Supporting Information

Fabricating Sandwich-Shelled ZnCdS/ZnO/ZnCdS Dodecahedral Cages with "One Stone" as Z-scheme Photocatalysts for Highly Efficient Hydrogen Production

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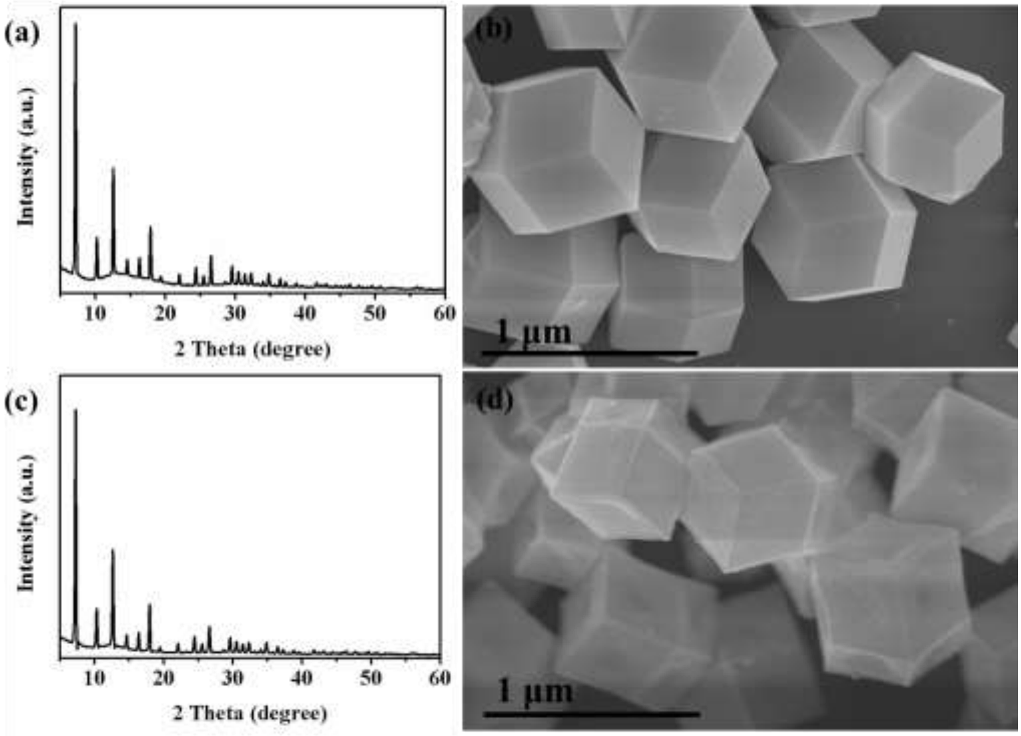

Fig. S1 XRD patterns (a and c) and SEM images (b and d) of ZIF-8 crystals before and after tannic acid etching for 30 min, respectively.

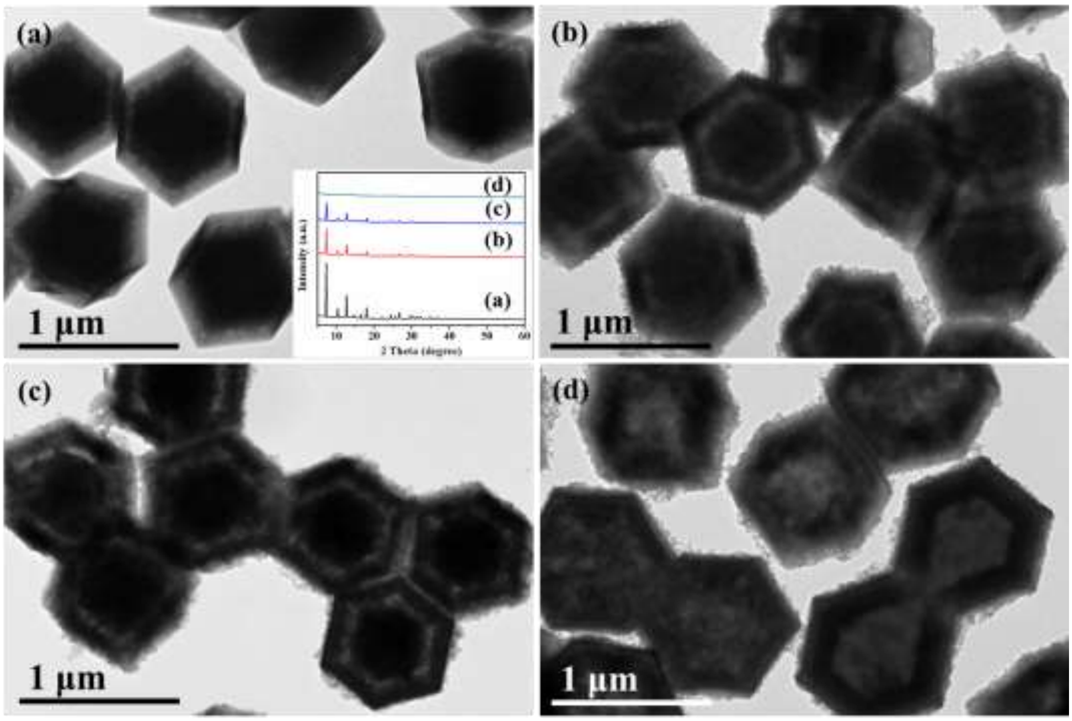

Fig. S2 TEM images of ZIF-8 with etching duration of 0.5 h (a), 1 h (b), 2 h (c), and 3 h (d), respectively, using tannic acid. The inset in (a) shows the corresponding XRD patterns.

