Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic supplementary information

Engineering highly active $Cd_{1-x}Zn_xS$ nanopopcorns via zinc blende/wurtzite phase junctions for enhanced photocatalytic H_2 evolution without co-catalyst

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Figures

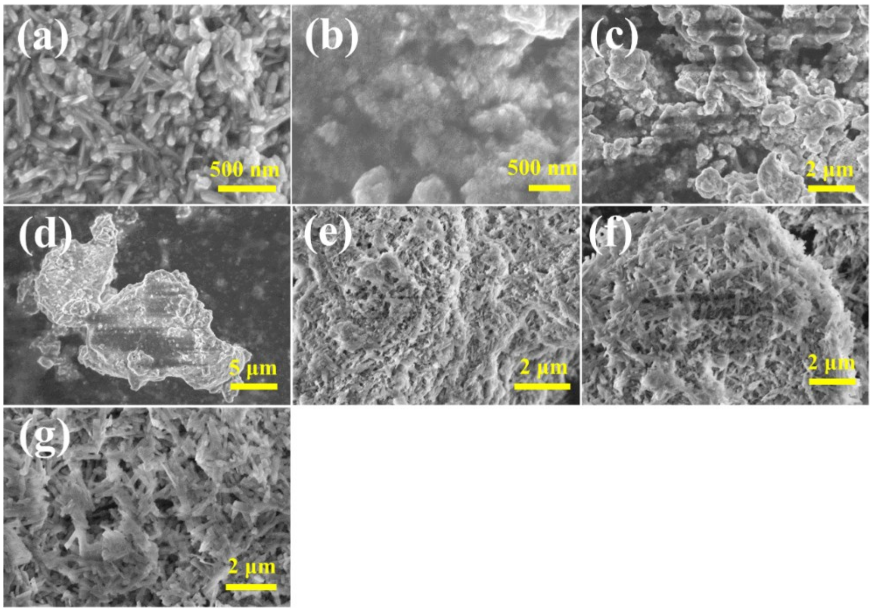

Fig. S1 SEM images of $Cd_{1-x}Zn_xS$-10 samples. (a) CdS-10, (b) $Cd_{0.9}Zn_{0.1}S$-10, (c) $Cd_{0.7}Zn_{0.3}S$-10, (d) $Cd_{0.5}Zn_{0.5}S$-10, (e) $Cd_{0.3}Zn_{0.7}S$-10, (f) $Cd_{0.1}Zn_{0.9}S$-10 and (g) ZnS-10.

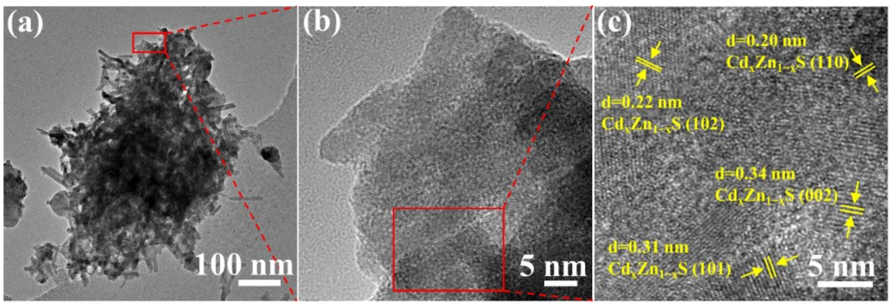

Fig. S2 (a) TEM and (b and c) HRTEM images of $Cd_{0.5}Zn_{0.5}S$-10. The lattice fringes with a spacing of ca. 0.20, 0.22, 0.31 and 0.34 nm can be indexed to the (110), (102), (101) and (002) plane of WZ $Cd_{1-x}Zn_xS$ solid solution, respectively.

