Electronic Supplementary Information

for

Engineering cation defects–mediated Z–scheme photocatalyst for highly efficient and stable photocatalytic hydrogen production

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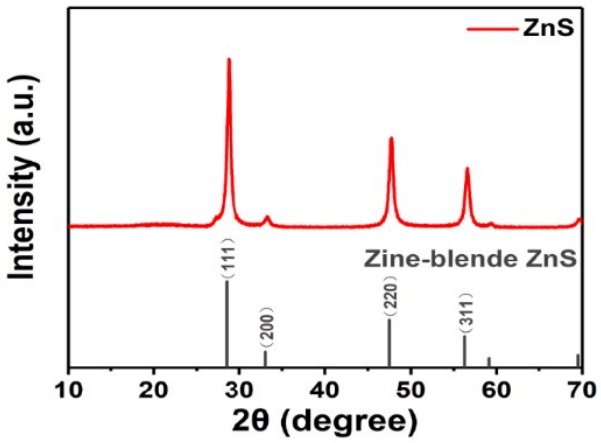

Fig. S1. XRD patterns of ZnS sample.

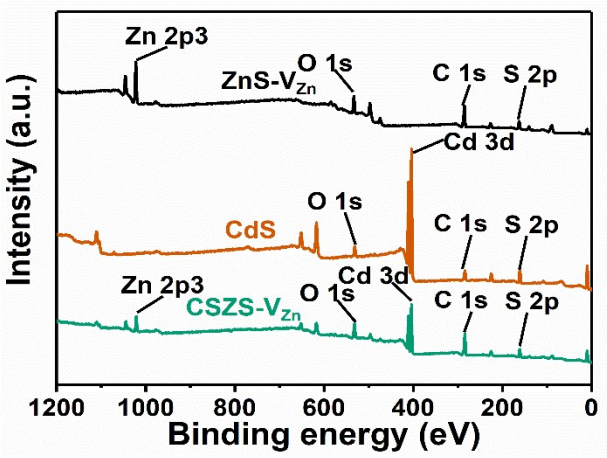

Fig. S2. XPS survey spectrum of CdS, ZnS–V_{Zn}, and CSZS–V_{Zn}.

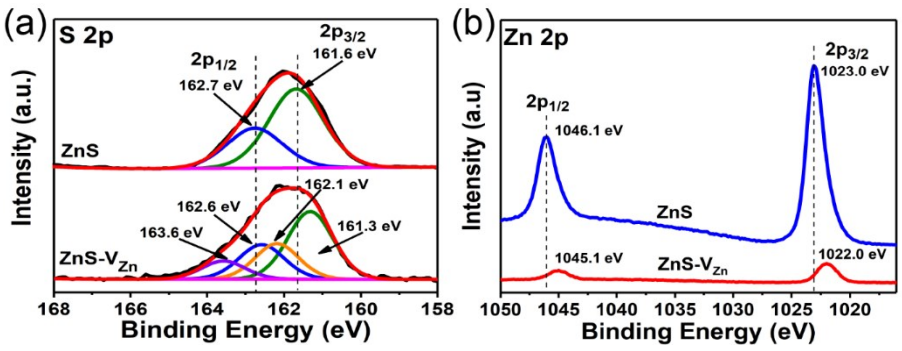

Fig. S3. High–resolution XPS spectra of (a) S 2p, (b) Zn 2p spectra of ZnS–V_{Zn} and ZnS.