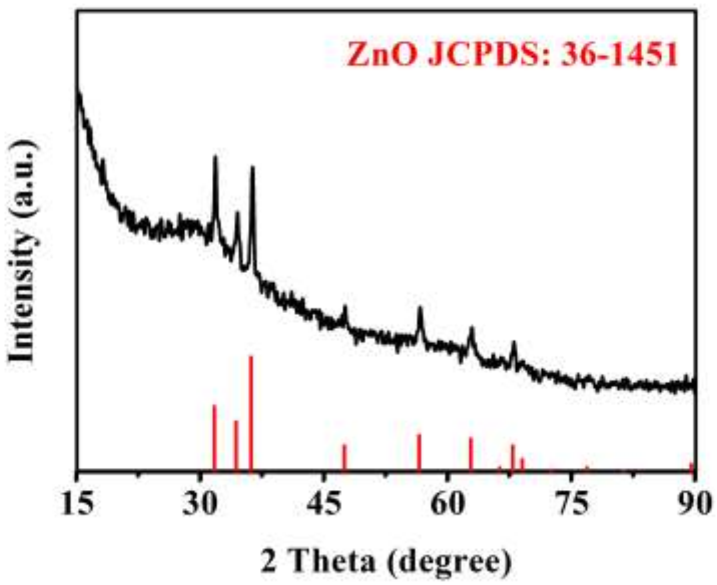

Fig. S3 XRD pattern of hollow ZnO cages after calcination at 500 ^{o}C for 4 h in the Ar atmosphere. Thermal annealing treatment was used to obtain better XRD patterns for characterizing the material.

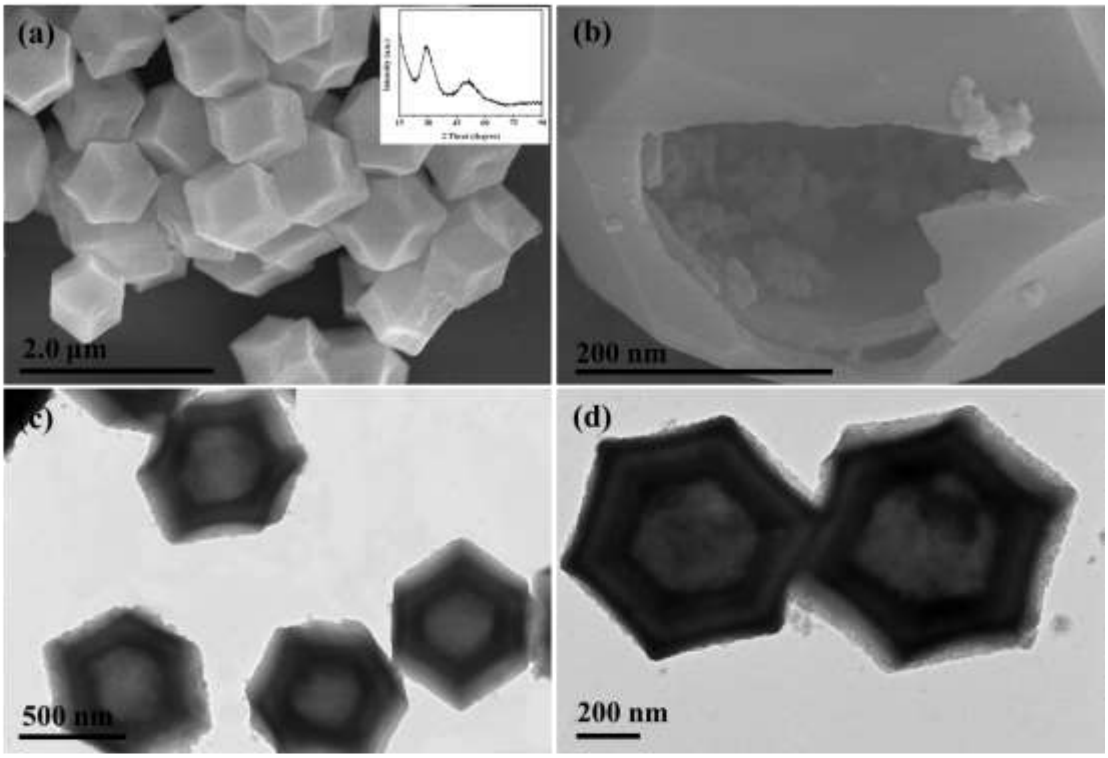

Fig. S4 SEM (a and b) and TEM images (c and d) of sandwich-shelled ZnS/ZnO/ZnS cages. The inset in (a) shows the corresponding XRD pattern.