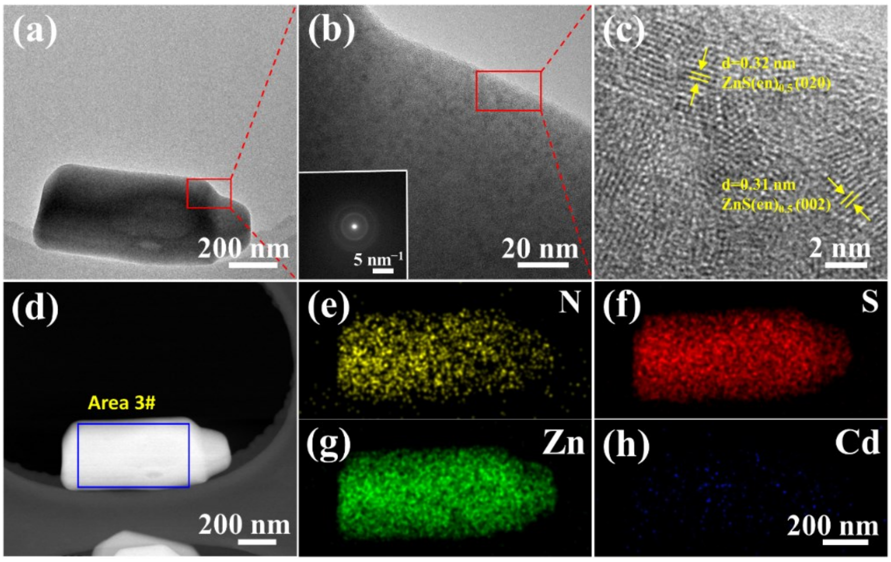

Fig. S3 (a) TEM, (b and c) HRTEM images of ZnS-16. (d) Dark-field TEM and (e–h) corresponding EDX elemental mapping images of ZnS-16. The inset in b is the SAED pattern of ZnS-16. The lattice fringes with a spacing of ca. 0.31 and 0.32 nm can be indexed to the (002) and (020) plane of $ZnS(en)_{0.5}$,[1] respectively.

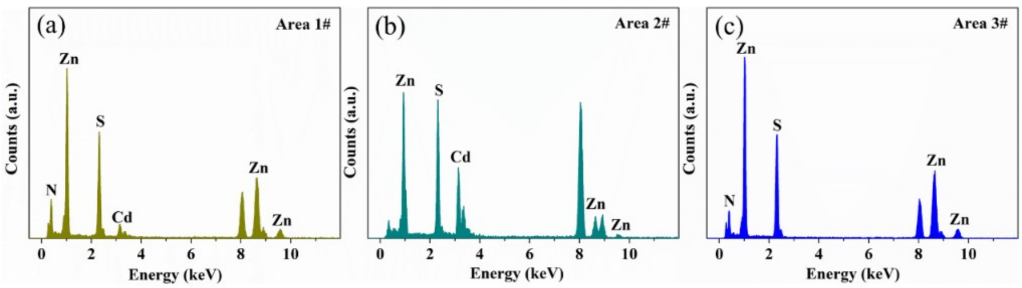

Fig. S4 EDX spectra of nanoplates, nanopopcorns and ZnS-16 in Area 1# (Fig. 3g), Area 2# (Fig. 3g) and Area 3# (Fig. S3d), respectively.

