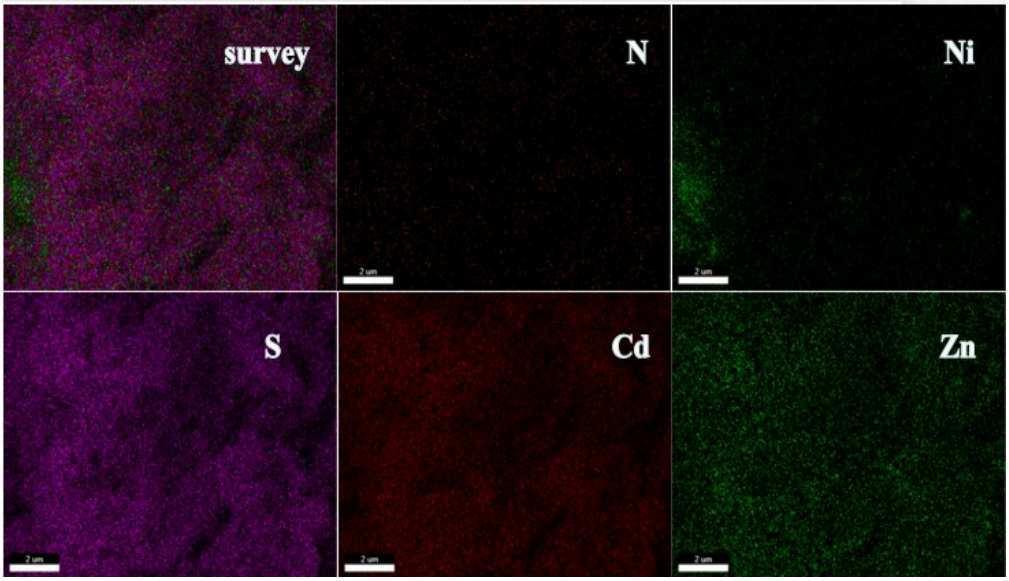


Fig. S5. SEM-Mapping images for nitrogen, nickel, sulphur, cadmium, zinc.

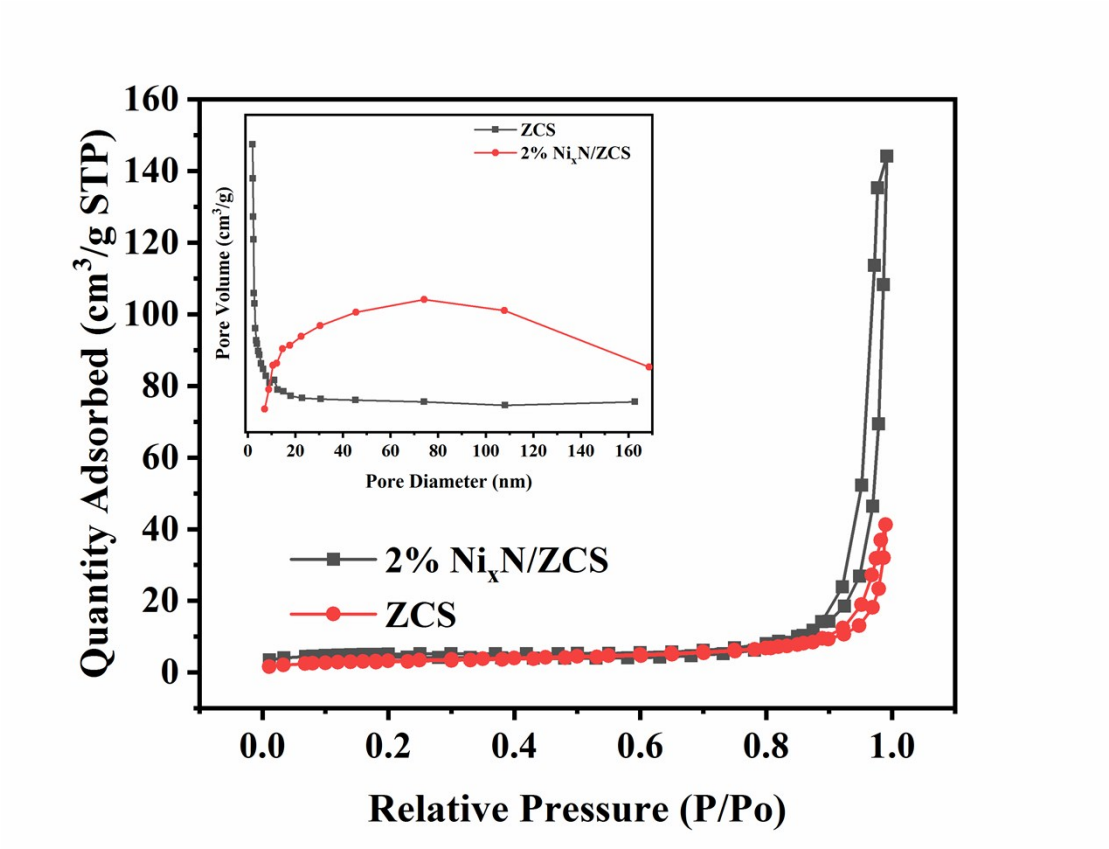


Fig. S6. Nitrogen adsorption-desorption isotherms.