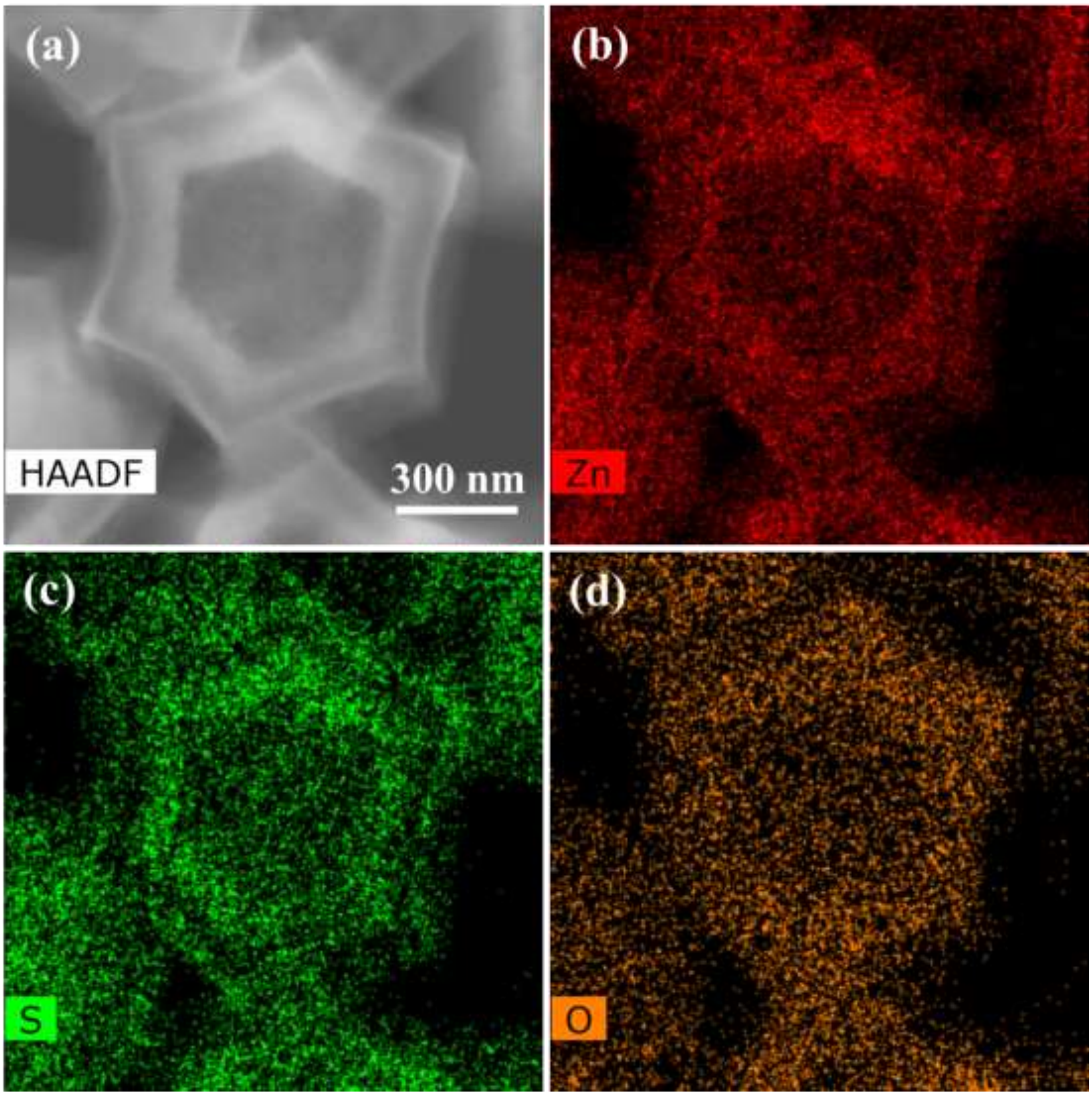

Fig. S5 (a) HAADF-STEM and (b-d) EDX mapping images of sandwich-shelled ZnS/ZnO/ZnS cages.