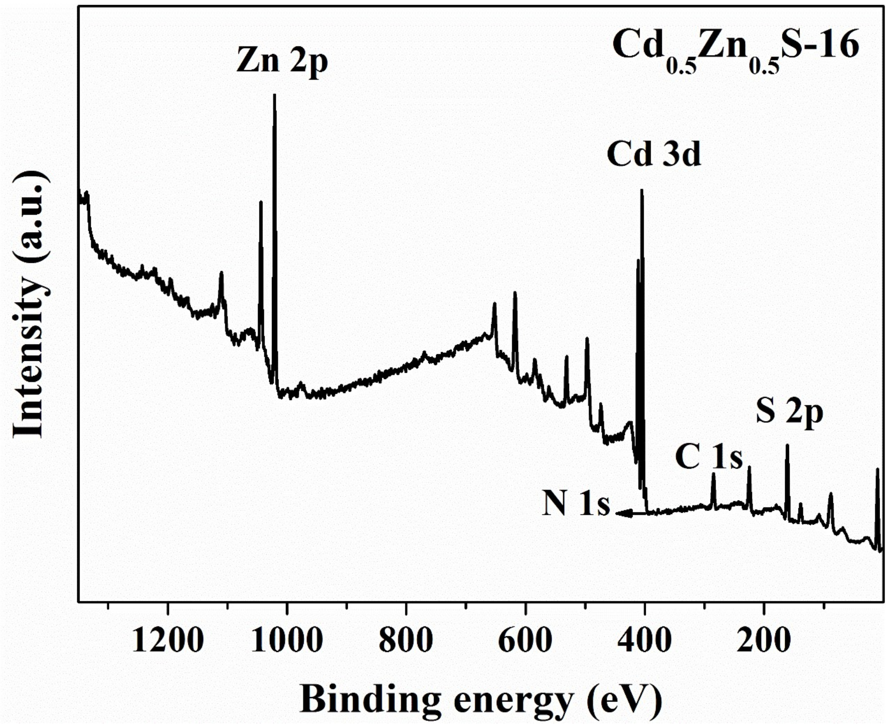

Fig. S5 The overall survey XPS spectrum of $Cd_{0.5}Zn_{0.5}S$-16.

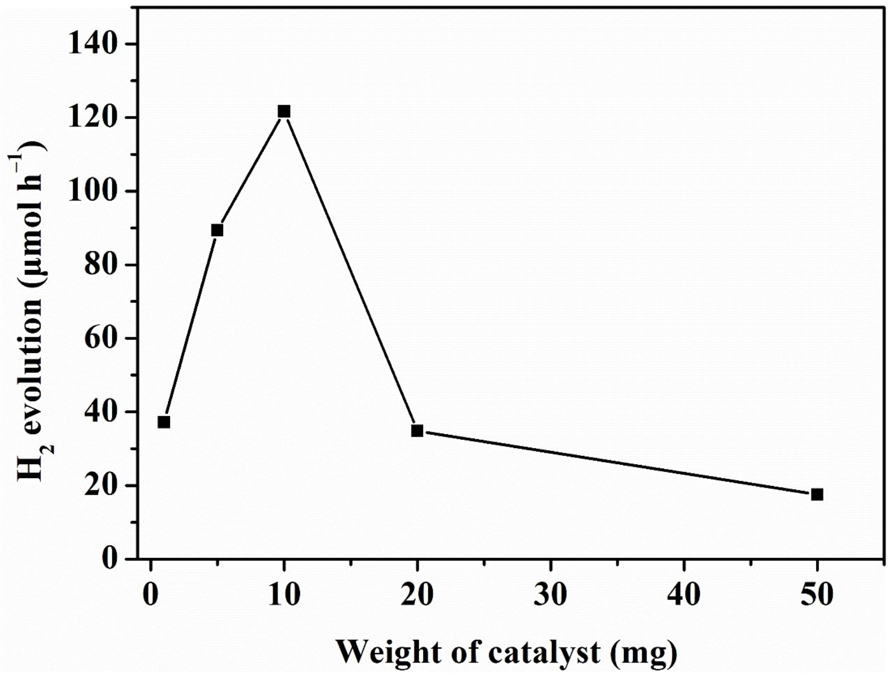

Fig. S6 H_2-evolution rates of $Cd_{0.5}Zn_{0.5}S$-16 with different weights using 420-nm LED light.