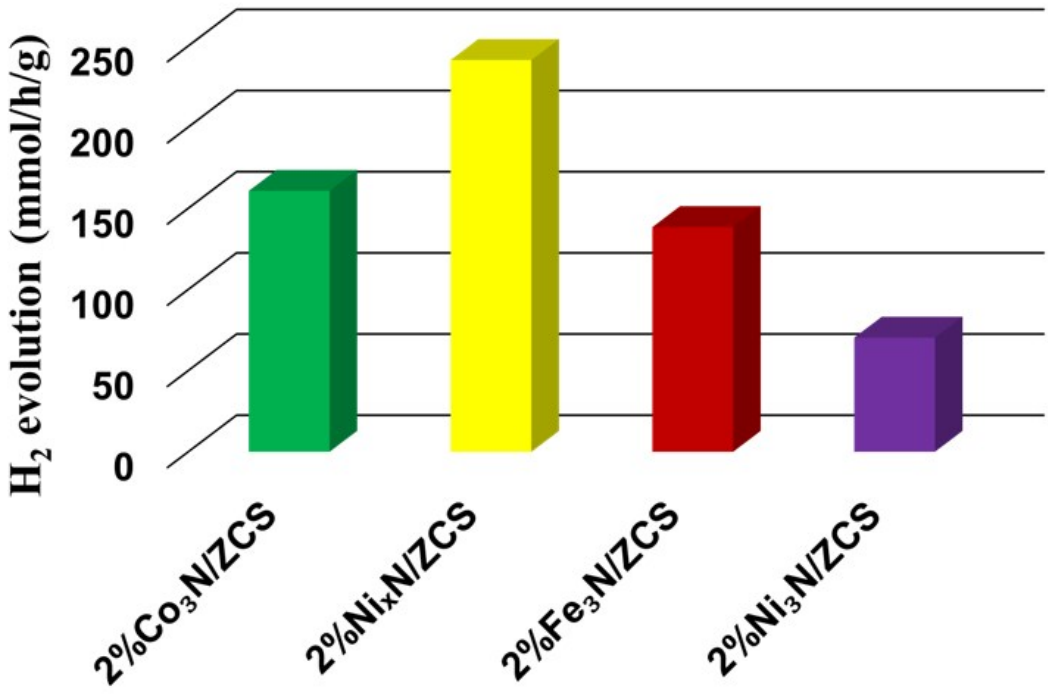


Fig. S7. Rate of H_2 evolution of 2% Co_3N/ZCS, 2% Ni_xN/ZCS, 2% Fe_3N/ZCS and

2%Ni_3N/ZCS

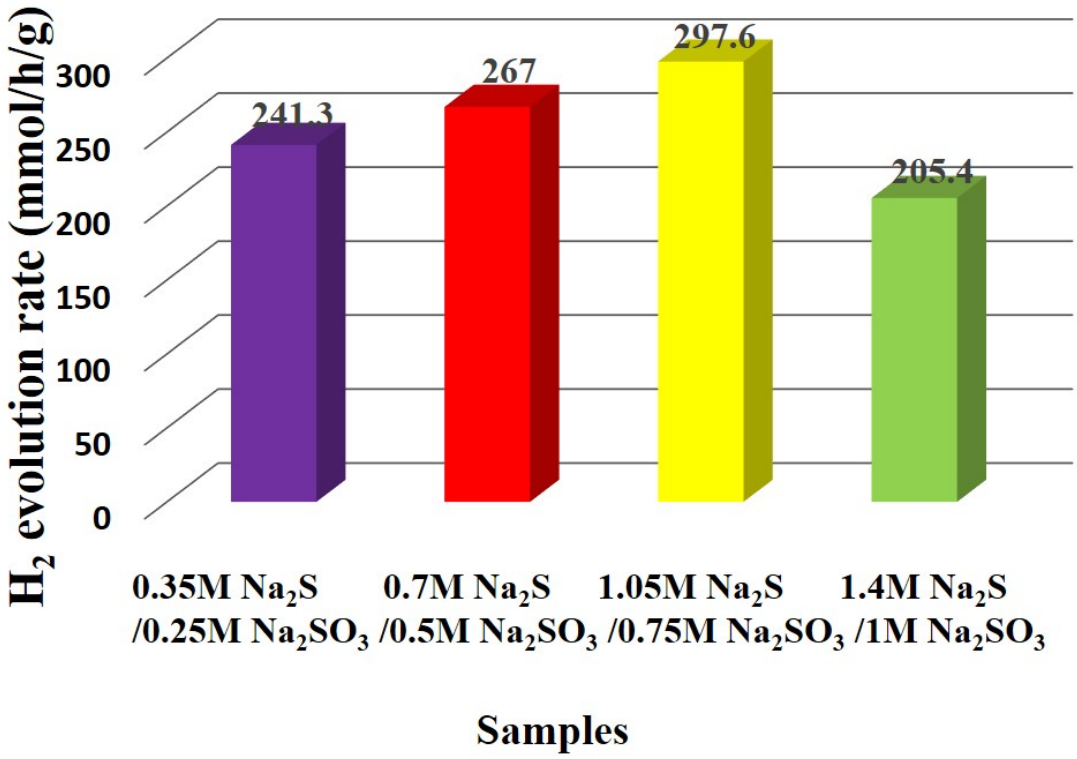


Fig. S8 Rate of H_2 evolution over the 2% Ni_xN/ZCS sample with different concentrations of sacrificial