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

Supplementary data

Few-Layered 1T-MoS_2-Modified ZnCoS Solid-Solution Hollow Dodecahedra for Enhanced Photocatalytic Hydrogen Evolution

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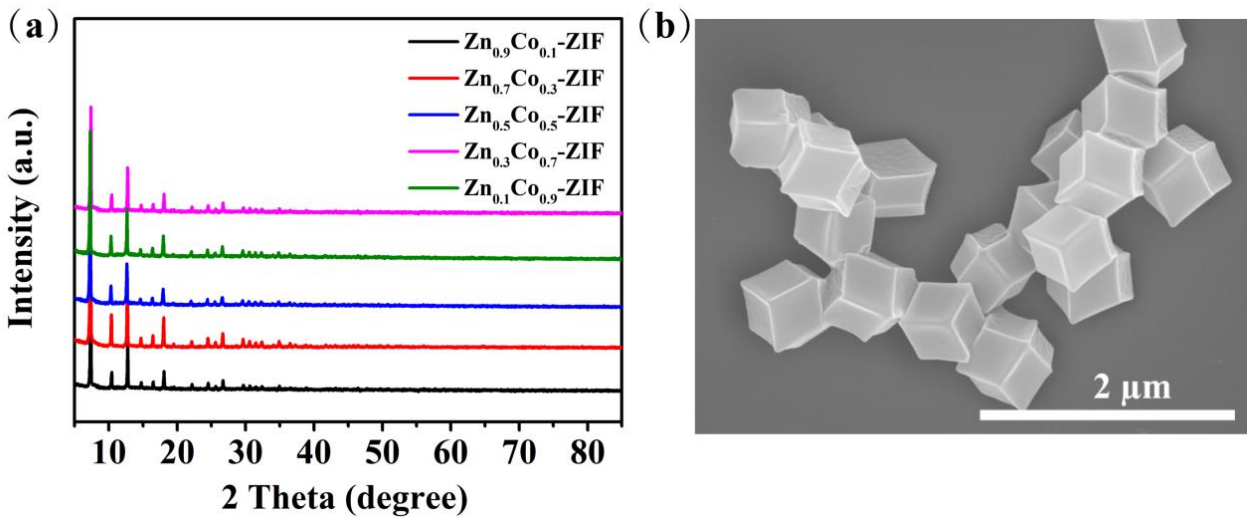

Fig. S1. (a) XRD patterns of Zn_xCo_{1-x}-ZIF crystals (x= 0.9, 0.7, 0.3, 0.1); (b) SEM image of $Zn_{0.5}Co_{0.5}$-ZIF.

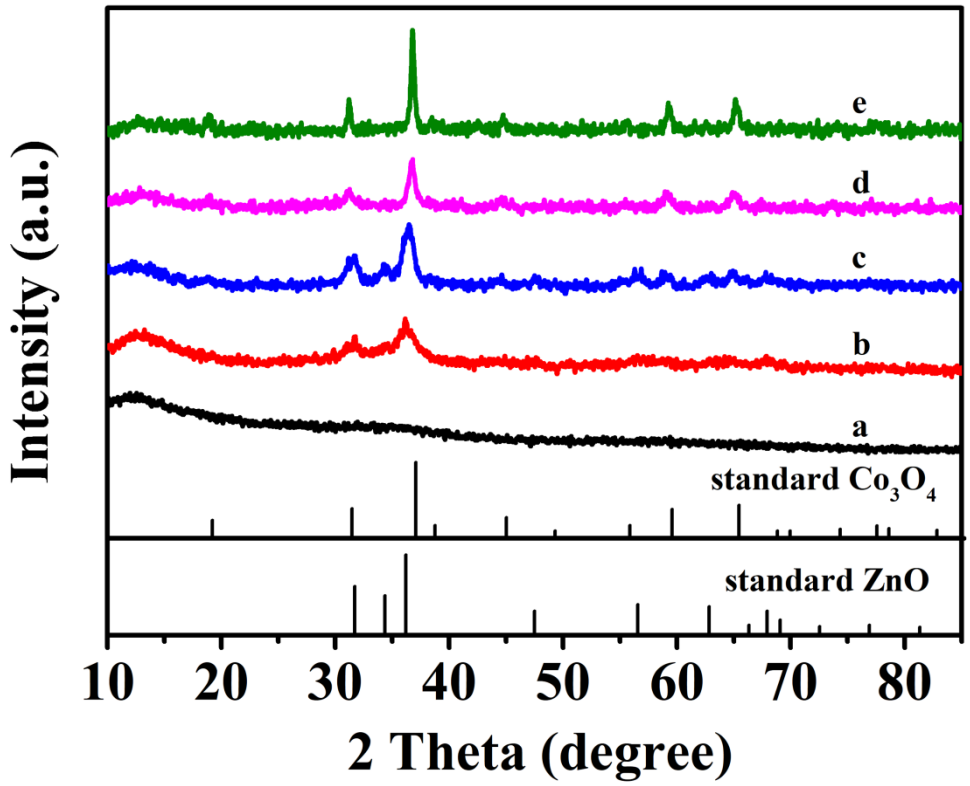

Fig. S2. XRD patterns of the Zn_xCo_{1-x}-ZIF derivatives: x = 0.9 (a), 0.7 (b), 0.5 (c), 0.3 (d) and, 0.1 (e).

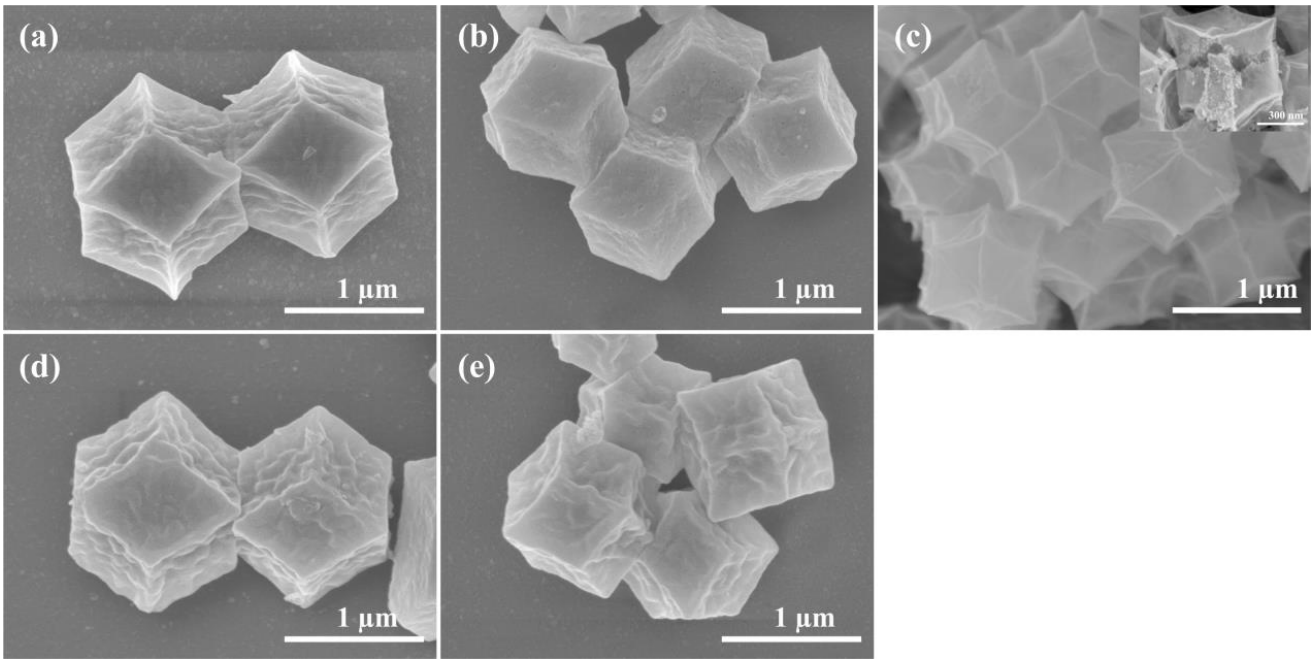

Fig. S3. SEM images of the Zn_xCo_{1-x}-ZIF derivatives: x = 0.9 (a), 0.7 (b), 0.5 (c), 0.3 (d) and 0.1(e).