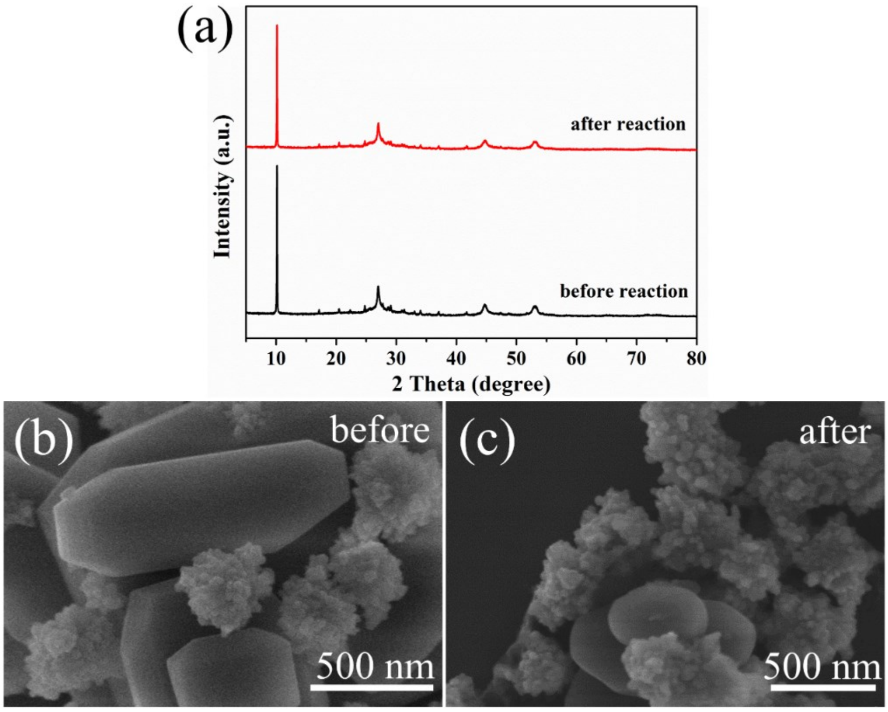

Fig. S7 (a) XRD patterns and (b–c) SEM images of $Cd_{0.5}Zn_{0.5}S$-16 before and after photocatalytic reaction.

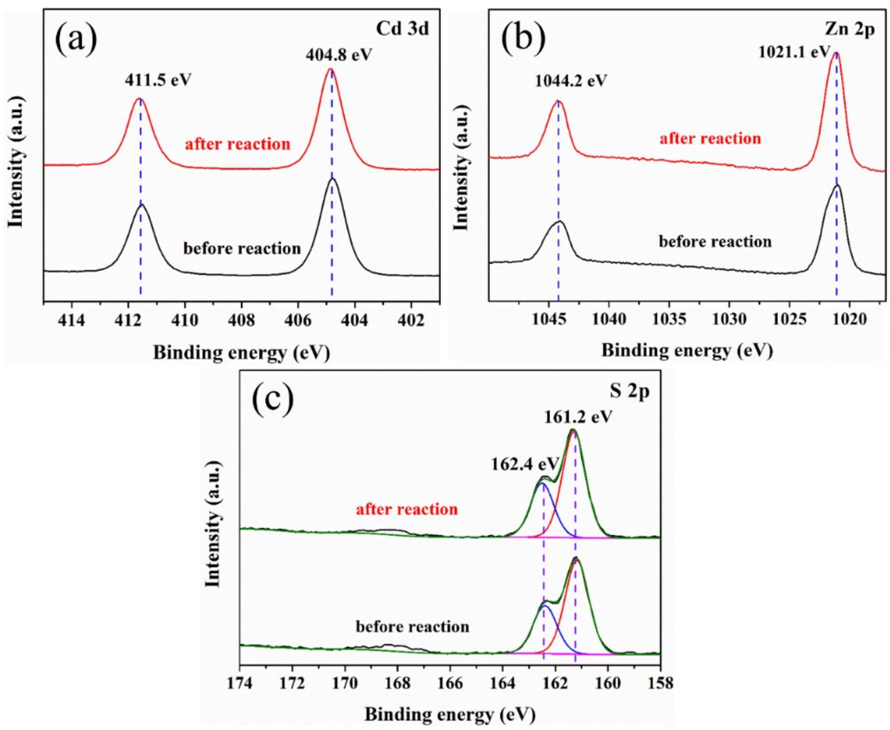

Fig. S8 XPS spectra of $Cd_{0.5}Zn_{0.5}S$-16 before and after photocatalytic reaction. (a) Cd 3d, (b) Zn 2p, and (C) S 2p.