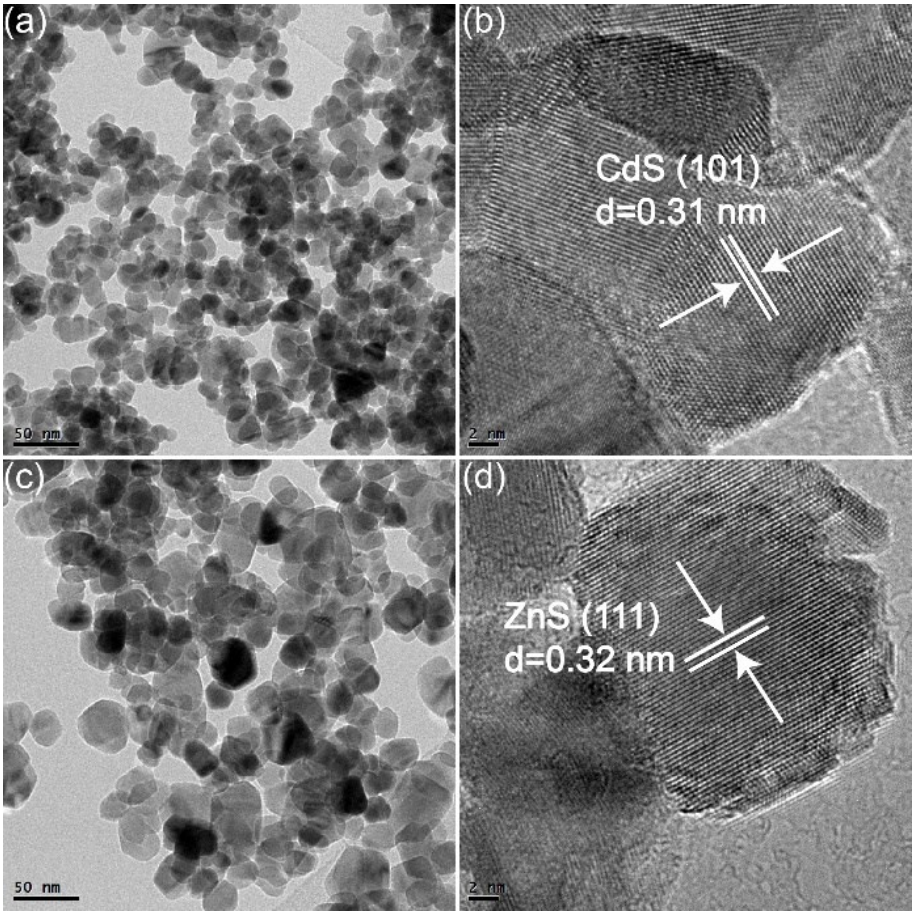

Fig.S4.TEM and HRTEM images of (a,b) CdS, (c,d) ZnS–V_{Zn}.

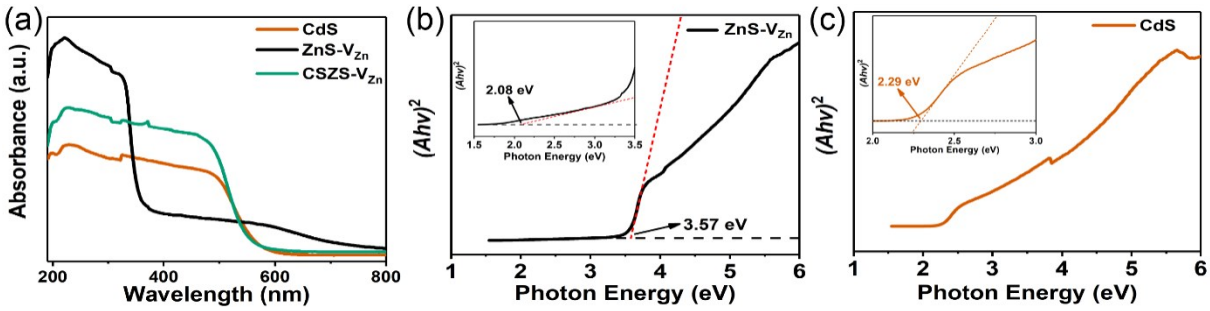

Fig.S5. (a) UV−vis absorption DRS spectra of CdS, ZnS–V_{Zn}, and CSZS–V_{Zn}. K–M plots of (b) ZnS–V_{Zn} and (c) CdS.

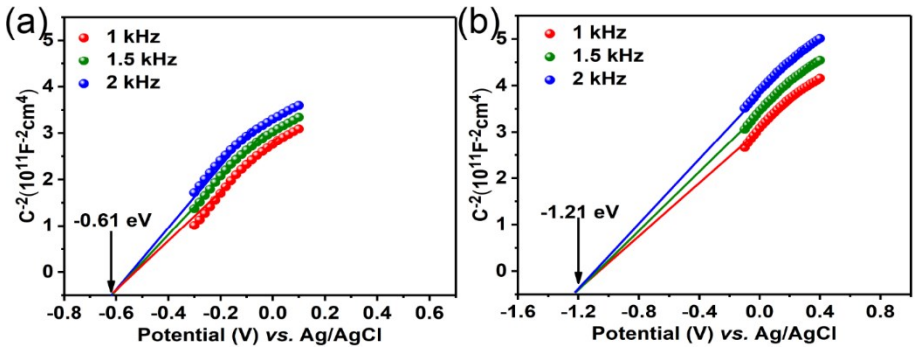

Fig. S6. Mott–Schottky plots of (a) CdS and (b) ZnS–V_{Zn} at frequencies 2.0, 1.5 and 1.0kHz.