reagents: a: 0.35 M Na_2S/0.25 M Na_2SO_3, b: 0.7 M Na_2S/0.5 M Na_2SO_3, c: 1.05 M Na_2S/0.75 M Na_2SO_3, and d: 1.4 M Na_2S/1.0 M Na_2SO_3

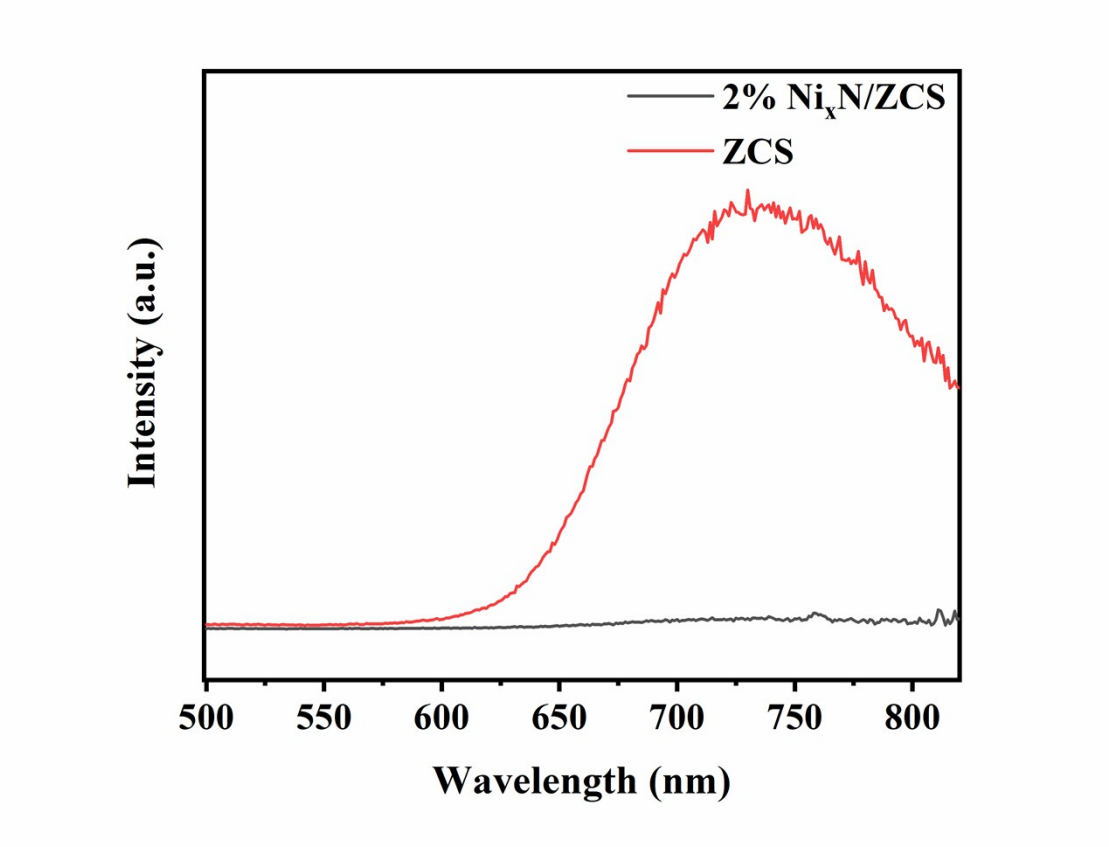


Fig. S9. Photoluminescence spectra of ZCS and 2% Ni_xN/ZCS and the excitation wavelength was 410 nm.