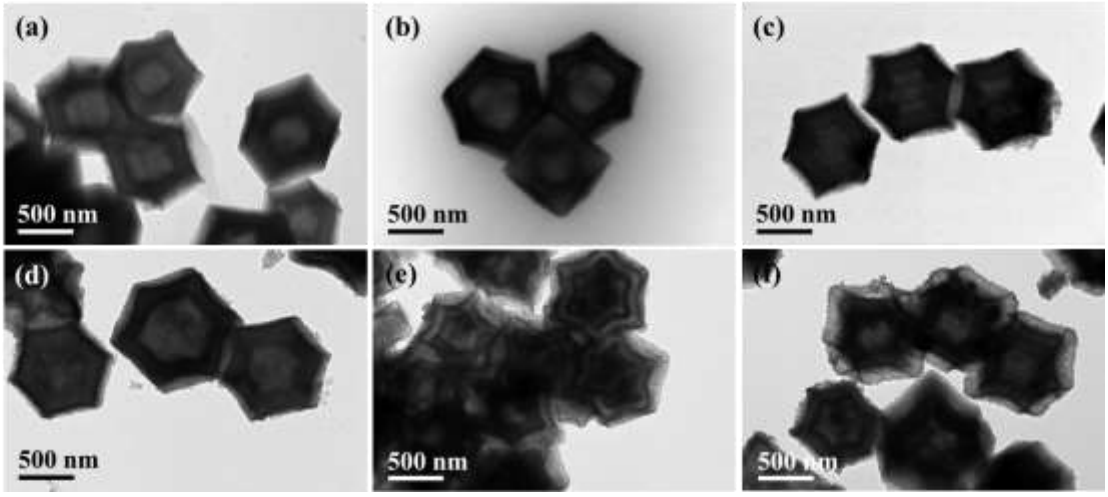

Fig. S6 TEM images of sandwich-shelled $Zn_{1-x}Cd_xS/ZnO/Zn_{1-x}Cd_xS$ cages: x = 0.1 (a); 0.3 (b); 0.5 (c); 0.7 (d); 0.9 (e); and 1 (f).

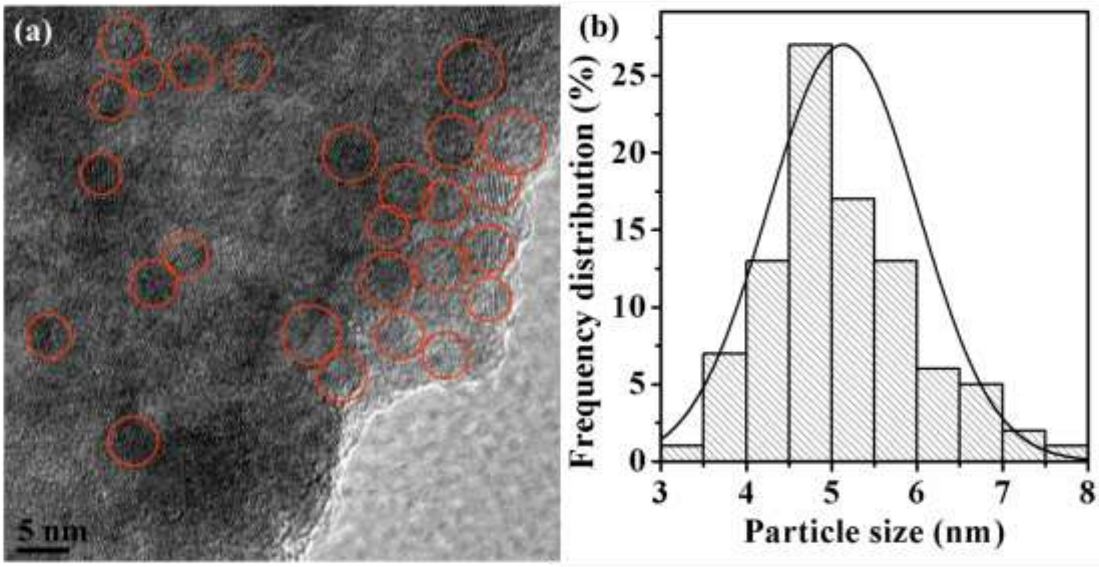

Fig. S7 (a) HRTEM image of sandwich-shelled $Zn_{0.5}Cd_{0.5}S/ZnO/Zn_{0.5}Cd_{0.5}S$ cages and (b) the particle size distribution of $Zn_{0.5}Cd_{0.5}S$ NPs.

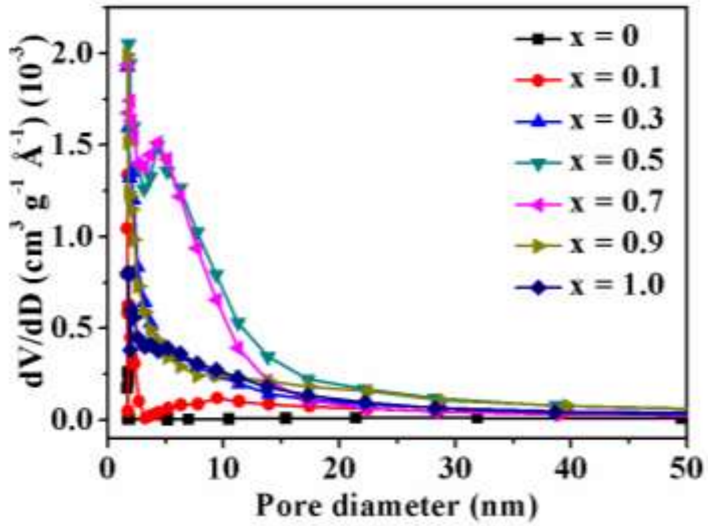

Fig. S8 The pore size distribution for the $Zn_xCd_{1-x}S/ZnO/Zn_xCd_{1-x}S$ cages.

