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Supporting Information

Direct synthesis of sulfide capped CdS and CdS/ZnS colloidal nanocrystals for efficient hydrogen evolution under visible light irradiation

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1. Materials.

CdS (98%) bulk material and terephthalic acid (98%) was obtained from Alfa Aesar. $Cd(NO_3)_2\cdot 4H_2O$ (99%), $Na_2S\cdot 9H_2O$ (98%), $ZnAc_2\cdot 7H_2O$ (99%), $NiCl_2\cdot 6H_2O$ (97%), isopropanol (IPA, 99.7%), acetone (99.5%) and others were obtained from a variety of sources. Reagents were all used as received. Deionized water with resistivity of 18.2 MΩ·cm (Barnstead 3750) was used throughout the experiment.

2. Characterization.

High-resolution transmission electron microscopy (HRTEM) and EDS element mapping was performed by JEM 2100F. XRD spectra were taken on a Bruker D8 Focus under Cu-Kα radiation at (λ = 1.54056 Å). UV-Vis absorption spectra were recorded with Shimadzu 1601PC spectrophotometer. UV-Vis diffuse reflectance spectra (DRS) were recorded by Cary 5000 UV-visible-NIR spectrophotometer employing a lab-sphere diffuse reflectance accessory. Elemental analysis was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian 710-OES, USA). XPS measurement was performed on an ESCALAB 250 spectrophotometer with Al-Kα radiation. The binding energy scale was calibrated using the C 1s peak at 284.6 eV. pH value was measured with a Model pHS-3C meter (Mettler Toledo FE20). Zeta potential value was measured with Zetasizer Nano-ZS ZEN3600 (Malvern Instruments). Steady state emission spectra were recorded by the Edinburgh instrument FLS-920 with a built-in emission correction, the excitation wavelength is 420 nm. Time-resolved emission measurements were carried out on Edinburgh instrument FLS-920 with time-correlated single photon counting (TCSPC) technology, the excitation wavelength is 406 nm and the detection wavelength is 480 nm for the bandgap emission of NCs.

3. Synthesis of CdS (1:1), CdS-S^{2-} and CdS/ZnS-S^{2-} NCs.

The synthesis of CdS, CdS-S^{2-} and CdS/ZnS-S^{2-} NCs were derived from the literature report with some modification.[1] For synthesis of CdS/ZnS-S^{2-} NCs, 154 mg (0.5 mmol) $Cd(NO_3)_2{\cdot}4H_2O$ was added into 55 mL H_2O. Under an inertia environment and continuous stirring, the solution was heated to 80 °C. Then, a freshly prepared Na_2S solution (5 mL water containing 600 mg (2.5 mmol) $Na_2S{\cdot}9H_2O$) was quickly injected to the above solution and instantly orange-yellow precipitates were obtained immediately. The reaction was held at 80 °C for 2 h with stirring and refluxing. Then Zn^{2+} precursor (5 mL water contains 55 mg (0.25 mmol) $Zn(CH_3COO)_2{\cdot}2H_2O$) was dropped into the reaction solution slowly within about 10 min. The mixture was maintained at 80 ºC for another 1 h. The obtained NCs was collected by centrifugation, washed with ethanol/water to get rid of any unreacted ions, and finally dispersed in water by ultrasound. The concentration of NCs was then adjusted to 1 mg/mL.

For synthesis of CdS-S^{2-} NCs, the process was similar to CdS/ZnS-S^{2-} NCs above with continuous heating of 3 h at 80 ºC without the additional introduction of Zn^{2+}. Moreover, we also synthesized the CdS (1:1) NCs with the same stoichiometric ratio of Cd^{2+} and S^{2-} as 154 mg $Cd(NO_3)_2{\cdot}4H_2O$ (0.5 mmol) and 120 mg Na_2S (0.5 mmol). The obtained NCs were purified by the same procedure above.

We also synthesized other CdS NCs and CdS/ZnS NCs of different stoichiometric ratio of precursors, and they are named as the stoichiometric ratio for Cd:S:Zn. For example CdS/ZnS (1:5:1) means 154 mg $Cd(NO_3)_2{\cdot}4H_2O$ (0.5 mmol), 600 mg Na_2S (2.5 mmol) and 110 mg $ZnAc_2{\cdot}7H_2O$ (0.5 mmol) was added during synthesis. The other procedure for synthesis of these NCs was the same as the description above.