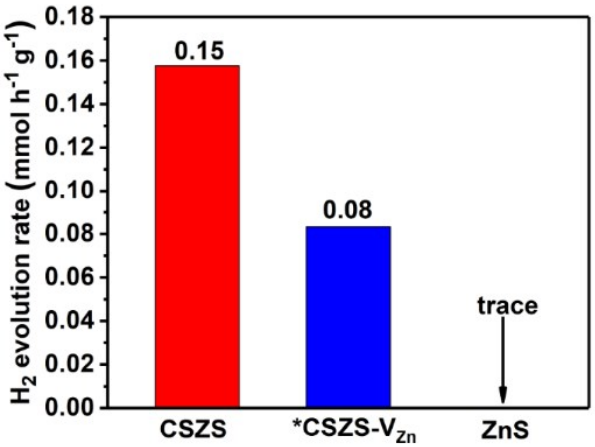

Fig. S7. Photocatalytic H_2 generation activities of CSZS, *CSZS–V_{Zn} andZnS.

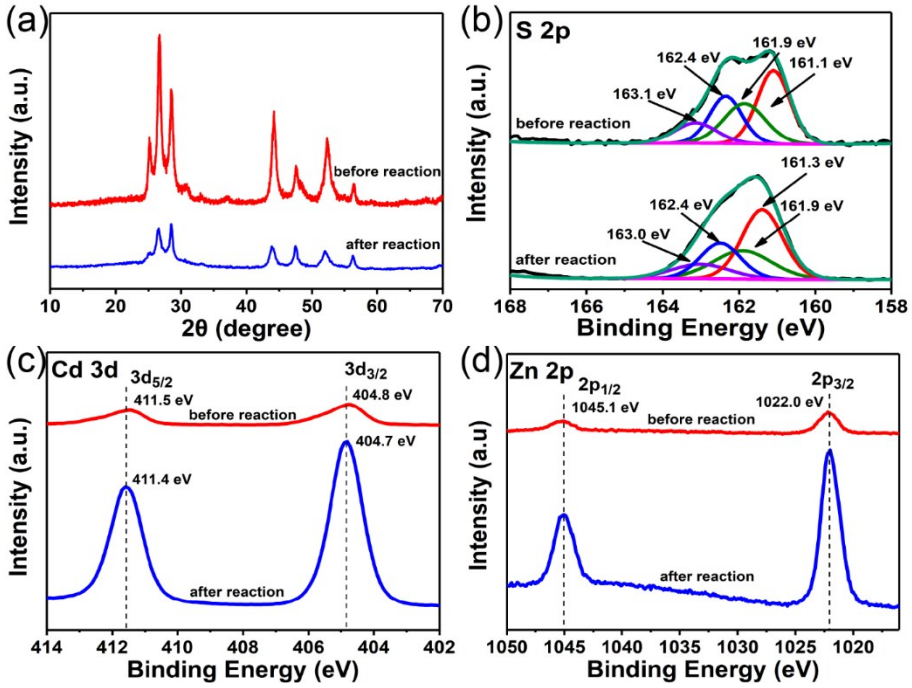

Fig. S8. (a) XRD patterns and the high–resolution XPS spectra of (b) S 2p, (c) Cd 3d, and (d) Zn 2p spectra of the as–prepared and recycledCSZS–V_{Zn}.