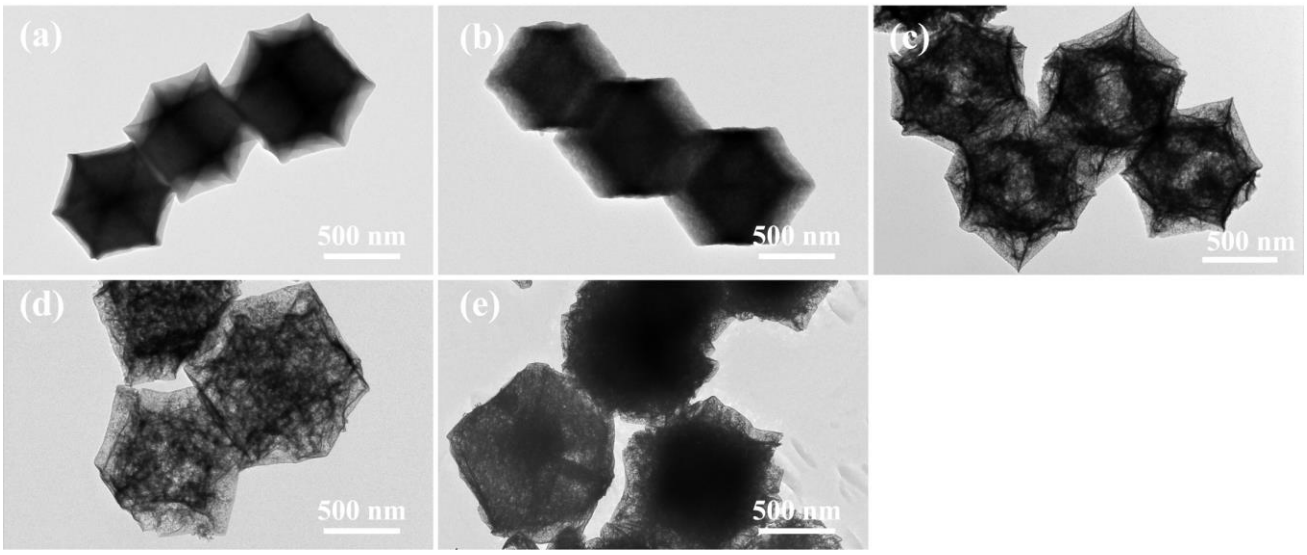

Fig. S4. TEM images of the Zn_xCo_{1-x}-ZIF derivatives: x = 0.9 (a), 0.7 (b), 0.5 (c), 0.3 (d) and 0.1(e).

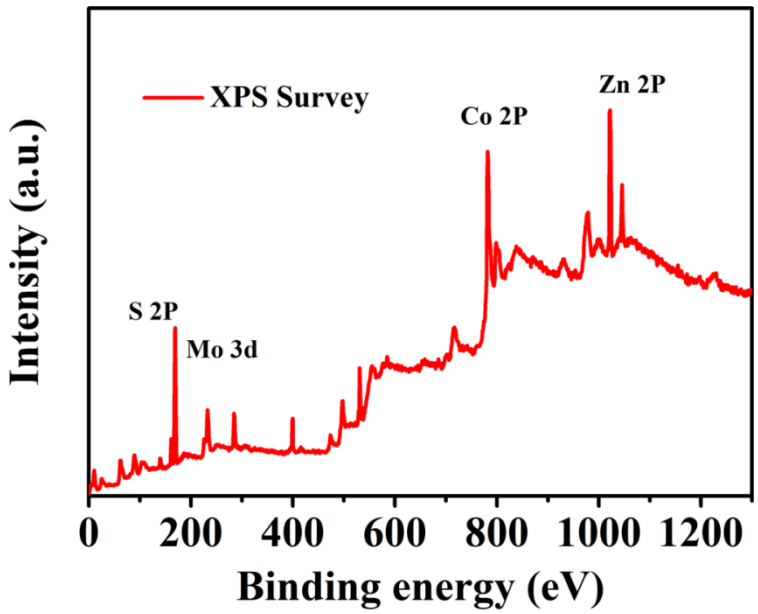

Fig. S5. XPS survey spectra of 2%$MoS_2/Zn_{0.5}Co_{0.5}S$.

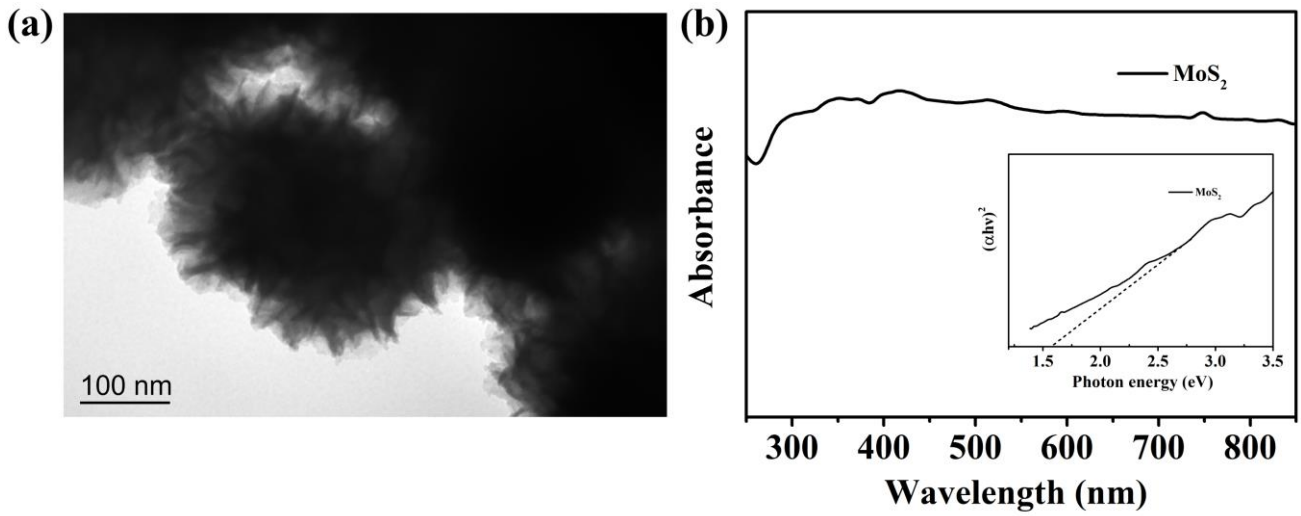

Fig. S6. (a) TEM image and (b) UV-vis DRS spectrum of the pure MoS_2; the inset of (b) shows the plot of transforming the Kubelka–Munk function versus the energy of light.

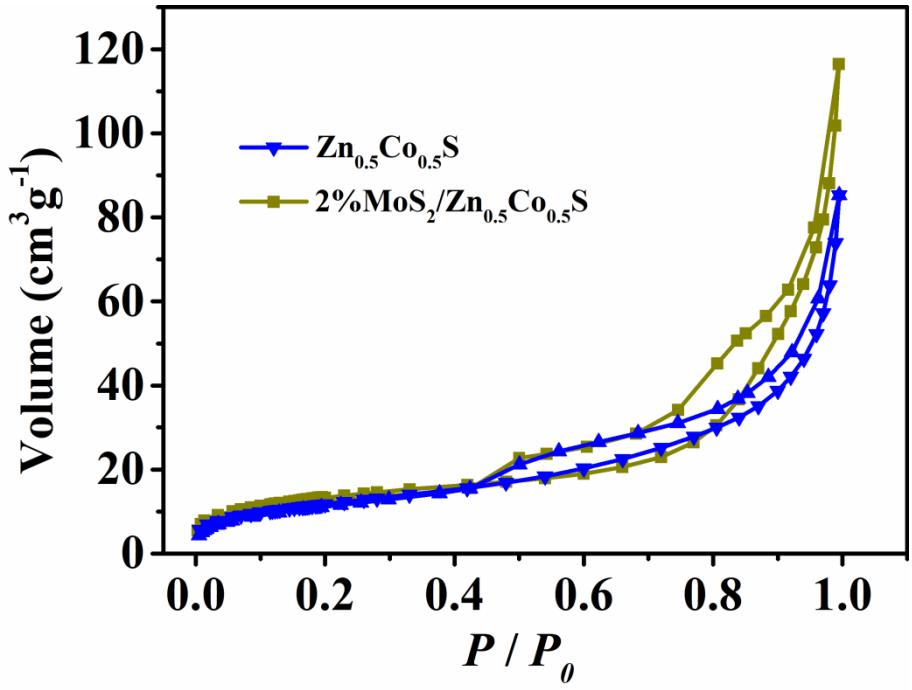

Fig. S7. Nitrogen adsorption-desorption isotherms for 2%MoS_2/$Zn_{0.5}Co_{0.5}S$ and $Zn_{0.5}Co_{0.5}S$ recorded at 77 K.