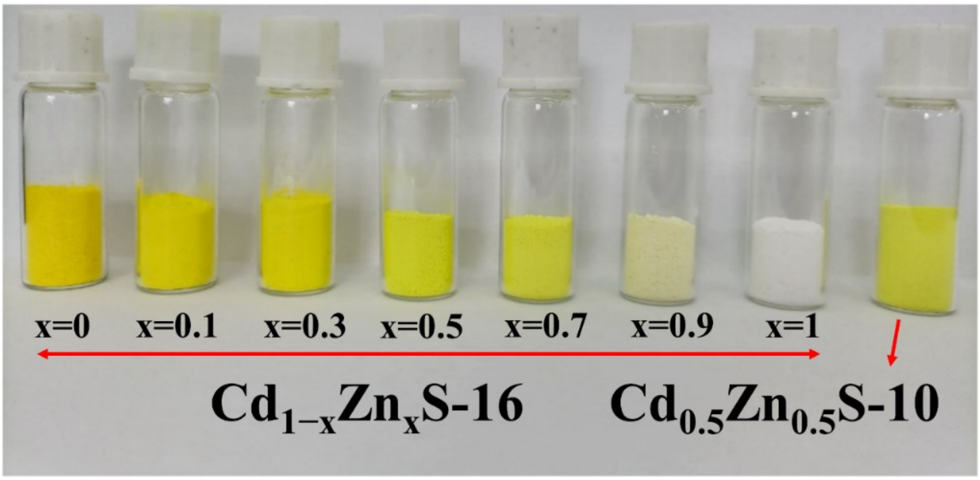

Fig. S9 Photographs of $Cd_{1-x}Zn_xS$-16 and $Cd_{0.5}Zn_{0.5}S$-10.

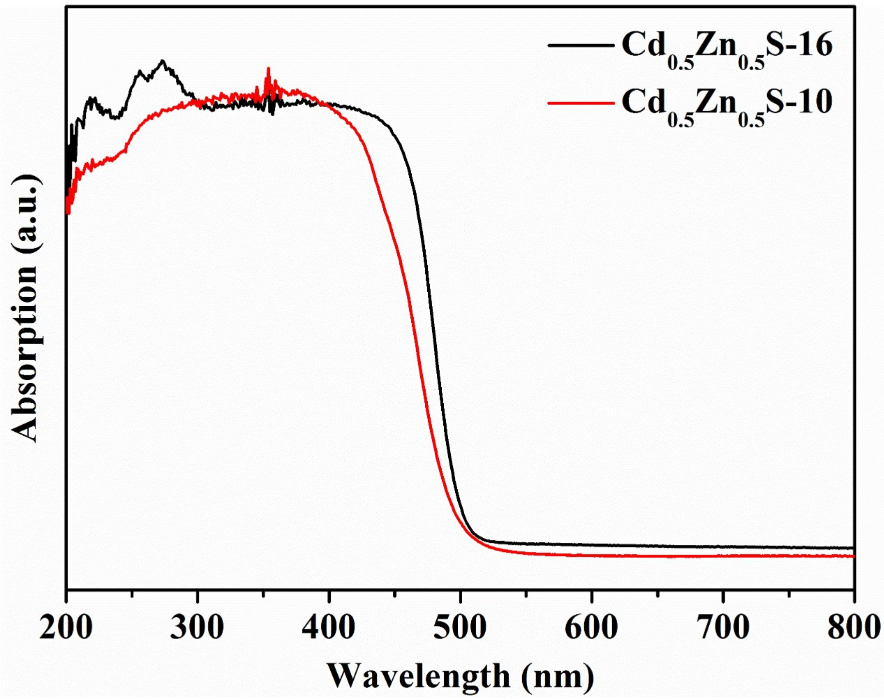

Fig. S10 UV–vis absorption spectra of $Cd_{0.5}Zn_{0.5}S$-10 and $Cd_{0.5}Zn_{0.5}S$-16.

