Supplementary Information

Accumulated photogenerated holes in Type-II ZnSe/CdS nanotetrapods for efficient photocatalytic hydrogen evolution

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Characterization

Powder X-ray diffraction (XRD) patterns were obtained by using Bruker D8-ADVANCE (Bruker Corp, Billerica, MA, USA) with Cu-Kα radiation. X-ray photoelectron spectroscopy (XPS) were recorded on an ESCALAB 250 spectrophotometer (Thermo Fisher Scientific Corp, Waltham, MA, USA) with Al-Kα radiation. The binding energy scale was calibrated using the C1s peak at 284.60 eV. Elemental analysis data were obtained from Inductively coupled plasma-mass spectrometry (ICP-MS, 7890A+5975C, Agilent, USA). TEM images were obtained from JEM 2100 (JEOL Co. Ltd., Tokyo, Japan). UV-vis absorption spectra were recorded on a Shimadzu UV-2600PC spectrophotometer (Shimadzu Corp, Kyoto, Japan). Photoluminescence (PL) spectra were obtained by Hitachi (F-4600) spectrophotometer (Hitachi High-Tech Corp., Tokyo, Japan). The content of H_2 in the product was determined by gas chromatography (GC, GC-2014, Shimadzu Corp., Kyoto, Japan), and using Ar as the carrier gas with a molecular sieve column (5 Å; 30 m × 0.53 mm) and a thermal conductivity detector. The photoelectrochemical measurement was carried out on an electrochemical workstation (CHI 660B, Chinstruments, Shanghai, China). High angle annular dark field (HAADF)-scanning transmission electron microscopy (STEM) images and energy-dispersive X-ray spectroscopy (EDS) maps were acquired using an aberration-corrected JEM-ARM300F (JEOL Co. Ltd., Tokyo, Japan) operated at 80 kV. The steady-state surface photovoltage (SPV) measurement system includes computer, lock-in amplifier, monochromatic light and photovoltaic cell. The monochromatic light was provided by Xe lamp (300 W) and a double-prism monochromator. Femtosecond transient absorption (TA) spectroscopy was measured with pump pulse at 360 nm and probing with white light, the 360 nm pulse was produced by second-harmonic generation of the fundamental output of the Ti:sapphire regenerative amplifier (Coherent Legend Elite, 4 mJ, 25 fs, 1KHz).

Apparent Quantum Yield (AQY)

The apparent quantum yield (AQY) of ZnSe/CdS NTPs was measured under the monochromatic LED light sources (λ = 460 nm, 100 mW cm^{-2}) with the irradiation area of 2.0 × 1.2 cm^2. 344.8 μmol of H_2 was produced under 1 h irradiation for the ZnSe/CdS NTPs. The AQY was calculated as 20.8 % according to the following equation (S1):

$$AQY = \frac{N_e}{N_p} \times 100\% = \frac{10^9 \times \nu \times N_A \times K \times h \times c}{I \times A \times \lambda} \times 100\% \#(S1)$$

Where N_e is number of reacted electrons; N_p is number of incident photons; ν is reaction rate (mol s^{-1}); N_A is the Avogadro constant (6.022 × 10^{23} mol^{-1}); K is number of electrons transferred (K=2 for photocatalytic H_2 evolution); h is the Plank constant (6.626 × 10^{-34} J s); A is the irradiation area (m^2); I is the monochromatic light intensity (W m^{-2}); λ is the wavelength of the monochromatic light (nm); c is the speed of light (3 × 10^8 m s^{-1}).

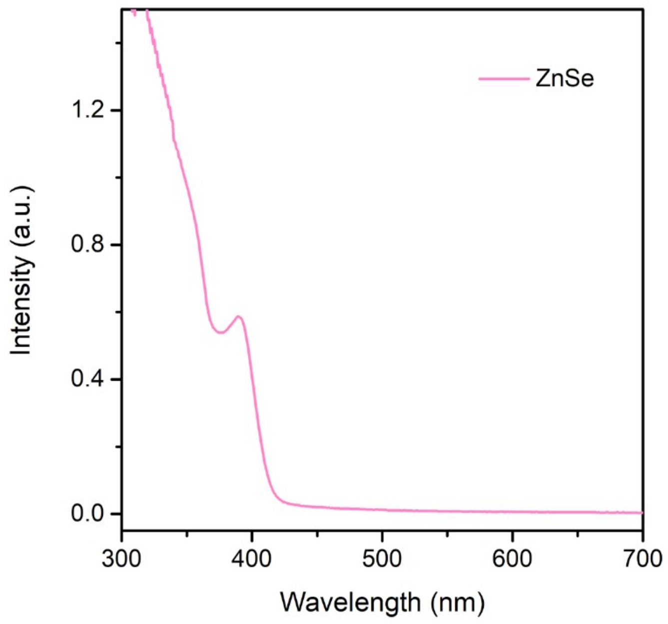

Fig. S1 The UV-vis absorption spectrum of ZnSe QDs.