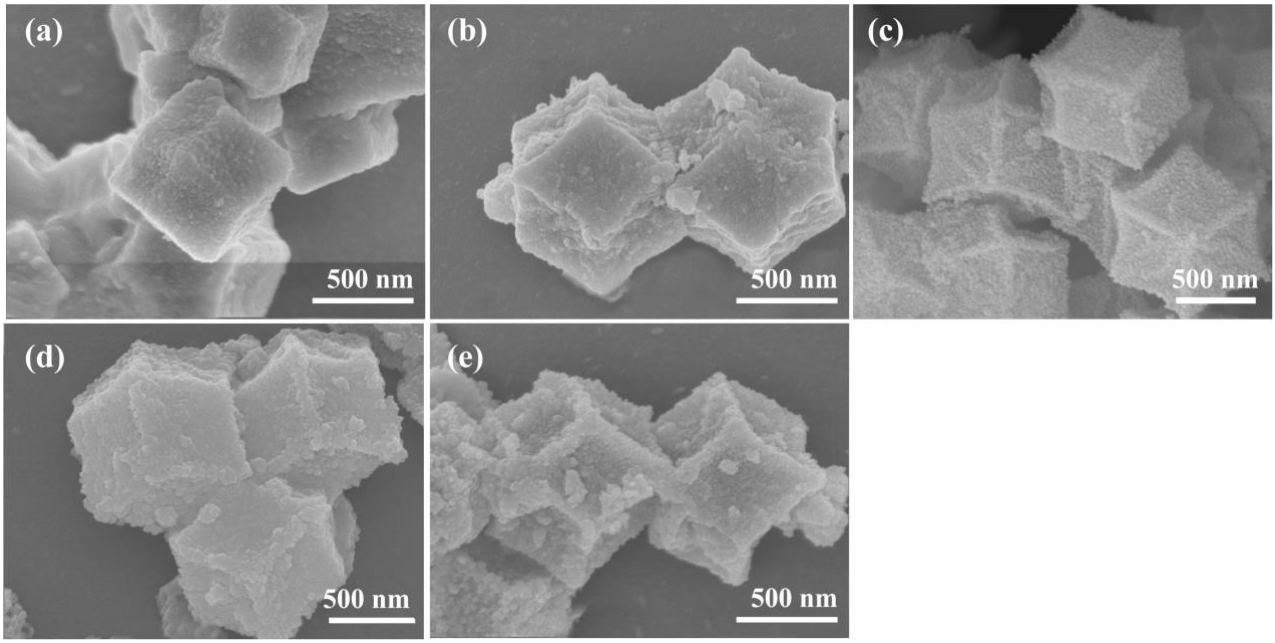

Fig. S8. SEM images of 2%MoS_2/$Zn_xCo_{1-x}S$: x = 0.9 (a), 0.7 (b), 0.5 (c), 0.3(d) and 0.1(e).

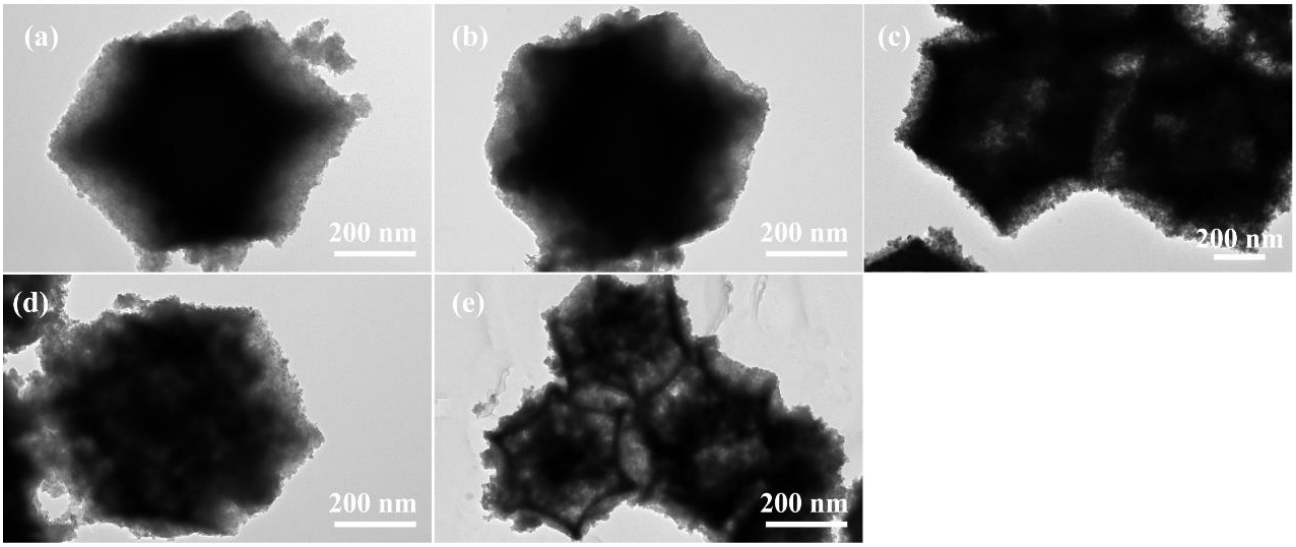

Fig. S9. TEM images of 2%MoS_2/$Zn_xCo_{1-x}S$: x = 0.9 (a), 0.7 (b), 0.5 (c), 0.3(d) and 0.1(e).

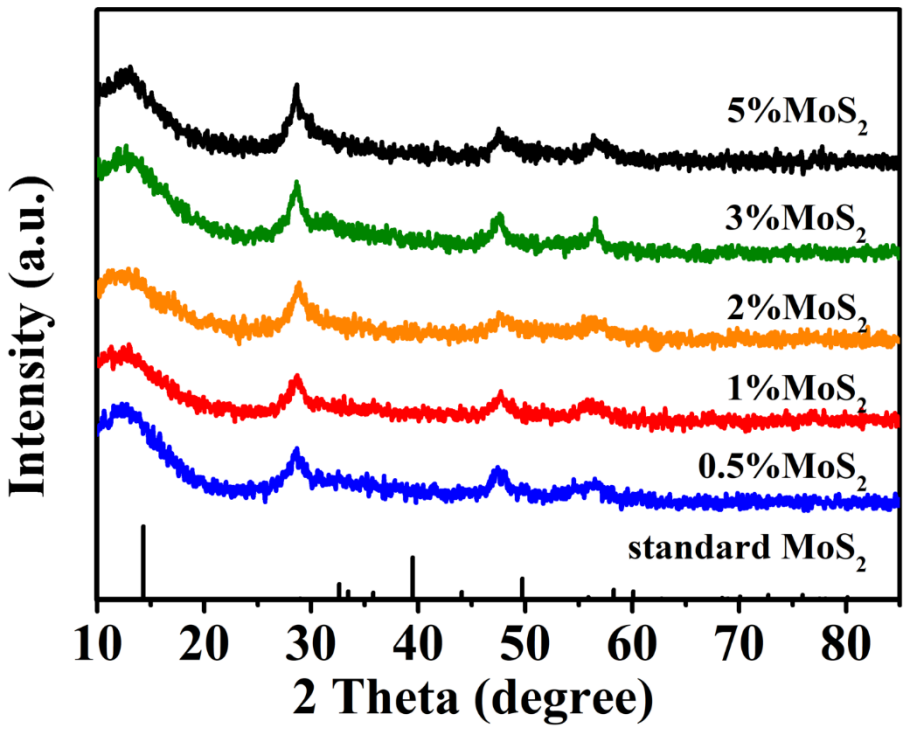

Fig. S10. XRD patterns of *m*%MoS_2/$Zn_{0.5}Co_{0.5}S$ with different loading amount of MoS_2.