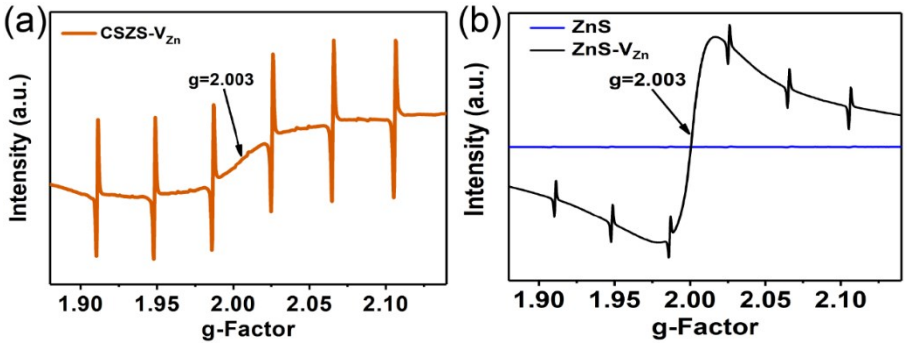

Fig. S9. ESR spectra of CSZS–V_{Zn}, ZnS and ZnS–V_{Zn}.

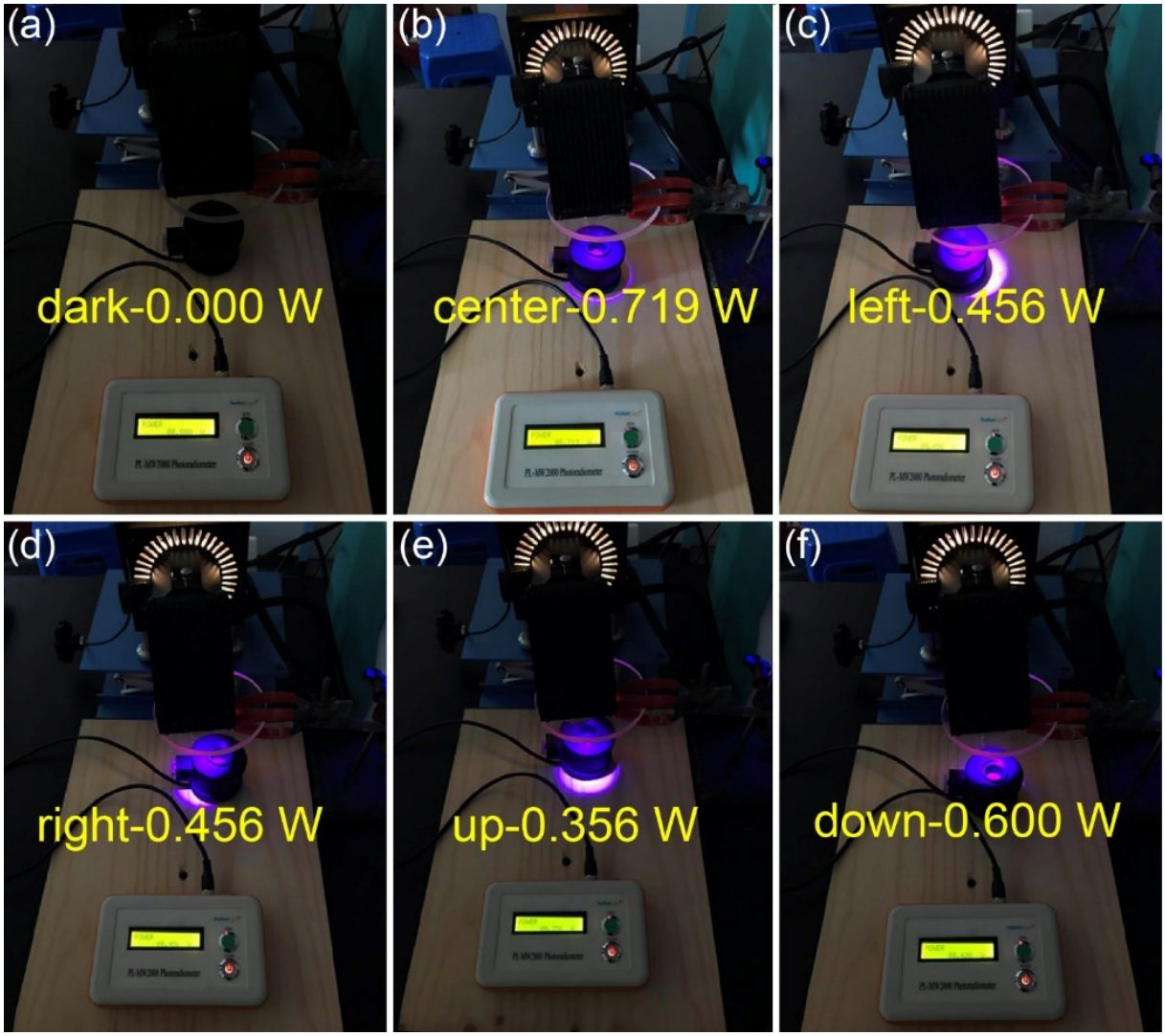

Fig. S10. Measurement of power of Xe–lamp by digital optical controller (using the 400 nm band pass filter):

(a) blank; (b) center; (c) left; (d) right; (e) up; (f) down.