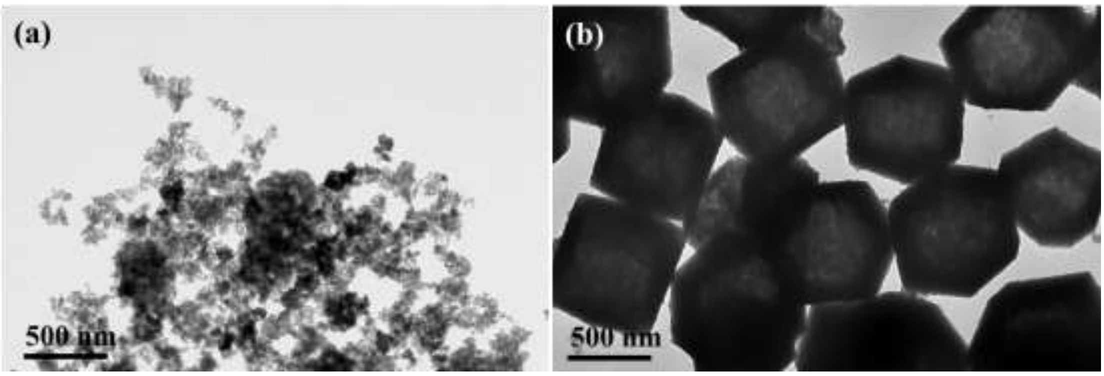

Fig. S9 (a) TEM images of (a) $Zn_{0.5}Cd_{0.5}S$ solid and (b) single-shelled $Zn_{0.5}Cd_{0.5}S$ cages.

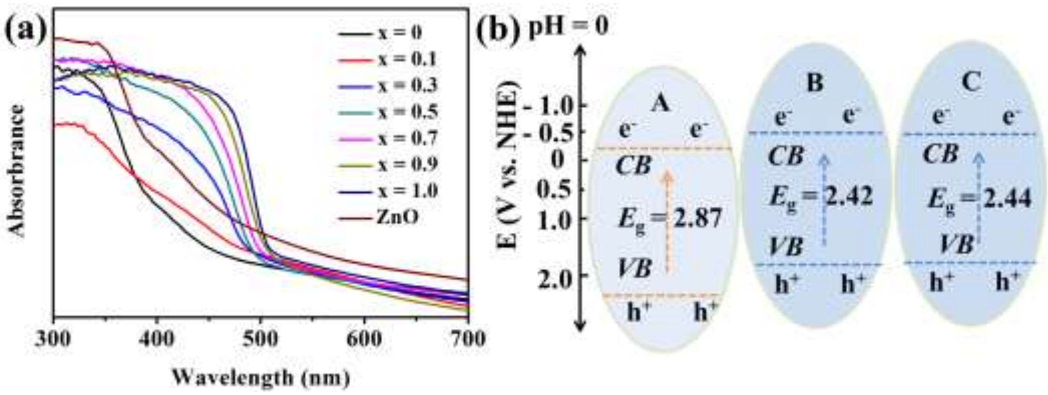

Fig. S10 (a) UV-Vis DRS spectra of the as-synthesized sandwich-shelled $Zn_xCd_{1-x}S/ZnO/Zn_xCd_{1-x}S$ cages ($0 \leqslant x \leqslant 1$) with different metal ratios and ZnO hollow cages; (b) The E_g and band positions of ZnO (A), single-shelled $Zn_{0.5}Cd_{0.5}S$ (B), and sandwich-shelled $Zn_{0.5}Cd_{0.5}S/ZnO/Zn_{0.5}Cd_{0.5}S$ (C).

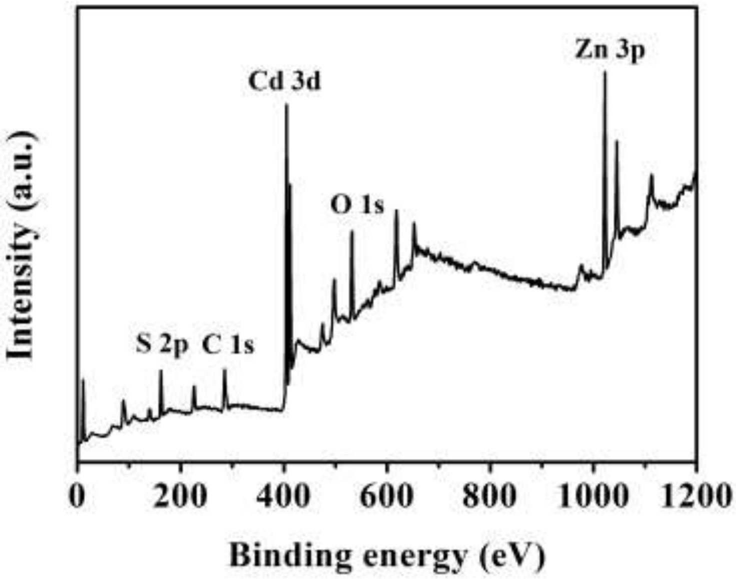

Fig. S11 The XPS spectrum of the $Zn_{0.5}Cd_{0.5}S/ZnO/Zn_{0.5}Cd_{0.5}S$ cages.