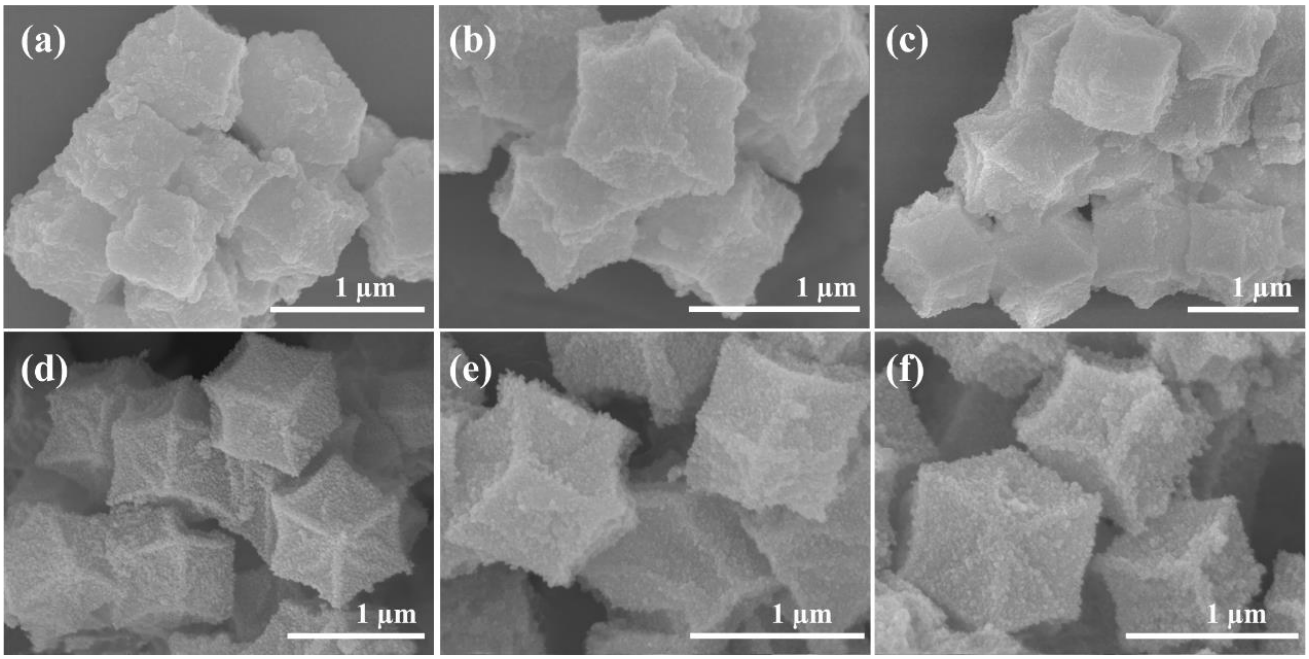

Fig. S11. SEM images of *m*%MoS_2/$Zn_{0.5}Co_{0.5}S$: *m* = 0 % (a), 0.5 % (b), 1 % (c), 2 % (d), 3 % (e) and 5 % (f).

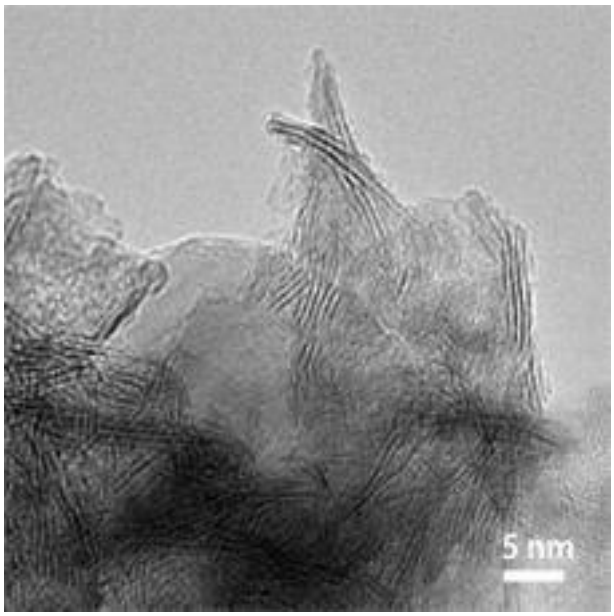

Fig. S12. TEM image of 15%$MoS_2/Zn_{0.5}Co_{0.5}S$.

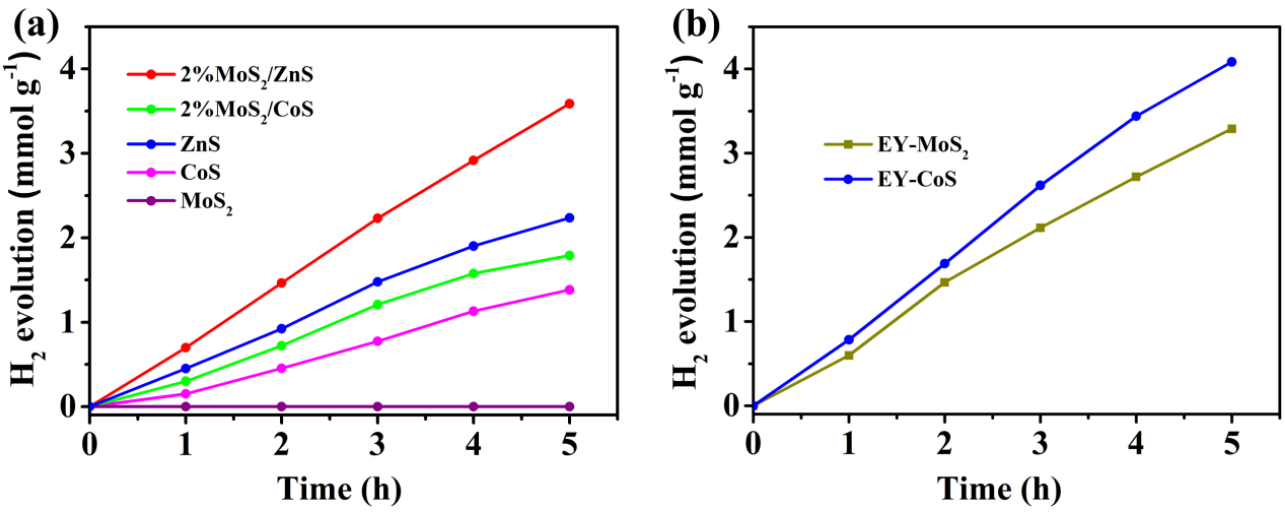

Fig. S13. Photocatalytic hydrogen evolution curves of (a) 2%MoS_2/ZnS ,2%MoS_2/CoS, ZnS, CoS and MoS_2 within 5 h under light irradiation of a 300 W Xe lamp (5 ml TEA, 10 ml H_2O, 35 ml CH_3CN); (b) Photocatalytic hydrogen evolution curves of EY-CoS and EY-MoS_2 (5 ml TEA, 10 ml H_2O, 35 ml CH_3CN, 25 mg eosin Y), respectively.