4. Photocatalytic hydrogen evolution experiment.

For a typical hydrogen evolution experiment, 6 mL solution with H_2O/IPA (V/V = 1:1) contains 0.5 mg NCs, and 0.25 mg $NiCl_2·6H_2O$ were added into a Schlenk tube. The pH of the mixed solution was adjusted to 6 by HCl and NaOH aqueous solution. After deoxygenation with argon for 20 min, the system was irradiated to 4 pcs of 465 nm LED bulbs (4 × 3 W, about 160 mW/cm^2; Tao Yuan, China) under constant stirring and fan cooling. The generated amount of H_2 was quantitatively measured by drainage gas-collecting method using a gas-tight acid burette, and then confirmed by GC analysis (Shimadzu GC-2014C) using argon as the carrier gas with a molecular sieve column (5 Å) and a thermal conductivity detector. For each condition of hydrogen evolution experiment, three or more independence measurements were operated, which are shown as the error bar in the graphs.

5. Electrodes preparation of CdS (1:1), CdS-S^{2-} and CdS/ZnS-S^{2-} NCs.

The CdS (1:1), CdS-S^{2-} and CdS/ZnS-S^{2-} NCs electrodes are prepared by the methods reported before with small modification.[2, 3] Briefly, the electrode was prepared by coating on indium tin oxide (ITO) conductor glass with viscous pastes of CdS (1:1), CdS-S^{2-} or CdS/ZnS-S^{2-} NCs by doctor blade method. The pastes were prepared using 3 mg of NCs, 3 mg of ethyl cellulose, 2 mg of lauric acid and 25 mg terpineol. The coated films were subsequently annealed at 200 °C for 1 h to improve their adhesion. The exposed area of the electrode was confined to 1 cm^2.

6. Measurement of internal quantum efficiency.

To measure the internal quantum efficiency, the absorbed light intensity was decreased compared to the normal photocatalytic experiment. With monochromatic LED light source (λ = 465 nm), the accurate illumination power for a certain place (1 cm^2) was measured using a digital photodiode power meter (Newport, model 842-PE). Then photocatalytic hydrogen evolution was performed in a specially-made spectro-cell with a total volume of 7 mL and a path-length of 1 cm. The cuvette was filled with 2.0 mL solution of H_2O/IPA (V/V = 1:1), containing CdS/ZnS NCs (0.1 mg), $NiCl_2·6H_2O$ (0.05 mg) under pH 6. After sealing and deoxygenation with argon for 15 min, 300 μL CH_4 was added into the spectro-cell as an internal standard for H_2 detection. Under constant stirring, the solution was irradiated at the same place and area (1 cm^2) for power measurement. The number of absorbed photons was calculated from the illumination power and absorbance of the reaction solution; the number of generated H_2 was obtained by GC.

Based on the measurement of three independent experiments, the illumination power was 58.0 ± 1 mW/cm^2, the absorbance of the reaction solution in 465 nm was 0.186 ± 0.003, the hydrogen evolution for 30 min is 846 ± 37 μL. The internal quantum efficiency can be calculated as follow[4]:

H_2 generated in 30 min: 846 μL

Molar amount of H_2 in 30 min: 3.78×10^{-5} mol

$k = 3.78 \times 10^{-5}$ mol / 1800 s= 2.10×10^{-8} mol/s

$T_a = 1 - 10^{-abs} = 0.348$

$q_p = T_a P\lambda / ch = 0.348 \times [(0.058 \text{ J/s}) \times (465 \times 10^{-9} \text{ m})] / [(3.0 \times 10^8 \text{ m/s}) \times (6.626 \times 10^{-34} \text{ J/s})] = 4.72 \times 10^{16} \text{ s}^{-1} = 7.84 \times 10^{-8}$ mol/s

$\Phi_{H2} = 2k/q_p = 2 \times (2.10 \times 10^{-8} \text{ mol/s}) / (7.84 \times 10^{-8} \text{ mol/s}) = 53.6\%$