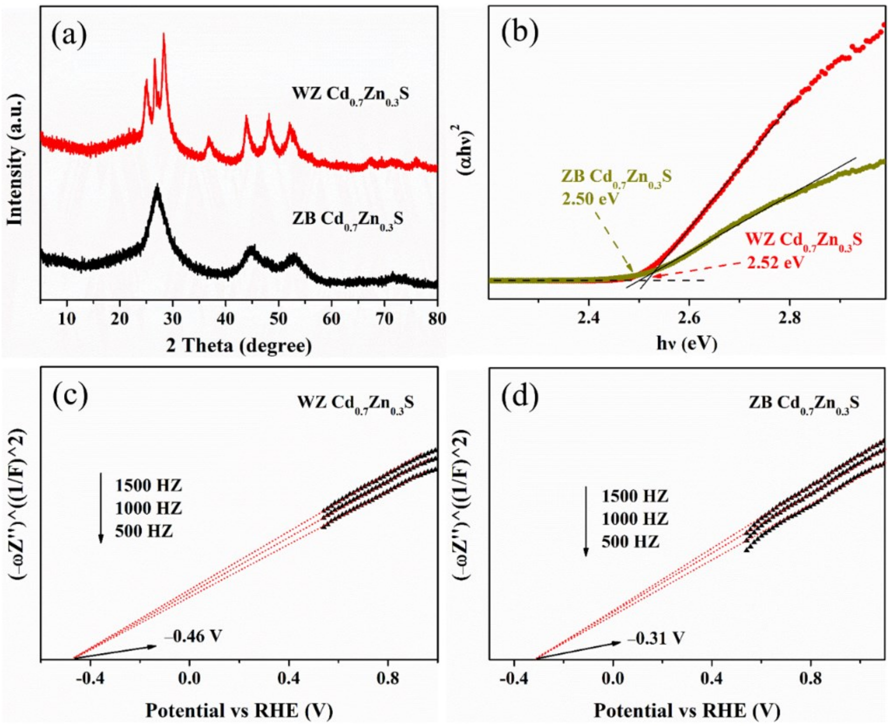

Fig. S11 (a–b) XRD patterns and determined bandgaps of WZ $Cd_{0.7}Zn_{0.3}S$ and ZB $Cd_{0.7}Zn_{0.3}S$. (c–d) Mott–Schottky plots of WZ $Cd_{0.7}Zn_{0.3}S$ and ZB $Cd_{0.7}Zn_{0.3}S$ at different frequencies of 1500, 1000 and 500 Hz.

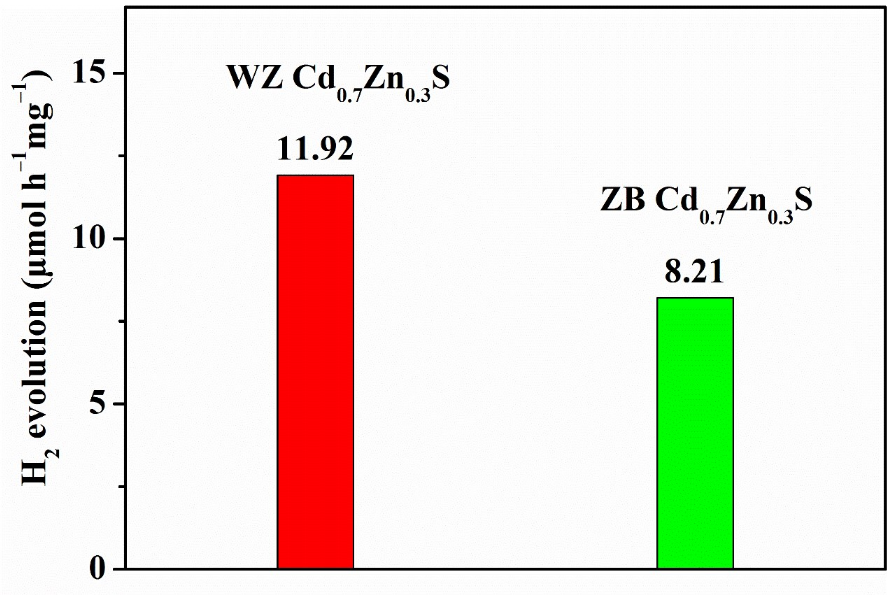

Fig. S12 Photocatalytic H_2-evolution activities of WZ $Cd_{0.7}Zn_{0.3}S$ and ZB $Cd_{0.7}Zn_{0.3}S$.

Tables

Table S1 EDX experimental data of nanoplates (Fig. 3g, Area 1#), nanopopcorns (Fig. 3g, Area 2#) and ZnS-16 (Fig. S3d, Area 3#).

sample	Weight percentage (wt%)				Atomic percentage (at%)			
	N	Cd	Zn	S	N	Cd	Zn	S
nanoplates (Area 1#)	9.05	10.04	51.35	29.55	25.45	3.93	33.13	37.49
nanopopcorns (Area 2#)	1.48	49.86	13.98	34.68	5.43	25.46	11.76	57.35
ZnS-16 (Area 3#)	6.55	1.06	60.45	31.93	18.72	0.42	39.66	41.20

Table S2 ICP-OES experimental data for $Cd_{0.5}Zn_{0.5}S$-16.

sample	Weight percentage (wt%)			Mole ratio
	Cd	Zn	S	Cd : Zn
$Cd_{0.5}Zn_{0.5}S$-16	46.54	27.36	14.81	1 : 1.01

Table S3 Absolute fluorescence quantum yield (Φ_f) of $Cd_{0.5}Zn_{0.5}S$-10 and $Cd_{0.5}Zn_{0.5}S$-16.