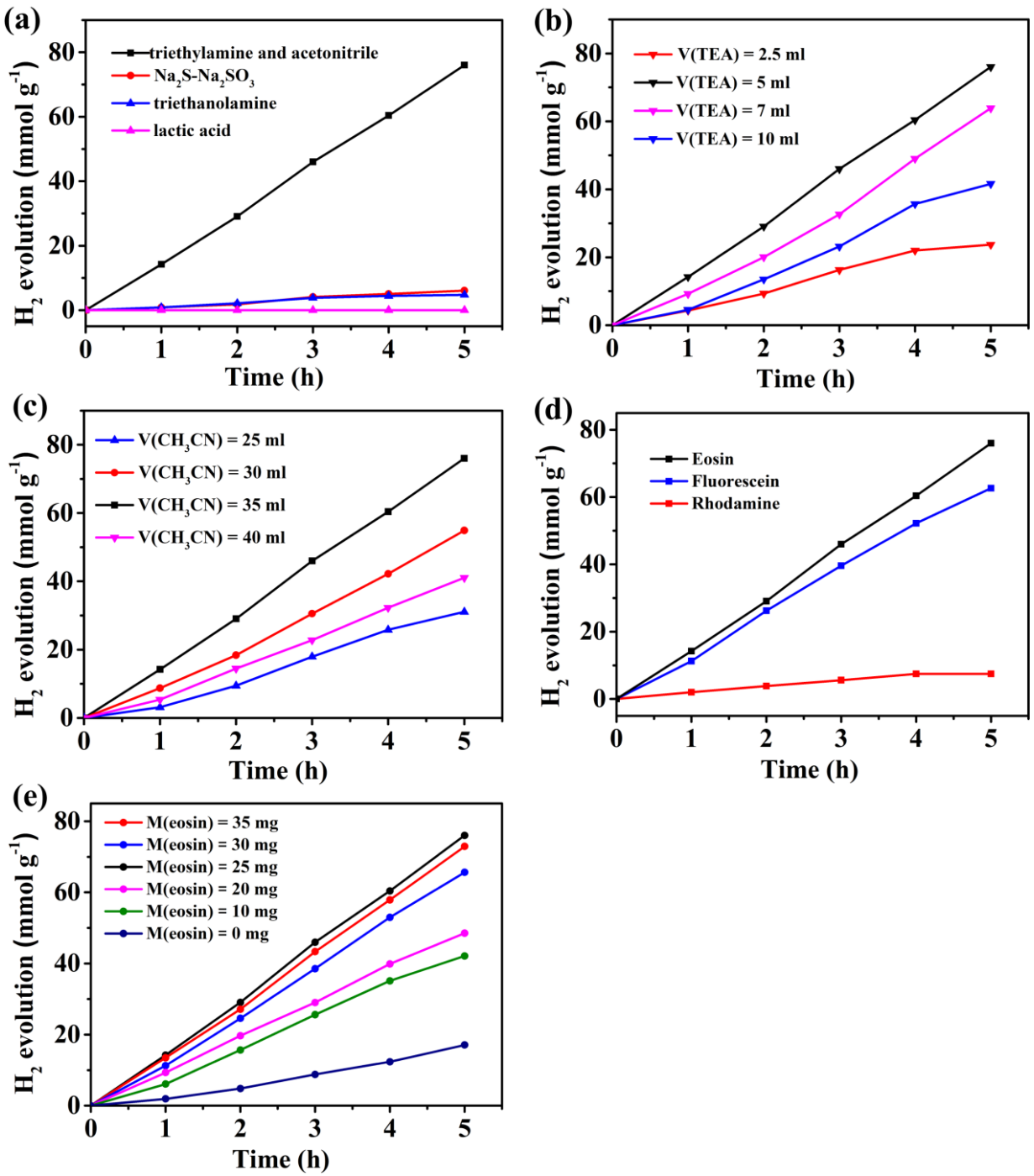

Fig. S14. Photocatalytic hydrogen evolution curves of 2%MoS_2/$Zn_{0.5}Co_{0.5}S$ under conditions of varied sacrificial agents (a), varied volume ratios of H_2O: CH_3CN: TEA (b and c), different photosensitizer (d) and different amounts of EY (e).

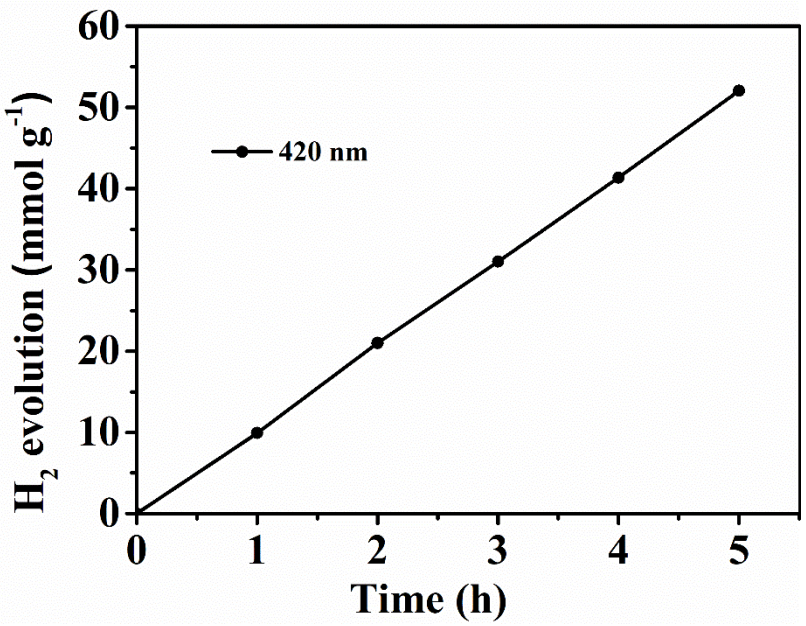

Fig. S15. Photocatalytic hydrogen evolution curves of 2%MoS_2/$Zn_{0.5}Co_{0.5}S$ under 420 nm irradiation.

The apparent quantum efficiency (QE) for 2%MoS_2/$Zn_{0.5}Co_{0.5}S$ at 420 nm was calculated as follows:

The solution containing 30 mg catalyst was irradiated by a 300W Xe lamp applying a 420±20 nm band-pass filter for 5 h. The average intensity of irradiation was determined to be 32.8 mW·cm^{-2} by an ILT 950 spectroradiometer (International Light Technologies) and the irradiation area was 5.06 cm^2. The number of incident photons (N) is calculated by equation (1). The amount of H_2 molecules generated in 5 hours was 1561 μmol. The quantum efficiency is obtained from equation (2).

$$N = \frac{E\lambda}{hc} = \frac{32.28 \times 10^{-3} \times 5.06 \times 3600 \times 5 \times 420 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 6.21 \times 10^{21} \qquad (1)$$

$$QE = \frac{2 \times \text{the number of evolved } H_2 \text{ molecules}}{\text{the number of incident photons}} \times 100\%$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 10^{-6} \times 1561}{6.12 \times 10^{21}} \times 100\% = 30.3\% \qquad (2)$$

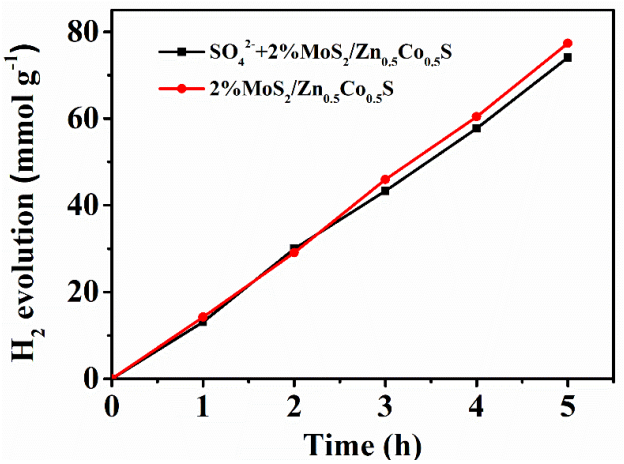

Fig. S16. Photocatalytic hydrogen evolution curves of 2%MoS_2/$Zn_{0.5}Co_{0.5}S$ and the physical mixed of 2%MoS_2/$Zn_{0.5}Co_{0.5}S$ and Na_2SO_4 (0.02 M) in the presence of EY.