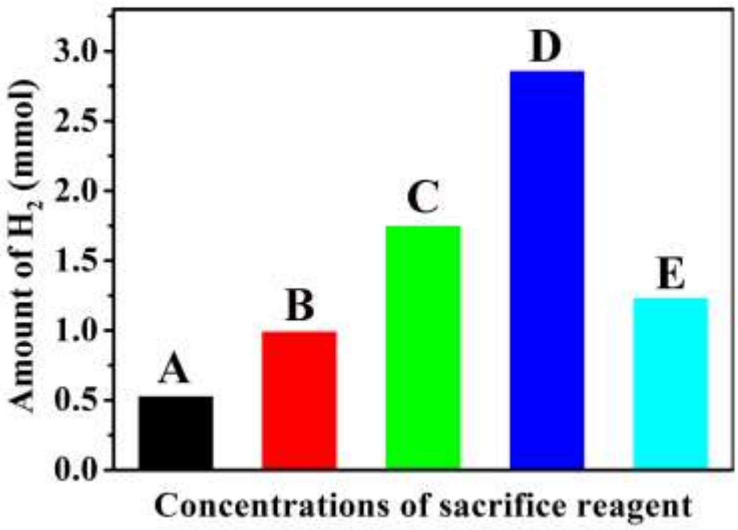

Fig. S12 Photocatalytic H_2 evolution on $Zn_{0.5}Cd_{0.5}S/ZnO/Zn_{0.5}Cd_{0.5}S$ cages in the presence of sacrificial reagents with various concentrations: **A**: 0.13 M Na_2S, 0.18 M Na_2SO_3; **B**: Na_2S, 0.35 M Na_2SO_3; **C**: 0.50 M Na_2S, 0.70 M Na_2SO_3; **D**: 0.75 M Na_2S, 1.05 M Na_2SO_3; **E**: 1.00 M Na_2S, 1.40 M Na_2SO_3.

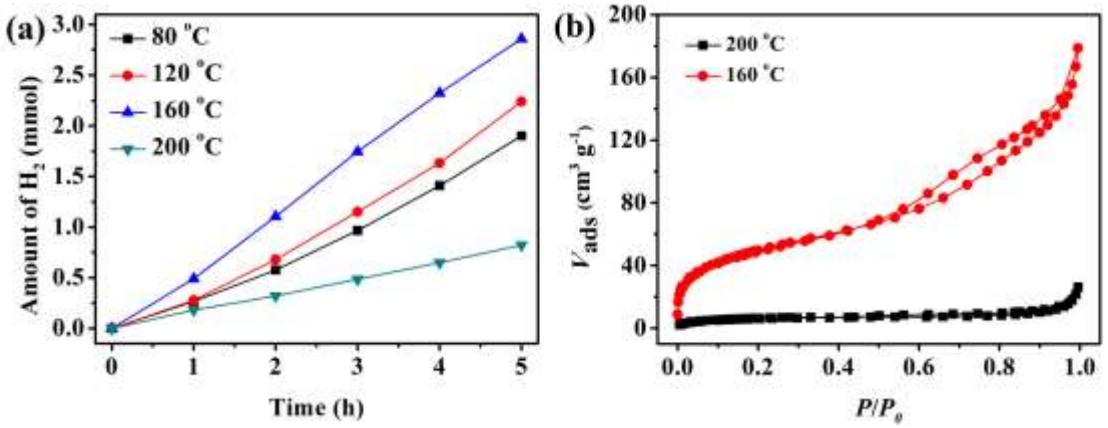

Fig. S13 (a) Photocatalytic hydrogen evolution curves of the sandwich-shelled $Zn_{0.5}Cd_{0.5}S/ZnO/Zn_{0.5}Cd_{0.5}S$ cages prepared at different cation-exchange temperatures in a solution containing 0.75 M Na_2S and 1.05 M Na_2SO_3. (b) Nitrogen adsorption/desorption isotherms recorded at 77 K for $Zn_{0.5}Cd_{0.5}S/ZnO/Zn_{0.5}Cd_{0.5}S$ cages prepared at different cation-exchange temperatures.

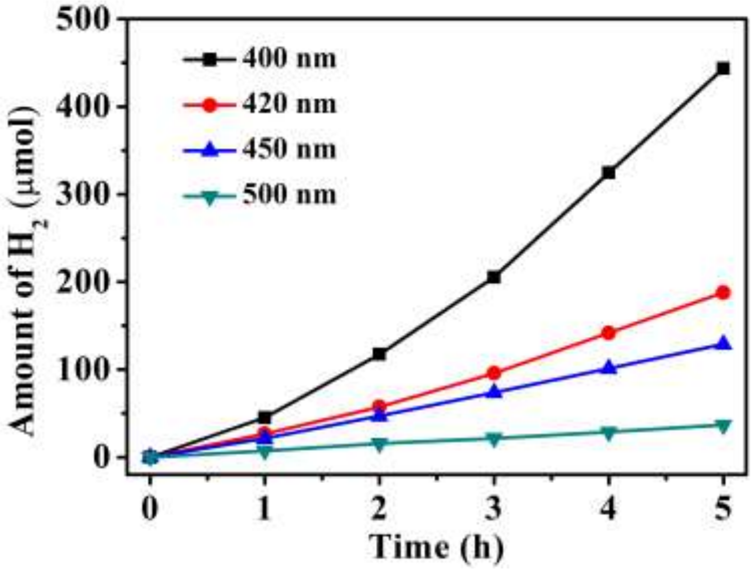

Fig. 14 Photocatalytic hydrogen evolution curves of sandwich-shelled $Zn_{0.5}Cd_{0.5}S/ZnO/Zn_{0.5}Cd_{0.5}S$ cages under different wavelength irradiation.