Sample	$Cd_{0.5}Zn_{0.5}S$-10	$Cd_{0.5}Zn_{0.5}S$-16
Φ_f (%)	1.47	0.21

Table S4 Comparison of $Cd_{1-x}Zn_xS$ phase junctions for photocatalytic H_2 evolution with Na_2S/Na_2SO_3 as sacrificial reagent.

Photocatalyst	Preparation method	Solvent/ Temperature	Activity (μmol h^{-1} mg^{-1})	AQY% (420 nm)	Ref
ZB/WZ $Cd_{1-x}Zn_xS$ nanopopcorns	solvothermal	en/180 °C	282.14 (λ≥420 nm)	64.4	This work
$Cd_{0.5}Zn_{0.5}S$ nanorod	microwave irradiation solvothermal	en+H_2O/ 230 °C	25.8 (λ≥430 nm)	62	2
$Cd_{0.5}Zn_{0.5}S$ nanospheres	solvothermal	en+H_2O/ 180 °C	83.5 (λ≥420 nm)	47.5	3
$Cd_{1-x}Zn_xS$	co-precipitation	H_2O/25 °C	30 (λ>400 nm) (Na_2S-K_2SO_3)	-	4
Twin-$Cd_{0.5}Zn_{0.5}S$	solvothermal	H_2O/180 °C	46.6 (λ>420 nm)	6.6	5
$Cd_{0.7}Zn_{0.3}S$	solvothermal	deta+H_2O/ 180 °C	31.3 (λ≥420 nm)	65.7	6
$Cd_{0.5}Zn_{0.5}S$ nanoparticles	hydrothermal	H_2O/180 °C	125.27 (λ≥420 nm)	21.5	7
$Cd_{0.4}Zn_{0.6}S$	reflux	H_2O+oleylamine+octadecene / 230 °C	1.93 (λ≥420 nm)	-	8
$Cd_{0.6}Zn_{0.4}S$	solvothermal	H_2O+TEOA/ 160 °C	9.44 (λ>420 nm)	9.8	9
ZB-WZ $Cd_{1-x}Zn_xS$	ultrasonic assisted precipitation	ethanol/160 °C	9.8 (λ≥430 nm)	48.7	10

Table S5 Comparison of $Cd_{1-x}Zn_xS$-based catalysts for photocatalytic H_2 evolution.