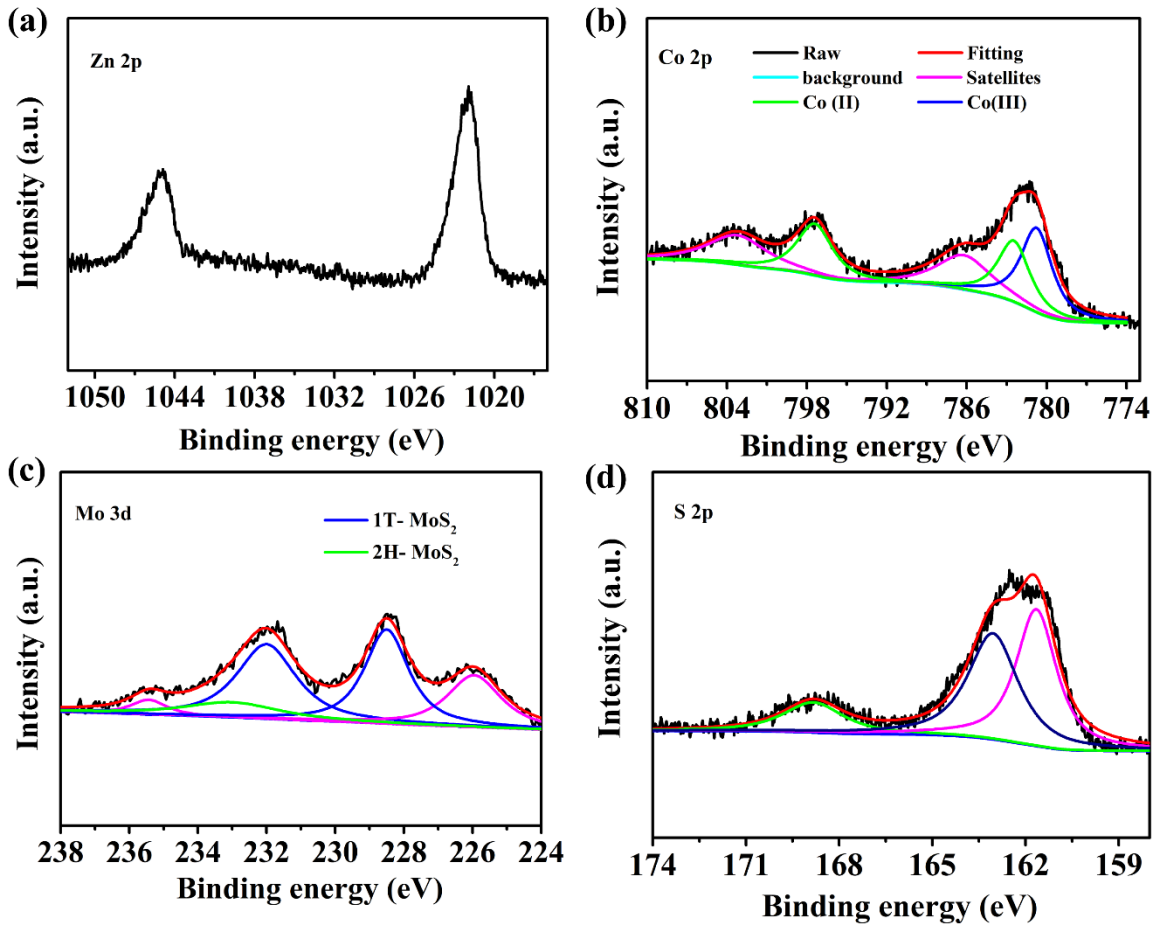

Fig. S17. XPS spectra of Zn 2p, Co 2p, Mo 3d and S 2p for 2%$MoS_2/Zn_{0.5}Co_{0.5}S$ after recycle test.

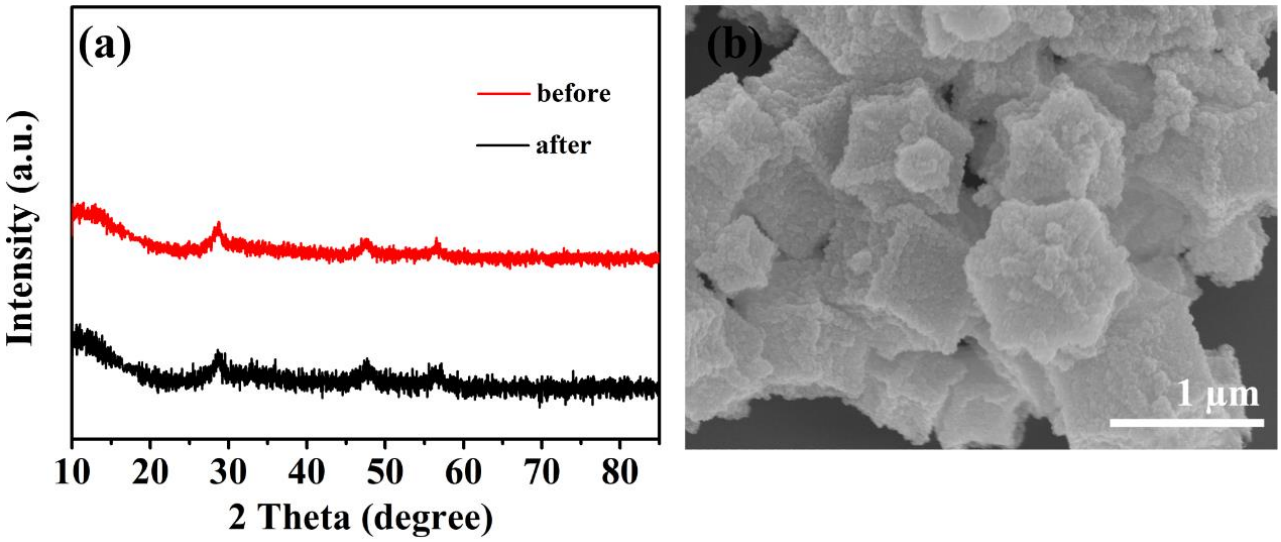

Fig. S18. (a) XRD patterns of 2%MoS_2/$Zn_{0.5}Co_{0.5}S$ before and after recycle test; (b) SEM image of 2%MoS_2/$Zn_{0.5}Co_{0.5}S$ after recycle test.

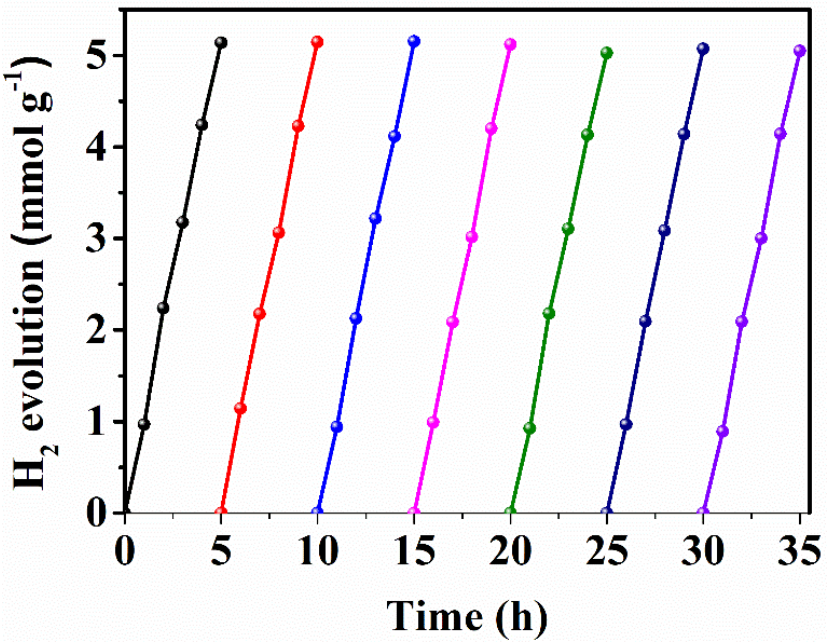

Fig. S19. Photocatalytic hydrogen generation curve as a function of irradiation time in seven consecutive cycles catalysed by 2%MoS_2/$Zn_{0.5}Co_{0.5}S$ in the presence of NaS_2-$NaSO_3$ (0.75 M-1.05 M) as the hole scavenger.