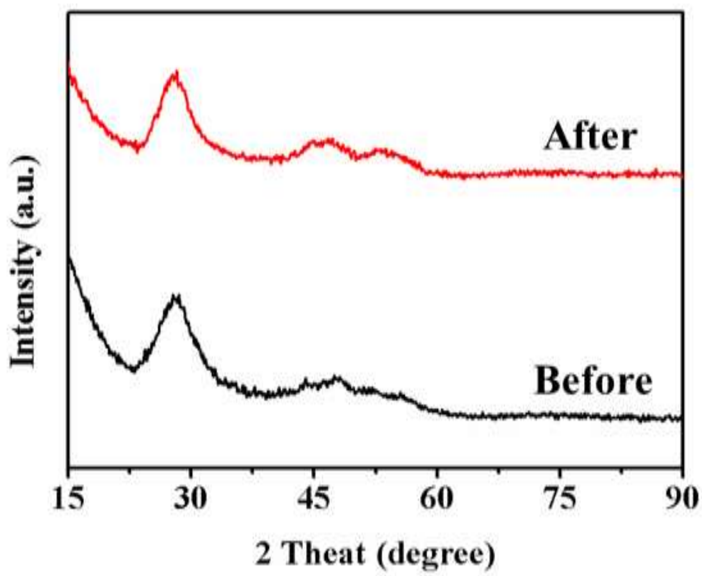

Fig. S15 XRD patterns of $Zn_{0.5}Cd_{0.5}S/ZnO/Zn_{0.5}Cd_{0.5}S$ cages before and after recycle test.

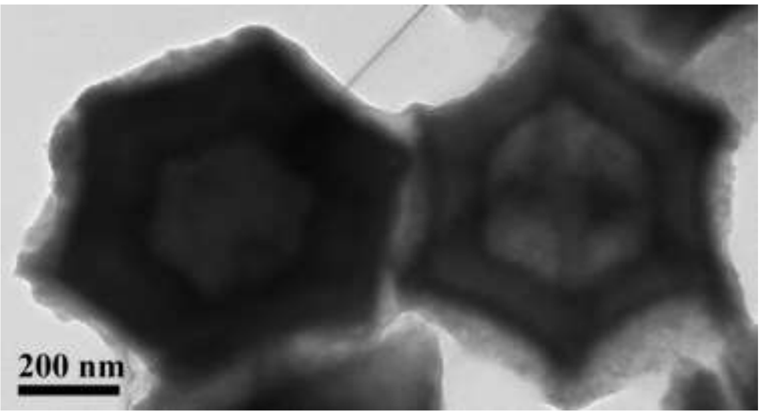

Fig. S16 TEM image of $Zn_{0.5}Cd_{0.5}S/ZnO/Zn_{0.5}Cd_{0.5}S$ cages after reaction.

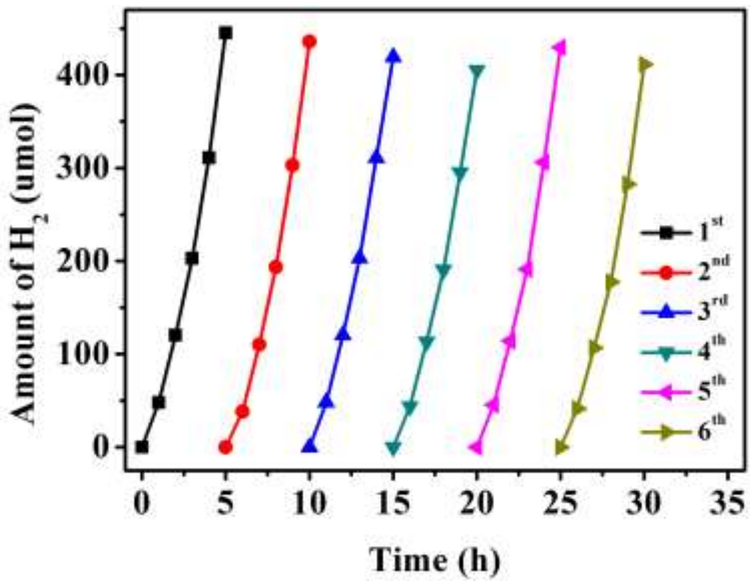

Fig. S17 Photocatalytic hydrogen generation curve as a function of irradiation time in six consecutive cycles catalysed by the $Zn_{0.5}Cd_{0.5}S/ZnO/Zn_{0.5}Cd_{0.5}S$ cages in the presence of triethanolamine as the hole scavenger.