7. Colloidal solution stability test for CdS/ZnS-S^{2-} NCs.

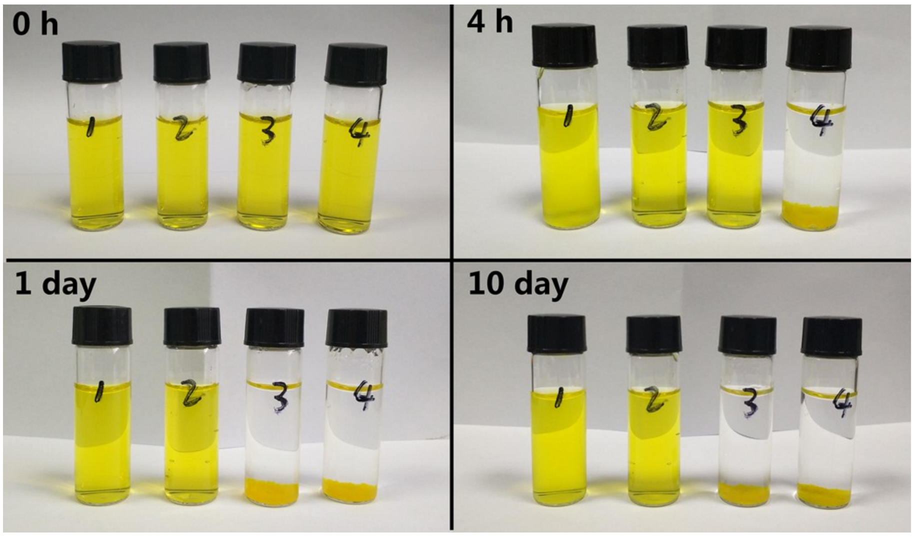

Figure S1. Stability of CdS/ZnS-S^{2-} NCs colloidal solution stored under different condition: 1. NCs stored in refrigerator (also in dark); 2. NCs stored in dark at room temperature; 3. NCs stored under incident room light at room temperature; 4. NCs stored under lamp irradiation at room temperature.

8. Statistic of size distribution for CdS-S^{2-} and CdS/ZnS-S^{2-} NCs.

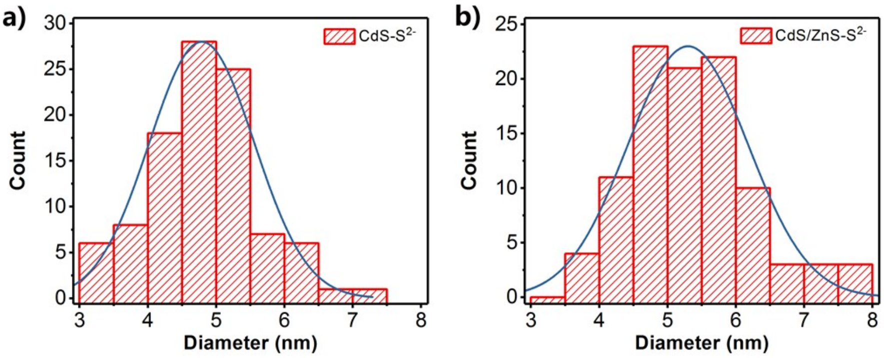

Figure S2. Statistic of size distribution for CdS-S^{2-} and CdS/ZnS-S^{2-} NCs. We do not make the analysis for the CdS (1:1) NCs due to its serious agglomeration.

9. HRTEM graph for CdS (1:1) NCs.

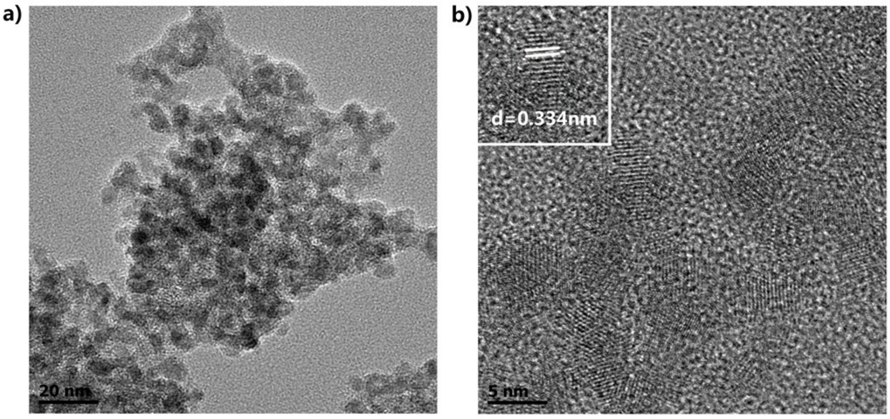

Figure S3. HRTEM graph of CdS (1:1) NCs, the inner graph show the interplanar spacing of CdS (1:1) NCs.