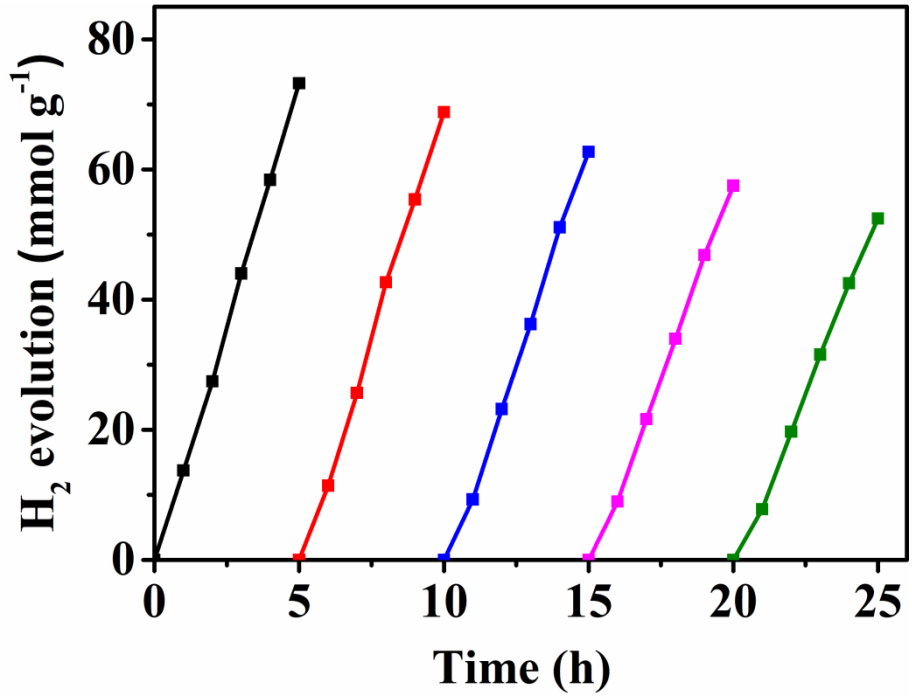

Fig. S20. Photocatalytic hydrogen generation as a function of irradiation time in five consecutive cycles over the hollow 2%MoS_2/$Zn_{0.7}Co_{0.3}S$ under light irradiation of a 300 W Xe lamp within 5 h (5 ml TEA, 10 ml H_2O, 35 ml CH_3CN, 25 mg eosin Y).

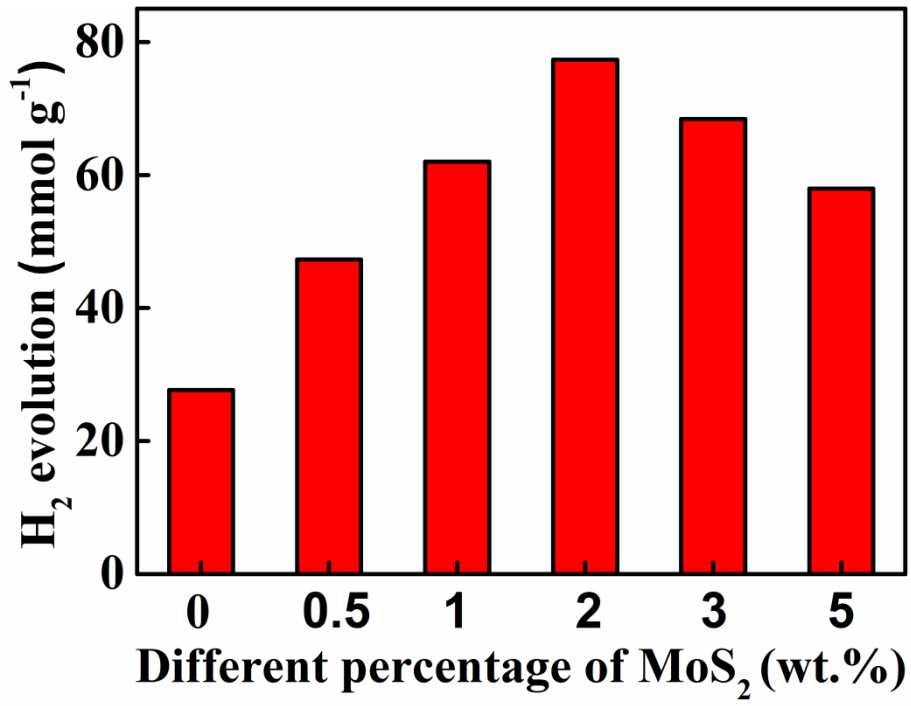

Fig. S21. Photocatalytic hydrogen evolution curves of *m*%MoS_2/$Zn_{0.5}Co_{0.5}S$ with different loading amounts of MoS_2 within 5 h under light irradiation of a 300 W Xe lamp (5 ml TEA, 10 ml H_2O, 35 ml CH_3CN and 25 mg eosin Y).

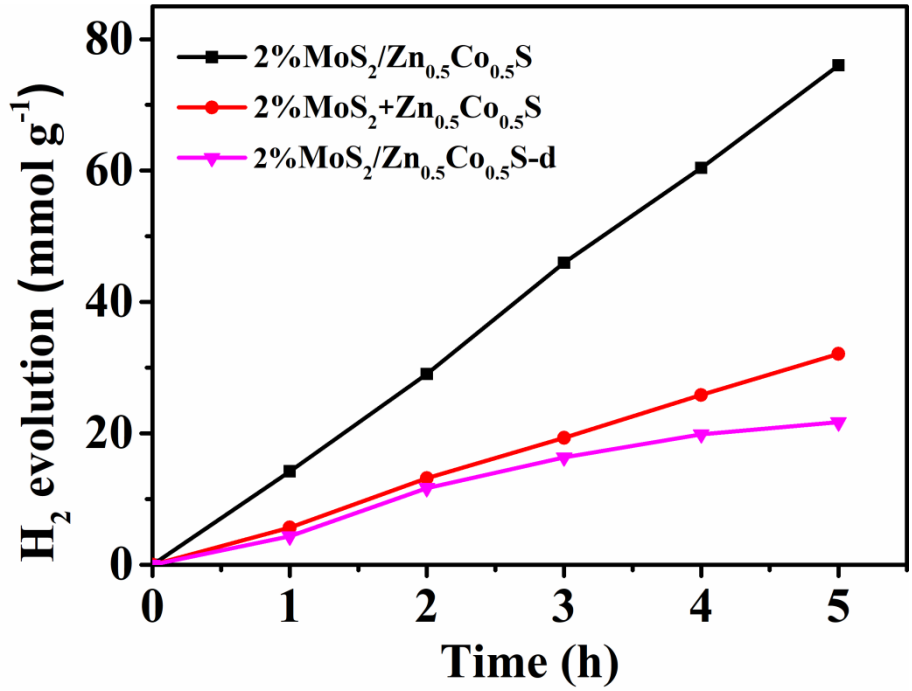

Fig. S22. Photocatalytic hydrogen generation as a function of the 2%MoS_2/$Zn_{0.5}Co_{0.5}S$, 2%MoS_2+$Zn_{0.5}Co_{0.5}S$ and 2%MoS_2/$Zn_{0.5}Co_{0.5}S$-d under light irradiation of a 300 W Xe lamp within 5 h (5 ml TEA, 10 ml H_2O, 35 ml CH_3CN, 25 mg eosin Y).