Table S1 Photocatalytic H_2 evolution activity over different ZCS photocatalysts

Cocatalysts	Light harvesting	Light source	Weight(mg)/ Solution (mL), sacrificial agent	Activity (mmol g^{-1} h^{-1})	A.Q.E. (%)	Ref.
Ni_xN	$Zn_{0.5}Cd_{0.5}S$	300 W Xe lamp with a 420 nm cut-off filter	1/200, 0.25 M Na_2SO_3 and 0.35 M Na_2S	241.3	43.8	This work
Fe_3N	$Zn_{0.5}Cd_{0.5}S$	300 W Xe lamp with a 420 nm cut-off filter	1/200, 0.25 M Na_2SO_3 and 0.35 M Na_2S	138.4	--	This work
Co_3N	$Zn_{0.5}Cd_{0.5}S$	300 W Xe lamp with a 420 nm cut-off filter	1/200, 0.25 M Na_2SO_3 and 0.35 M Na_2S	160.7	30.2	1
NiCoP	TiO_2	300 W Xe lamp	20/80, 20% vol methanol	1.54	--	2

Ni_2P	$Zn_{0.5}Cd_{0.5}S$	300 W Xe lamp with a 420 nm cut-off filter	50/100, 0.25 M Na_2SO_3 and 0.35 M Na_2S	41.26	--	3
NiO/Ni_2P	g-C_3N_4	300 W Xe lamp with a 420 nm cut-off filter	10/20, 10% triethanolamine	0.504	--	4
Ni_3N	g-C_3N_4	300 W Xe lamp with a 420 nm cut-off filter	5/250, 20 vol% triethanolamine	0.305	0.45	5
NiS_x	$Zn_{0.8}Cd_{0.2}S$/rGO	300 W Xe lamp with a 420 nm cut-off filter	50/50, 10% lactic acid	7.84	20.88	6
Ni_2P	CNTs	350 W Xe lamp	30/100, 10 vol% triethanolamine	19.25	5.8	7
Ni_2P	MIL-125-NH_2	300 W Xe lamp with a 420 nm cut-off filter	17/25, 20 vol% triethanolamine	3.878	27	8
Ni_3N	g-C_3N_4	300 W Xe lamp with a 420 nm cut-off filter	50/100, 10 vol% triethanolamine	0.169	0.11	9

Ni_2P	CdS	300 W Xe lamp with a 420 nm cut-off filter	10/75, 10% lactic acid	17.95	4.2	10

1. Z. B. Jin, T. T. Wei, L. X. Li, F. Y. Li, R. Tao and L. Xu, *Dalton. Trans.*, 2019, **48**, 2676-2682.
2. R. Song, W. Zhou, B. Luo and D. W. Jing, *Appl. Surf. Sci.* 2017, **416**, 957–964.
3. T. P. Yu , Y. Y Si, Z. H. Lv, K. H. Wang, Q. Zhang, X. Liu, G. X. Wang, G. W. Xie and L. H. Jiang, *Int. J. Hydrogen Energy*, 2019, **44**, 31832-31840.
4. J. W. Shi, Y. J. Zou, L. H. Cheng, D. D. Ma, D. K. Sun, S. M. Mao, L. W. Sun, C. He and Z. Y. Wang, *Chem. Eng. J.,* 2019, **378**, 122161.
5. J. H Ge, Y. J. Liu, D. C. Jiang, L. Zhang and P. W. Du, *Chinese J. Catal.*, 2019, **40**, 160–167.
6. C. Xue, H. Li, H. An, B. L. Yang, J. J. Wei, and G. D. Yang, *ACS Catal.*, 2018, **8**, 1532−1545.
7. Z. X. Lin, Y. Zhao, J. H. Luo, S. J. Jiang, C. Z. Sun and S. Q. Song, *Adv. Funct. Mater.,* 2019, **1908797**.
8. S. Kampouri, T. N. Nguyen, C. P. Ireland, B. Valizadeh, F. M. Ebrahim, G. Capano, D. Ongari, A. Mace, N. Guijarro, K. Sivula, A. Sienkiewicz, L. Forro, B. Smit and K. C. Stylianou, *J. Mater. Chem. A*, 2018, **6**, 2476-2481.
9. L. Chen, H. J. Huang, Y. H. Zheng, W. H. Sun, Y. Zhao, P. S. Francis and X. X. Wang, *Dalton Trans.*, 2018, **47**,12188-12196.
10. C. Liu, M. H. Xiong, B. Chai, J. T. Yan, G. Z. Fan and G. S. Song, *Catal. Sci. Technol.*, 2019, **9**, 6929-6937.