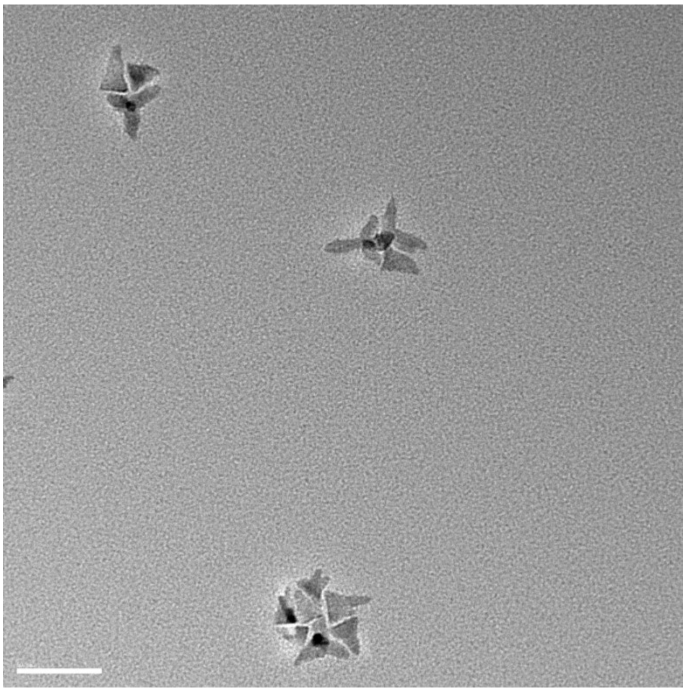

Fig. S2 The TEM images of thick ZnSe/CdS NTPs. Scale bar: 50 nm.