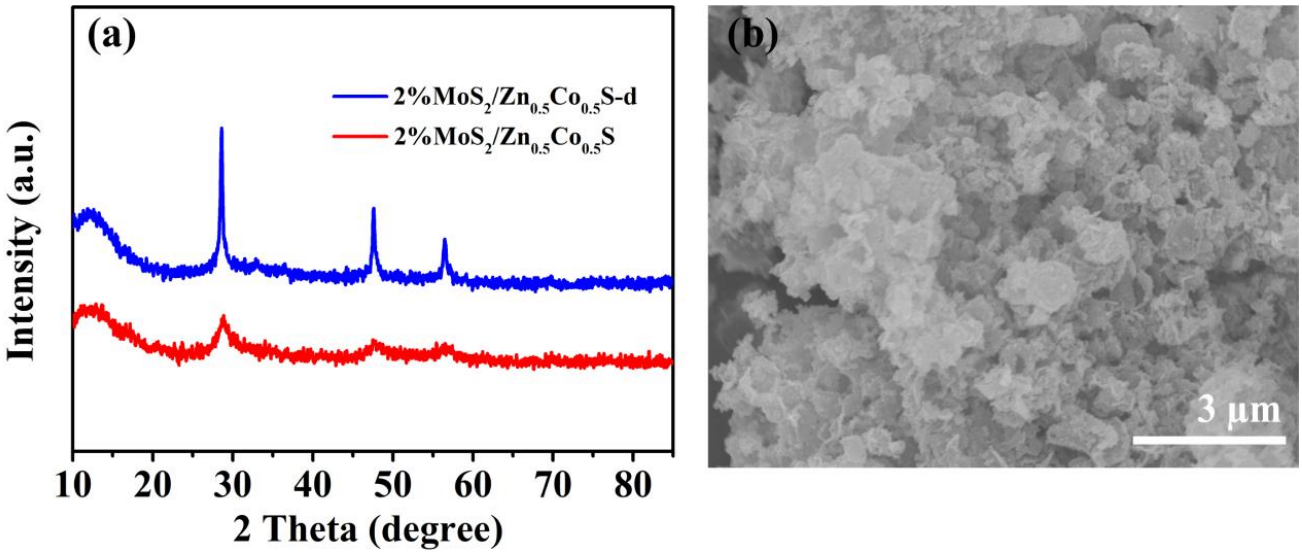

Fig. S23. (a) XRD patterns of hollow 2%$MoS_2/Zn_{0.5}Co_{0.5}S$ and 2% $MoS_2/Zn_{0.5}Co_{0.5}S$-d; (b) SEM image of 2%$MoS_2/Zn_{0.5}Co_{0.5}S$-d.

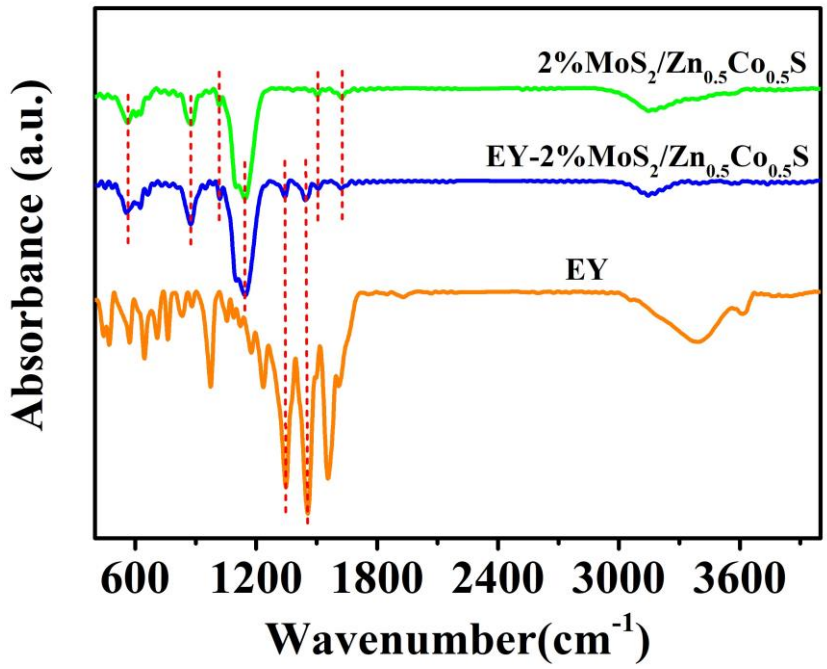

Fig.S24. FT-IR spectra of $Zn_{0.5}Co_{0.5}S$, 2% $MoS_2/Zn_{0.5}Co_{0.5}S$ and EY-2%$MoS_2/Zn_{0.5}Co_{0.5}S$. The absorption peaks of EY-2%$MoS_2/Zn_{0.5}Co_{0.5}S$ appeared at identical wavenumbers with EY and 2%$MoS_2/Zn_{0.5}Co_{0.5}S$, implying the ignorable chemical interaction be EY and 2%$MoS_2/Zn_{0.5}Co_{0.5}S$. EY should be absorbed on 2%$MoS_2/Zn_{0.5}Co_{0.5}S$.

Table S1 Characterization results of catalysts

Catalyst	S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})	Content (wt%)							
			Zn[a]	Co[a]	Mo[b]	S[c]	C[c]	N[c]	H[c]	O[d]
$Zn_{0.5}Co_{0.5}S$	42	0.13	27.02	27.54	-	34.5	3.71	2.78	3.15	1.30
$2\%MoS_2/Zn_{0.5}Co_{0.5}S$	57	0.30	26.41	25.59	1.98	34.88	3.65	2.87	3.15	1.47

[a] Measrued by AAS. [b] Measured by ICP. [c] Measured by elemental analysis. [d] Calculated.

Table S2 Summary of Co/Zn ratio

Catalyst	Content (wt%)		Co:Zn (molar ratio)	
	Zn[a]	Co[a]	Theoretic	Experimental
$Zn_{0.5}Co_{0.5}S$	27.02	27.54	1	1.13
$2\%MoS_2/Zn_{0.9}Co_{0.1}S$	39.65	3.66	0.11	0.10
$2\%MoS_2/Zn_{0.7}Co_{0.3}S$	29.41	13.30	0.43	0.50
$2\%MoS_2/Zn_{0.5}Co_{0.5}S$	26.41	25.59	1	1.07
$2\%MoS_2/Zn_{0.3}Co_{0.7}S$	12.30	27.03	2.33	2.43
$2\%MoS_2/Zn_{0.1}Co_{0.9}S$	6.23	43.35	9	7.72

[a] Measrued by AAS.

Table S3 The quantum efficiency of hydrogen evolution of different photocatalysts.

Catalyst	Incident light	Light source	Quantum yield	Ref
2%$MoS_2/Zn_{0.5}Co_{0.5}S$	420 nm	Xe lamp (300W)	30.3%	This work
1% MoS_2/CdS-TiO_2	420 nm.	Xe lamp (300W)	19.3%	S1
MoS_2/CdS core-shell	420 nm	Xe lamp (300W)	14.7%	S2
Au/ZnO@ZnS	365 nm	Xe arc lamp (225 W)	25.47%	S3
ZnS/$CdIn_2S_4$/rGO	430 nm	Xe lamp (300W)	19.34%	S4
CuS/ZnS nanoflower	420 nm	Xe lamp (350W)	26.2%	S5
MoS_2/rGO/TiO_2	365 nm	UV–Vis (Xenon lamp)	9.7%	S6
MoS_2-graphene/$ZnIn_2S_4$	420 nm	Xe lamp (300W)	28.1%	S7
0.2 wt% MoS_2/mpg-CN.	420 nm.	Xe lamp (300W)	2.1%	S8
16 wt.% WS_2/CdS	420 nm	Xe lamp (150W)	40.5%	S9
2.0 wt.% Mo-Mo2C/g-C_3N_4	420 nm	Xe lamp (300W)	8.3%	13
Ni-NG/CdS	420 nm	Xe lamp (300W)	48.2%	14
Co_4S_3/CdS	425 nm	Xe lamp (150W)	1.22%	S10

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