10. EDS elemental mapping for CdS/ZnS-S^{2-} NCs.

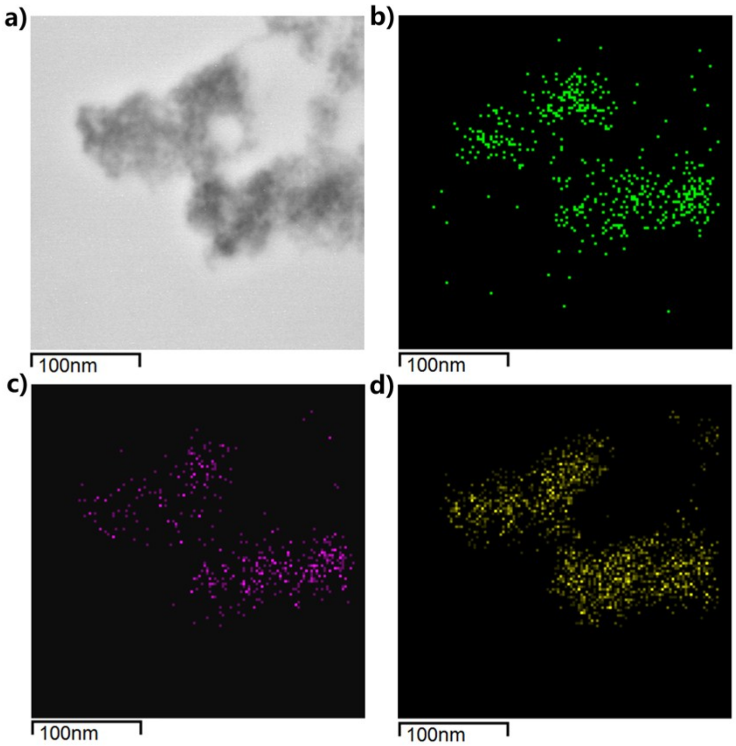

Figure S4. TEM EDS mapping of CdS/ZnS-S^{2-} NCs: a) overall morphology, b) Cd, c) Zn, d) S.

11. ICP-OES results for CdS (1:1), CdS-S^{2-} and CdS/ZnS-S^{2-} NCs.

Table S1. ICP-OES data for CdS (1:1), CdS-S^{2-} and CdS/ZnS-S^{2-} NCs.

	Cd w%	S w%	Zn w%	S/(Cd+Zn) atomic ratio
CdS	74.69	20.55	/	0.965
CdS-S^{2-}	72.40	22.53	/	1.091
CdS/ZnS-S^{2-}	54.37	24.97	15.42	1.082