Photocatalyst	Light source (Xe lamp)	Sacrificial reagent	Activity (μmol h^{-1} mg^{-1})	AQY% (420 nm)	Ref
ZB/WZ $Cd_{1-x}Zn_xS$ nanopopcorns	λ⩾420 nm	Na_2S-Na_2SO_3	282.14	64.4	This work
$Zn_{0.5}Cd_{0.5}S$	λ⩾400 nm	Na_2S-Na_2SO_3	7.42	9.6	11
Twin-$Zn_{0.5}Cd_{0.5}S$	λ⩾430 nm	Na_2S-Na_2SO_3	17.9	43 (425 nm)	12
NiS_x-$Zn_{0.5}Cd_{0.5}S$	λ⩾430 nm	Na_2S-Na_2SO_3	44.6	100 (425 nm)	13
$Zn_{0.5}Cd_{0.5}S$/ $PdP_{\sim0.33}S_{\sim1.67}$	λ>420 nm	Na_2S-Na_2SO_3	246	16.5	5
		Ascorbic acid	372	19.7	
$Cd_{0.5}Zn_{0.5}S$ nanorod	λ⩾430 nm	Na_2S-Na_2SO_3	25.8	62 (425 nm)	2
$Cu_{1.94}S$-$Zn_xCd_{1-x}S$	λ>420 nm	Na_2S-Na_2SO_3	7.74	8.5	14
Pt/$Cu_{1.94}S$-$Zn_xCd_{1-x}S$	λ>420 nm	Na_2S-Na_2SO_3	13.53	26.4	14
NiS/$Zn_{0.5}Cd_{0.5}S$	λ>420 nm	Na_2S-Na_2SO_3	16.78	-	15
$Zn_{1-x}Cd_xS$/ D-$ZnS(en)_{0.5}$	λ>420 nm	Na_2S-Na_2SO_3	15.5	50 (440 nm)	16
$Zn_{0.5}Cd_{0.5}S$@ HNTs-10	λ>400 nm	Na_2S-Na_2SO_3	25.67	32.3	17
Pt-PdS/ $Zn_{0.5}Cd_{0.5}S$-P	λ>420 nm	Na_2S-Na_2SO_3	~ 7	89	18
Ni_2P/ $Zn_{0.5}C_{d0.5}S$	λ>420 nm	Na_2S-Na_2SO_3	23.44	19	19
$Cd_{0.5}Zn_{0.5}S$/TNTs	λ>430 nm	Na_2S-Na_2SO_3	1.74	38.1	20
Hollow $Zn_{0.6}Cd_{0.4}S$ cage	λ>420 nm	Na_2S-Na_2SO_3	5.68	-	21

Twin-$Cd_{1-x}Zn_xS$/ MoS_2	λ>420 nm	Na_2S-Na_2SO_3 Lactic acid	69.25 37.22	55.2 36.3	22
Pt/$Zn_xCd_{1-x}S$ hollow nanospheres	λ>420 nm	Lactic acid	4.11	~ 23	23
Ni_xCo_{1-x}/ $Zn_{0.75}Cd_{0.25}S$	λ>420 nm	Na_2S-Na_2SO_3-TEOA	84.7	13.3 (365 nm)	24
Ni/NiS/ $Zn_{0.2}Cd_{0.8}S$	λ⩾420 nm	Lactic acid	4.15	11.1	25
$Zn_{0.5}Cd_{0.5}S$@ PAN	λ⩾420 nm	Na_2S-Na_2SO_3	9.5	27.4	26
Pt/Twin-$Cd_{1-x}Zn_xS$	λ > 400 nm	ascorbic acid	5.5	8.6	27
$Zn_{0.8}Cd_{0.2}S$@ g-C_3N_4	λ⩾420 nm	Na_2S-Na_2SO_3	23.51	1.4	28
Pt/$Cd_{0.5}Zn_{0.5}S$/ $BiVO_4$	λ>420 nm	Na_2S-Na_2SO_3	2.35	24.1	29
Twin-$Cd_{0.5}Zn_{0.5}S$/ CoO	λ>420 nm	Na_2S-Na_2SO_3	178	37.1	30
MoS_2-$Cd_{0.5}Zn_{0.5}S$	λ⩾420 nm	Lactic acid	11.49	1.3	31
$CoFe_2O_4$/ $Cd_{0.9}Zn_{0.1}S$	λ>400 nm	Na_2S-Na_2SO_3	3.5	27	32
$Zn_{0.5}Cd_{0.5}S$/ $Ni_{0.1}Co_{0.9}P$	λ>400 nm	Na_2S-Na_2SO_3	19.52	19.7	33
Cu-doped $Zn_{0.5}Cd_{0.5}S$	λ⩾420 nm	Na_2S-Na_2SO_3	21.4	18.8(428 nm)	34
Zn-Cd-S (surface defects)	λ>420 nm	Na_2S-Na_2SO_3	11.42	16.9	35

$BP_x/Zn_{0.5}Cd_{0.5}S$	λ>420 nm	Na_2S-Na_2SO_3	137.17	36.3	[36]
$Cd_{1-x}Zn_xS$ /CdS	λ⩾420 nm	Na_2S-Na_2SO_3	133.5	50.1	[37]
$Cd_{1-x}Zn_xS$@ O-MoS_2/Ni_2O_3	λ>420 nm	Na_2S-Na_2SO_3	223.17	64.1	[38]
		Lactic acid	66.08	41.2	

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