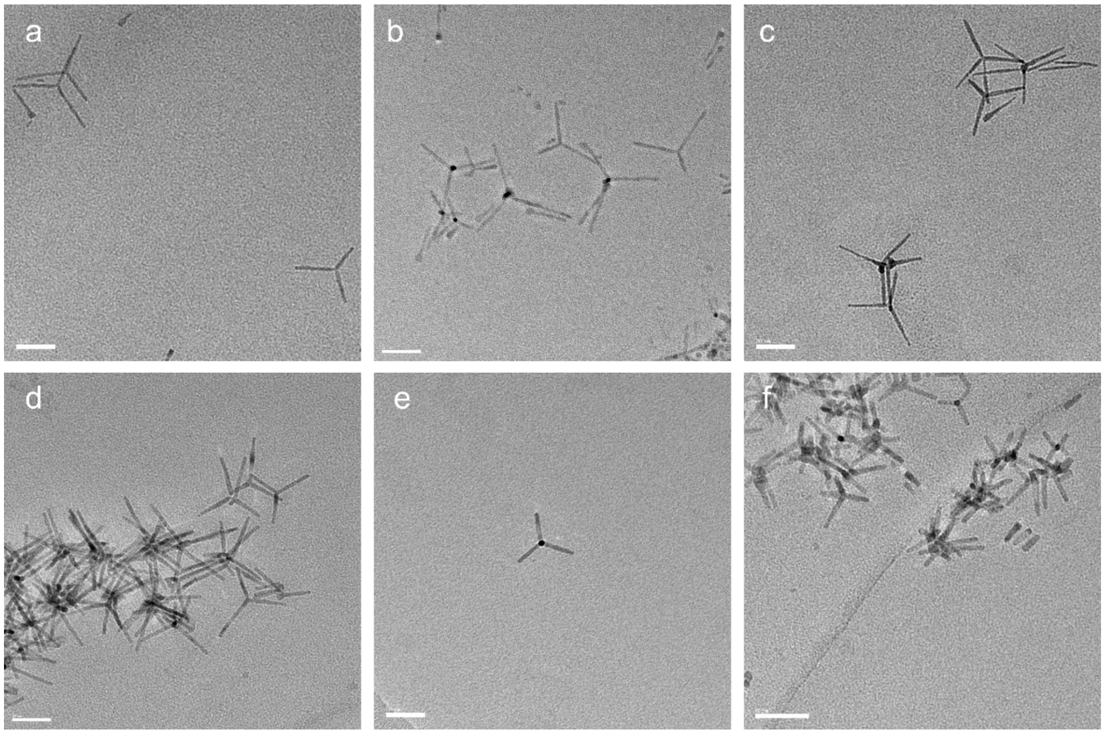

Fig. S3 The TEM images of (a) CdS NTPs and (b-f) $ZnSe_x$/CdS NTPs with different amounts of ZnSe seed during the synthetic process. The amount of ZnSe seed from b to f is 1.25×10^{-9} mol, 2.5×10^{-9} mol, 5.0×10^{-9} mol, 7.5×10^{-9} mol, and 10.0×10^{-9} mol, respectively. Scale bar: 50 nm.

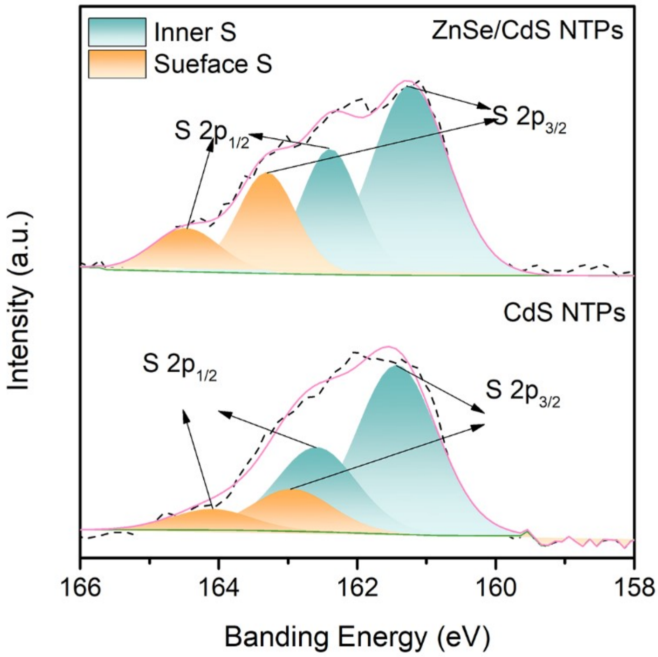

Fig. S4 High-resolution XPS analysis of S 2p spectra for CdS and ZnSe/CdS NTPs.

Table S1 Inductively coupled plasma-mass spectrometry (ICP-MS) results of ZnSe/CdS NTPs.

Elements	**Dilution Multiple[a]**	**Raw data (mg/L)**	**Element content (mg/g)**	**Element content (wt%)**
Cd	50	7.49	394.0	39.4%
S	50	2.37	124.4	12.4%
Se	1	7.28	7.66	0.8%
Zn	1	2.06	2.17	0.2%

[a]: The solution was diluted by 50 times for the concentration test of Cd and S, while Zn and Se were measured at the original solution.

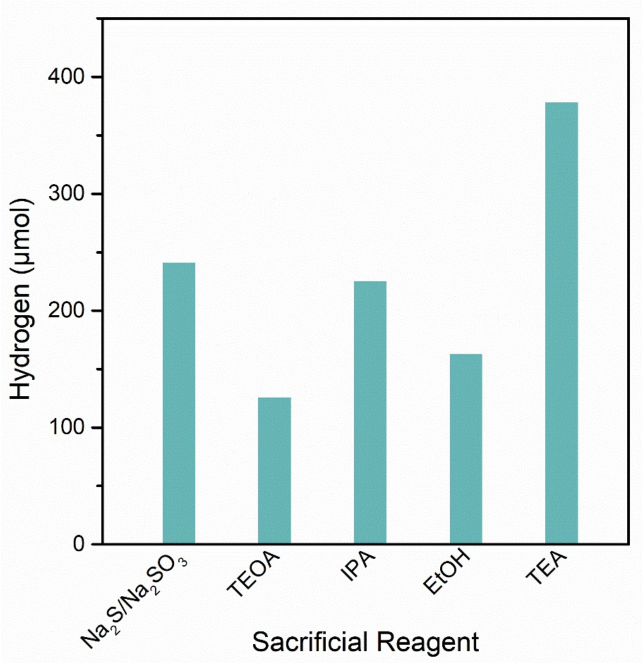

Fig. S5 Photocatalytic H_2 evolution for ZnSe/CdS NTPs under different sacrificial reagents within 4 h irradiation. The ZnSe/CdS NTPs would produce H2 efficiently under various sacrificial reagents. While the TEA gives the highest hydrogen production amount. Therefore, TEA serves as the sacrificial reagents throughout the entire reaction process.