Table S1 The chemical composition of ZnS–V_{Zn} and ZnS measured by XPS semi-quantitative.

Samples	Zn (at.%)	S (at.%)	Zn:S (at.%)
ZnS–V_{Zn}	43.49	56.51	0.77:1
ZnS	47.51	52.49	0.91:1

Table S2 The chemical composition of ZnS–V_{Zn} and ZnS measured by ICP analysis.

Sample	ICP(wt %)		Zn:S (molar ratio)
	Zn	S	
ZnS–V_{Zn}	61.06	38.94	0.77:1
ZnS	64.01	35.99	0.87:1

Table S3 Comparison of the photocatalytic H_2 evolution rates over different CdS/ZnS-based photocatalysts.

Catalyst	Co-catalyst	Light source	Sacrificial agent	H_2 evolution rate (μmol/g/h)[a]	Reference
ZnS/CdS/ZnO	Pt	225 W Xe lamp 320nm–700nm	0.25 M Na_2SO_3 and 0.35 M Na_2S	44700	S1
ZnS@CdS PNTs	Ni and CoO_x	300W Xe lamp λ > 420 nm	1.05 M Na_2SO_3 and 0.75 M Na_2S	20325	S2
CdS/ZnS-RGO	Au	300 W Xe lamp λ > 420 nm	0.25 M Na_2SO_3 and 0.35 M Na_2S	9960	S3
ZnO/CdS/ZnS		300 W Xe lamp λ > 400 nm	0.25 M Na_2SO_3 and 0.35 M Na_2S	2077	S4
CdS/ZnScore–shell	PbS	300 W Xe lamp λ > 400 nm	0.1 M Na_2SO_3 and 0.1 M Na_2S	2075	S5
CdS/ZnS-GO	Pt	300 W Xe lamp λ > 420 nm	0.1 M Na_2SO_3 and 0.1 M	1680	S6

			Na_2S		
ZnS/CuS/CdS		150 W xenon lamp AM 1.5 G	0.06 M Na_2S	837.6	S7
CdS/ZnS		300 W Xe lamp λ > 420 nm	0.1 M Na_2SO_3 and 0.1 M Na_2S	830.95	S8
CdS/ZnS	Au	300 W Xe lamp λ ≥ 400 nm	0.25 M Na_2SO_3 and 0.35 M Na_2S	675	S9
CdS/ZnS	Au	300 W Xe lamp λ > 400 nm	1.05 M Na_2SO_3 and 0.75 M Na_2S	610	S10
CdS/ZnS core-shell		300 W Xe lamp λ > 430 nm	0.25 M Na_2SO_3 and 0.35 M Na_2S	55.5	S11
Zn–vacancy ZnS/CdS		300 W Xe lamp λ ≥ 420 nm	0.25 M Na_2SO_3 and 0.35 M Na_2S	46630	**This work**

[b] converted value according the optimized activity in the corresponding literature.

Table S4 Time–resolved fluorescence decay parameters of ZnS–V_{Zn} and CSZS–V_{Zn}.

Sample	**τ_1 (ns)**		**τ_2 (ns)**		**τ_3 (ns)**		**Ave. τ (ns)[a]**
	Value/ns	**Rel A%**	**Value/ns**	**Rel A%**	**Value/ns**	**Rel A%**	
ZnS–V_{Zn}	0.32	69.59	1.66	22.96	15.78	7.45	1.77
CSZS–V_{Zn}	1.25	59.60	12.04	40.40			5.61

[a] Average lifetime (Ave.τ(ns)) was determined by using the following equation according to the literature[S12].

$$Ave.\tau(ns) = \sum_{i=1}^{i=n} A_i\tau_i^2 / \sum_{i=1}^{i=n} A_i\tau_i$$

Reference

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