12. XPS results for CdS (1:1), CdS-S^{2-} and CdS/ZnS-S^{2-} NCs.

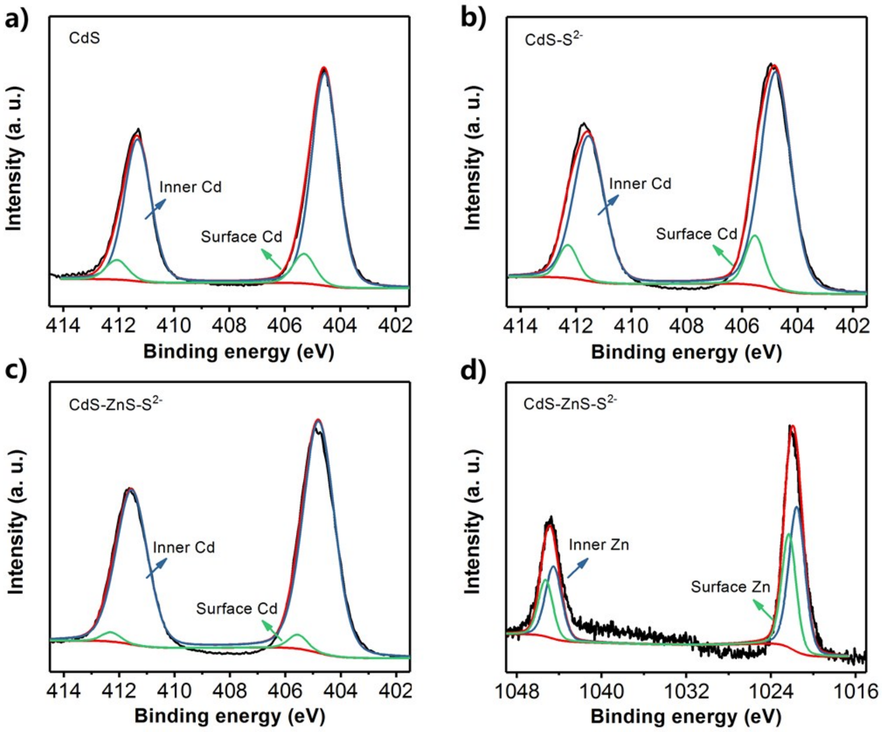

Figure S5. Fine XPS spectra of Cd and Zn from CdS (1:1), CdS-S^{2-} and CdS-ZnS-S^{2-} NCs. Black lines represent raw data; red lines represent the sum of the fitting XPS data; blue lines are the Gaussian curve fitting of bulk (inner) atoms and green lines are the Gaussian curve fitting of surface atoms.

Table S2. XPS results for CdS (1:1), CdS-S^{2-} and CdS/ZnS-S^{2-} NCs. Atoms ratio of Cd, S and Zn are calculated from integrated peak area fitted from Cd, S and Zn fine signals in XPS data.

	C at%	**O at%**	**Cd at%**	**S at%**	**Zn at%**
CdS	51.05	17.7	16.35	14.91	/
CdS-S^{2-}	41.79	16.04	22.12	22.19	/
CdS-ZnS-S^{2-}	49.82	17.08	11.85	16.77	4.47

Table S3. Detailed XPS peak analysis. Raw XPS data was fitted with Gaussian functions as shown in Figure 3 and S5. In each sample, Inn represents contributions to signals from inner atoms of Cd, S or Zn (also represented by the blue fitting curves), while Surf. represents contributions to signals from surface atoms (the green fitting curves).

Sample		**Peak**	**Binding Energy (eV)**	**FWHM**	**Area**	**%Conc.**
CdS	C	1s	284.60	1.69		
	Inn. Cd	3d 5/2	404.57	1.13	86577	**89.67**
		3d 3/2	411.32	1.13	57718	
	Surf. Cd	3d 5/2	405.32	0.93	9977	**10.33**
		3d 3/2	412.01	0.93	6651	
	Inn. S	2p 3/2	160.84	1.10	6664	**89.27**
		2p 1/2	162.04	1.10	3332	
	Surf. S	2p 3/2	161.56	1.01	801	**10.73**
		2p 1/2	162.76	1.01	400.1	
CdS-S^{2-}	C	1s	284.60	1.78		
	Inn. Cd	3d 5/2	404.79	1.29	180209	**87.55**
		3d 3/2	411.54	1.29	120139	
	Surf. Cd	3d 5/2	405.54	0.80	25630	**12.45**
		3d 3/2	412.29	0.80	17086	
	Inn. S	2p 3/2	161.07	1.19	14043	**74.20**
		2p 1/2	162.27	1.19	7022	
	Surf. S	2p 3/2	161.82	1.01	4883	**25.80**
		2p 1/2	163.02	1.01	2441	
CdS-ZnS -S^{2-}	C	1s	284.60	2.18		
	Inn. Cd	3d 5/2	404.80	1.34	199493	**96.52**
		3d 3/2	411.55	1.34	132995	
	Surf. Cd	3d 5/2	405.55	0.80	7194	**3.48**
		3d 3/2	412.30	0.80	4796	
	Inn. S	2p 3/2	160.72	1.24	10446	**75.42**
		2p 1/2	161.92	1.24	5223	
	Surf. S	2p 3/2	161.47	1.17	3404	**24.58**
		2p 1/2	162.67	1.17	1702	
	Inn. Zn	2p 3/2	1021.56	1.80	26184	**58.79**
		2p 1/2	1044.53	1.80	13092	
	Surf. Zn	2p 3/2	1022.31	1.61	18355	**41.21**
		2p 1/2	1045.28	1.61	9178	

Table S4. XPS Compositions of CdS (1:1), CdS-S^{2-} and CdS/ZnS-S^{2-} NCs on the surface.