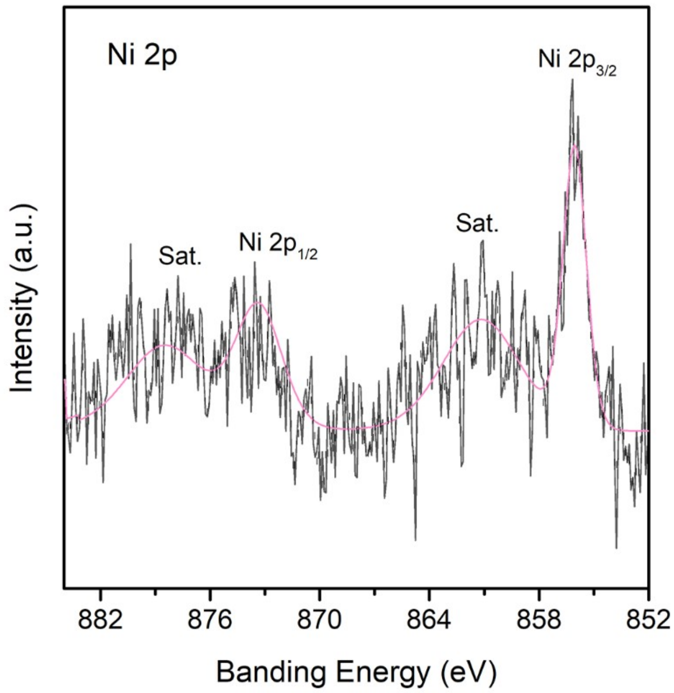

Fig. S6 High-resolution XPS analysis of Ni 2p spectra for ZnSe/CdS NTPs.

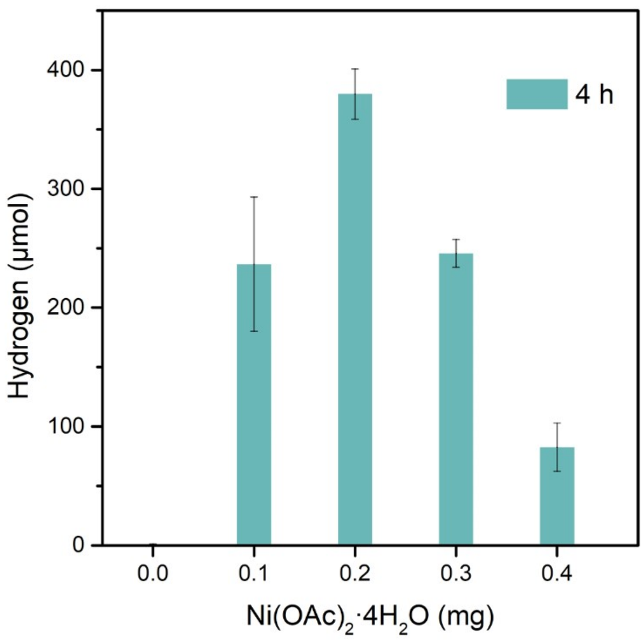

Fig. S7 Comparison of H_2 evolution for ZnSe/CdS NTPs under different amount of $Ni(CH_3COO)_2 \cdot 4 \cdot H_2O$. Error bars represent the mean ± s.d. of multiple independent experiments.

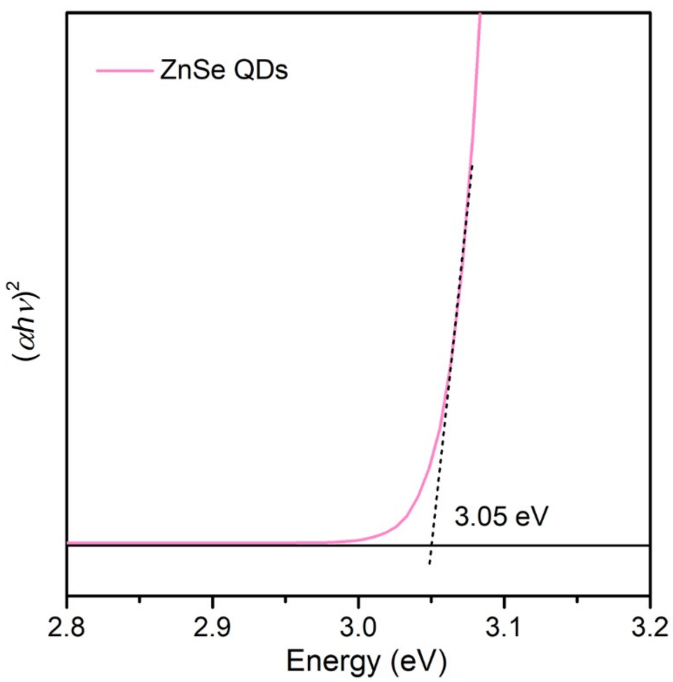

Fig. S8 Tauc plots of ZnSe QDs.