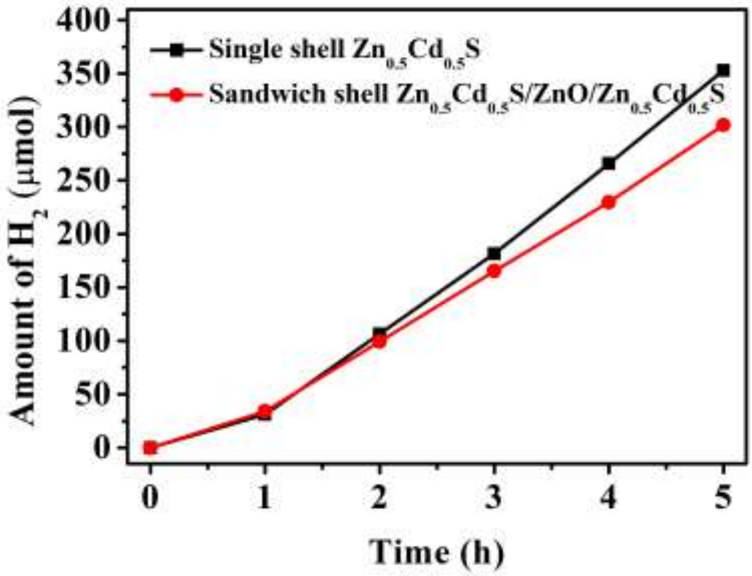

Fig. S18 Photocatalytic hydrogen evolution curves of sandwich-shelled $Zn_{0.5}Cd_{0.5}S/ZnO/Zn_{0.5}Cd_{0.5}S$ and single shell $Zn_{0.5}Cd_{0.5}S$ cages under visible light irradiation.

Table S1. AAS results of different catalysts and the corresponding BET surface area, pore volume, bandgap energy (E_g), and conduction band (CB) and valence band (VB) potentials.

Catalyst	**Zn:Cd (atomic ratio)**	S_{BET}[a] **(m^2 g^{-1})**	**Pore volume**[b] **(cm^3 g^{-1})**	E_g[c] **(eV)**	E_{CB} **(eV)**	E_{VB} **(eV)**
ZnS/ZnO/ZnS	-	17	0.024	2.94	-0.71	2.23
$Zn_{0.9}Cd_{0.1}S$/ZnO/$Zn_{0.9}Cd_{0.1}S$	0.91 : 0.09	48	0.083	2.59	-0.54	2.05
$Zn_{0.7}Cd_{0.3}S$/ZnO/$Zn_{0.7}Cd_{0.3}S$	0.72 : 0.28	102	0.154	2.49	-0.51	1.98
$Zn_{0.5}Cd_{0.5}S$/ZnO/$Zn_{0.5}Cd_{0.5}S$	0.51 : 0.49	176	0.276	2.44	-0.50	1.94
$Zn_{0.3}Cd_{0.7}S$/ZnO/$Zn_{0.3}Cd_{0.7}S$	0.31 : 0.69	132	0.193	2.42	-0.51	1.91
$Zn_{0.1}Cd_{0.9}S$/ZnO/$Zn_{0.1}Cd_{0.9}S$	0.12 : 0.88	96	0.167	2.40	-0.51	1.89
CdS/ZnO/CdS	-	58	0.129	2.38	-0.50	1.88
Single-shelled ZnCdS	0.53 : 0.47	102	0.090	2.42	-0.49	1.93
ZnO	-	-	-	2.87	-0.14	2.73

[a] BET surface area was calculated by using the Brunauer-Emmett-Teller equation. [b] Total pore volume was determined by using the adsorption branch of the N_2 isotherm at P/P_0 = 0.995. [c] Bandgap energy (E_g) was calculated by the Kubelka-Munk method.

Table S2. Comparison of the H_2-generation rates for various photocatalysts.

Catalyst	**Co-catalyst**	**Light source**	**TOF ($mmol_{H2}$ h^{-1} g^{-1})**	**Ref.**
ZnO/Pt/$Cd_{0.8}Zn_{0.2}S$	Pt	450 W Xe	31.20	54
ZnCdS/ZnO/ZnCdS	**-**	**300 W Xe**	**28.60**	**This work**
ZnO-CdS@Cd	Pt	300 W Xe	19.20	27
$Zn_{0.5}Cd_{0.5}S$	CoP	AM 1.5G	12.20	55
TiO_2	Pt	AM 1.5G	10.64	56
CdS/ZnO core/shell	-	300 W Xe	9.62	57
Pt-Zn_3P_2-CoP	Pt	300 W Xe	9.15	58
NiS/$Zn_{0.5}Cd_{0.5}S$/RGO	-	AM 1.5G	7.51	12
ZnO–CdS	RuO	300 W Xe	6.18	59
ZnO-CdS/RGO	Pt	300 W Xe	5.10	25
ZnS/graphene/MoS_2	RGO, MoS_2	300 W Xe	2.26	23
MoS_2/TiO_2	MoS_2	300 W Xe	2.15	60
TiO_2-MoS_2-graphene	-	350 W Xe	2.07	61
RGO-$Zn_{0.8}Cd_{0.2}S$	RGO	AM 1.5G	1.82	10
ZnO/CdS	Pt	300 W Xe	1.81	62
Pt_1-Au_2/TiO_2	-	AM 1.5G	1.23	63
Pt@UiO-NH_2-66	Pt	300 W Xe	0.35	64
ZnO/$Zn_xCd_{1-x}Te$	-	300 W Xe	0.27	20