	Cd$_{surf}$	**S$_{surf}$**	**Zn$_{surf}$**	Surface %

	at%	**at%**	**at%**	Cd	S	Zn
CdS	1.689	1.600	\	51.35	48.65	\
CdS-S^{2-}	2.754	5.725	\	32.48	67.52	\
CdS-ZnS-S^{2-}	0.412	4.122	1.842	6.46	64.65	28.89

13. Optimization of reaction condition for hydrogen evolution by CdS/ZnS-S^{2-} NCs.

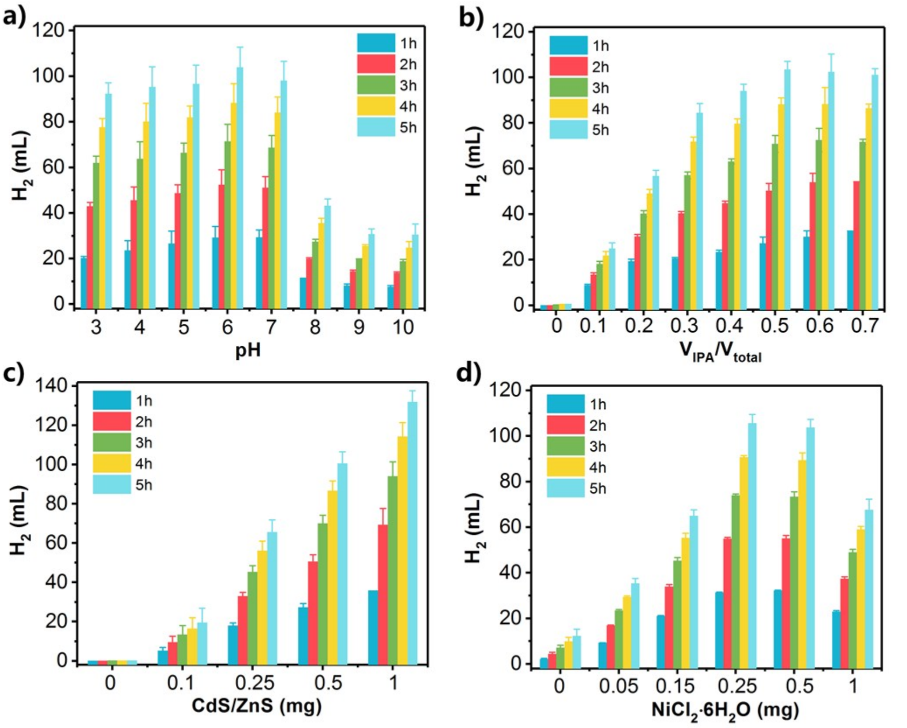

Figure S6. Photocatalytic performance of CdS/ZnS-S^{2-} NCs: (a) H_2 evolution from 6 mL solution of H_2O/IPA (V/V = 1:1), containing 0.25 mg $NiCl_2 \cdot 6H_2O$ and 0.5 mg CdS/ZnS-S^{2-} NCs under different pH; (b) H_2 evolution from 6 mL solution of different volume of IPA/H_2O containing 0.25 mg $NiCl_2 \cdot 6H_2O$ and 0.5 mg CdS/ZnS-S^{2-} NCs under pH 6; (c) H_2 evolution from 6 mL solution of H_2O/IPA (V/V = 1:1) containing 0.25 mg $NiCl_2 \cdot 6H_2O$ and different CdS/ZnS-S^{2-} NCs under pH 6; (d) H_2 evolution from 6 mL solution of H_2O/IPA (V/V = 1:1) containing different $NiCl_2 \cdot 6H_2O$ and 0.5 mg CdS/ZnS-S^{2-} NCs under pH 6. Light source: 465 nm LED (ca. 160 mW/cm^2)

14. Hydrogen evolution by commercial bulk CdS.

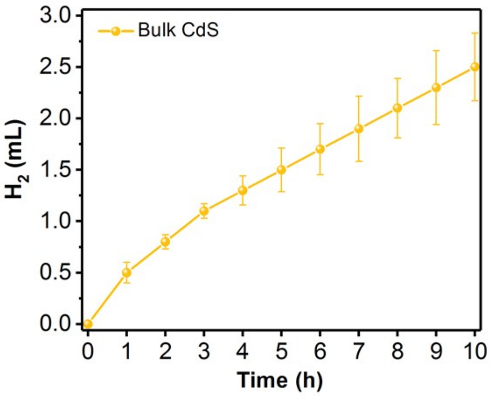

Figure S7. Photocatalytic hydrogen evolution of Ni^{2+} and commercial bulk CdS from 6 mL solution of H_2O/IPA (V/V = 1:1) containing 0.25 mg $NiCl_2 \cdot 6H_2O$ and 0.5 mg bulk CdS under pH 6. The commercial bulk CdS (98%) was obtained from Alfa Aesar, and dispersed in water by ultrasound for 30 min. Light source: 465 nm LED (ca. 160 mW/cm^2)