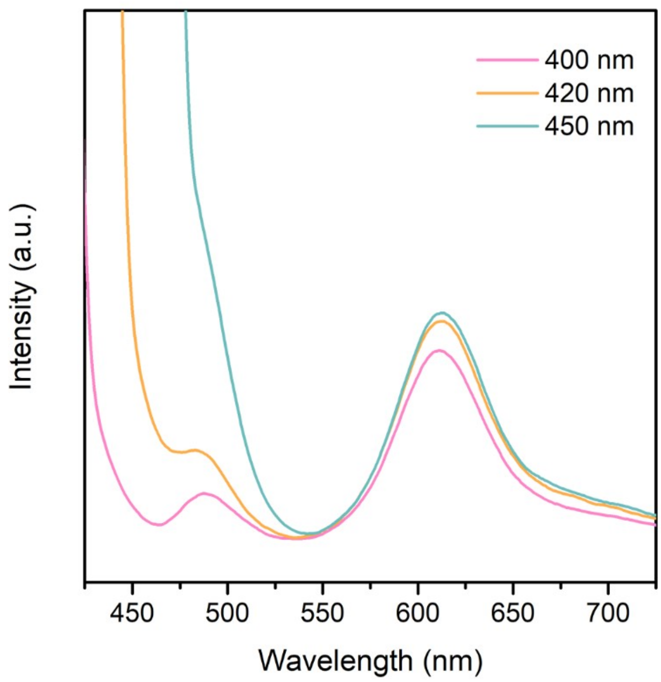

Fig. S9 Photoluminescence (PL) spectra of ZnSe/CdS NTPs with different excitation wavelength.

Table S2 Comparison of photocatalytic H_2 evolution with reported colloidal nanocrystals based systems.

Photocatalyst	Co-catalyst	Light Source	Donor	Rate of H_2 Evolution[a] (μmol h^{-1} mg^{-1})	TON	AQY (%)	Time (h)	Refer
Ni-CdS NRs	None	447 nm	EtOH	63	None	53	4	[1]
CdSe/CdS	None	>420 nm	TEOA	16.03	None	None	4	[2]
CdS QDs	Co^{2+}	>420 nm	Na_2SO_3	----	29000	None	88	[3]
CdS QDs	Ni^{2+}	>400 nm	Glycerol	74.6	38405	None	20	[4]
CdS QDs	Cobaloxime	>420 nm	TEOA	2.3[b]	171	None	15	[5]
CdS QDs	None	>400 nm	$N_2H_4 \cdot H_2O$	33	14.16	None	4	[6]
NiS_2-C/CdS NSs	None	>420 nm	Na_2S and Na_2SO_3	92.19	None	None	5	[7]
Pt_{SA+C}/CdS	None	>420 nm	Lactic acid	80.4	58818	None	6	[8]
CdS@MoS_2/Ti_3C_2	None	420 nm	Lactic acid	14.88	None	None	78	[9]
CdS/ZnS-ReS_2	None	≥420 nm	Na_2S and Na_2SO_3	10.72	None	1.7	2	[10]
CdS/TiO_2	None	300 W Xe lamp	Na_2S and Na_2SO_3	21.4	None	None	4	[11]
NiS/CdS NPs	None	≥420 nm	Lactic acid	7.49	None	None	16	[12]
CoP QDs/CdS NRs	None	>400 nm	Lactic acid	104.95	None	32.16	12	[13]
Co_3N/CdS	None	>420 nm	Na_2S and Na_2SO_3	137.33	None	14.9	48	[14]
CdS	None	≥420 nm	Na_2S and Na_2SO_3	9.58	None	4.12	15	[15]
CdS/Pt/Mo_2C	None	>400 nm	Na_2S and Na_2SO_3	1.83	None	9.39	20	[16]
ZnSe/CdS NTPs	Ni^{2+}	460 nm	TEA	142.89	1.71×10^8	20.8	100	This work

[a]: All units are converted to μmol h^{-1} mg^{-1} according to the results provided in the articles.

[b]: The data is calculated according to the data in the article.

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