15. Photocorrosion analysis for CdS/ZnS-S^{2-} NCs during hydrogen evolution.

Table S5. ICP-OES data for supernatant and precipitate of photocatalytic hydrogen evolution system before and after 10 h irradiation. Light source: 465 nm LED (ca. 160 mW/cm^2). Cd(Zn) % means the ratio of Cd(Zn) detected in supernatant to the total amount of Cd(Zn) in both supernatant and precipitate. The result show that after 10 h irradiation, about 3% of Cd and Zn in the system was detected in the supernatant, indicating that only a little photocorrosion has happened for CdS/ZnS-S^{2-} NCs.

	Cd / μg	Zn / μg	S / μg	Cd %	Zn %
Supernatant without *hv*	0.260	0.342	4.174	0.05	0.20
precipitate without *hv*	490	174	168		
Supernatant after *hv*	15.2	4.64	13.4	3.36	2.98
precipitate after *hv*	436	151	143		

16. Hydrogen evolution for NCs of different ratio of precursor.

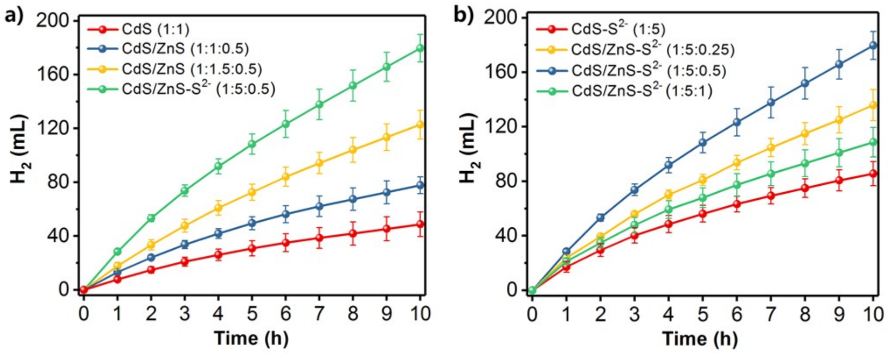

Figure S8. Photocatalytic hydrogen evolution of Ni^{2+} and different NCs from 6 mL solution of H_2O/IPA (V/V = 1:1) containing 0.25 mg $NiCl_2 \cdot 6H_2O$ and 0.5 mg CdS/ZnS-S^{2-} NCs under pH 6. The number in the bracket means the precursor ratio of Cd: S: Zn during synthesis. (a) Comparison of CdS (1:1) NCs and different ratio S precursor of CdS/ZnS NCs. (b) Comparison of CdS (1:1) NCs and different ratio Zn precursor of CdS/ZnS NCs. Light source: 465 nm LED (ca. 160 mW/cm^2).

17. Fitting results and average lifetime calculation of PL decay for CdS (1:1), CdS-S^{2-} and CdS/ZnS-S^{2-} NCs.

Table S6. Kinetic analyses of photoluminescence decay for CdS (1:1), CdS-S^{2-} and CdS/ZnS-S^{2-} NCs.

	τ_1(ns)	B_1	τ_2(ns)	B_2	τ_3(ns)	B_3	τ_{avg}(ns)
CdS	0.8533	2316	4.328	723.9	20.33	65.99	6.59
CdS-S^{2-}	0.7267	1994	3.445	1223	14.08	156.5	5.92
CdS/ZnS-S^{2-}	1.319	2422	5.551	790.7	48.72	53.08	15.2

18. Electrochemical impedance spectra for CdS (1:1), CdS-S^{2-} and CdS/ZnS-S^{2-} NCs.

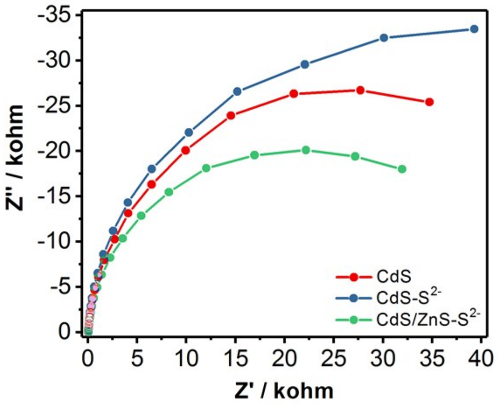

Figure S9. Electrochemical impedance spectra for CdS (1:1), CdS-S^{2-} and CdS/ZnS-S^{2-} NCs in 0.1 M Na_2SO_4 aqueous solution under irradiation of Xe lamp. The frequency range is from 50k Hz to 0.1 Hz with perturbation at 10 mV.

19. Steady state and time resolved photoluminescence spectra for CdS/ZnS-S^{2-} NCs after introduction of Ni^{2+}.

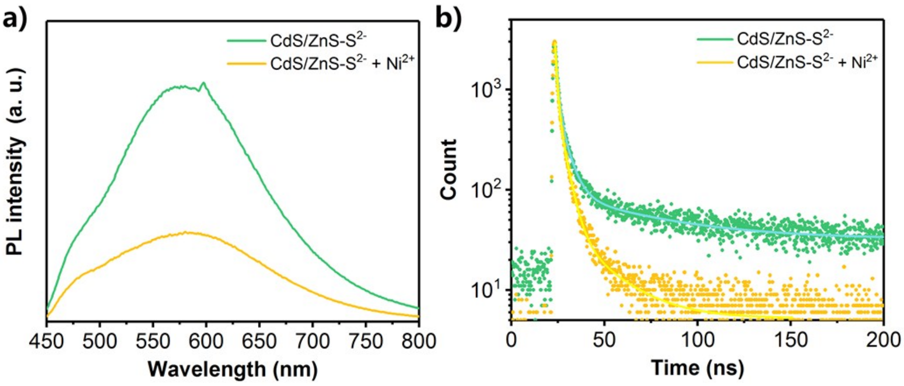

Figure S10. (a) Photoluminescence spectra and (b) corresponding photoluminescence decay for CdS/ZnS-S^{2-} NCs with and without Ni^{2+}.

Table S7. Kinetic analyses of photoluminescence decay for CdS/ZnS-S^{2-} NCs and CdS/ZnS-S^{2-} NCs with Ni^{2+}.

	τ_1(ns)	B_1	τ_2(ns)	B_2	τ_3(ns)	B_3	τ_{avg}(ns)
CdS-ZnS-S^{2-}	1.1176	2600	4.928	745.6	48.62	62.54	17.3
CdS-ZnS-S^{2-} + Ni^{2+}	0.9148	2537	3.900	860.5	20.60	44.39	5.17

20. ·OH radical detection in the NCs photocatalytic system.

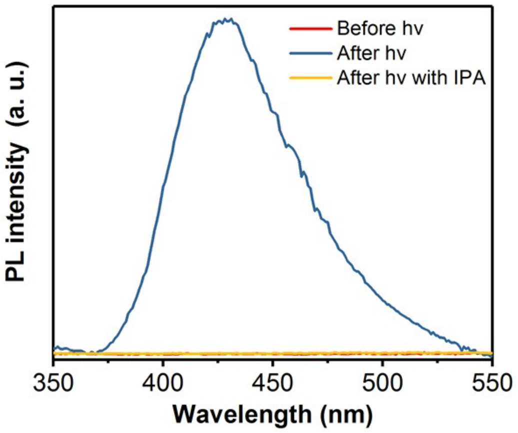

Figure S11. ·OH trapping emission spectra in the solution of CdS/ZnS-S^{2-} NCs (0.1 mg/mL), Ni^{2+} (2×10^{-4} M), terephthalic acid (5×10^{-4} M) and NaOH (1×10^{-3} M). pH before and after irradiation was around 6, Light source: 465 nm LED (ca. 160 mW/cm^2), 1 h for irradiation. For PL detection, the excitation wavelength was 315 nm.

Typically, hydroxide radicals yielded by photogenerated holes could combine with terephthalic acid, and a strong photoluminescence peak at 426 nm appears accordingly.[5, 6] In our system with CdS/ZnS-S^{2-} NCs, this peak could be obviously observed after light irradiation in the absence of IPA (Figure S11), which confirms the generation of hydroxide radicals by photogenerated holes from NCs. After introduction of IPA, the characteristic emission peak at 426 nm disappeared completely, indicating that hydroxide radicals are consumed in priority by IPA. It has demonstrated the effectiveness of IPA as hole scavenger in our system, which agrees well with our expectation and further confirms our proposed mechanism.

21. References.

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