

Supplementary Information for

Surface Stoichiometry Manipulation Enhances Solar Hydrogen

Evolution of CdSe Quantum Dots

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1. Apparent quantum yield (Φ) measurement

Quantum yield was one of most important parameters to judge the photocatalytic activity of an artificial photosynthetic system.^{1,2} For photocatalytic hydrogen production, the apparent quantum yield (AQY) was defined as the following equation (S1): the number of evolved hydrogen atom in H₂ gas divided by the number of incident photons. Light-driven H₂ reduction was performed in a standard spectro-cell with a total volume of 4 mL and a path-length of 1 cm. The cuvette was filled with 3.0 mL reaction solution of IPA-H₂O (V:V = 1:1) at pH 5.0 \pm 0.2 in the presence of NiCl₂·6H₂O (0.7×10^{-4} mol L⁻¹), and CdSe with surface Se ratio of ~4.9% (5.0×10^{-6} mol L⁻¹). The apparent quantum yield (Φ) was measured using LED as light source ($\lambda > 410$ nm; light intensity: ~89 mW cm⁻² at spectro-cell surface) with constant stirring by a magnetic stirrer.

$$\text{AQY} = \frac{2 \times \text{Number of evolved H}_2 \text{ molecules}}{\text{Number of incident photons}} \times 100\%$$

(S1)

2. DLS measurements

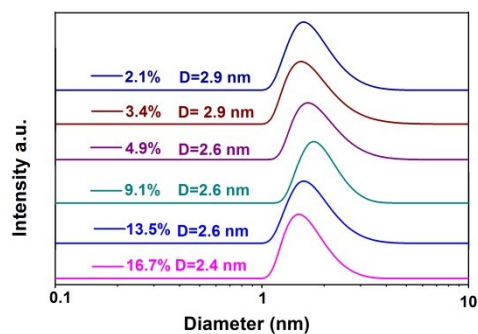


Figure S1 The size distribution of QDs with different surface stoichiometry characterized by DLS under the same conditions, see corresponding data in **Table S1**.

Table S1. Size distribution of CdSe QDs with different surface Se.

Surface Se%	16.7	13.5	9.1	4.9	3.4	2.1
D ^[a] (nm)	2.4	2.6	2.6	2.6	2.9	2.9
D ^[b] (nm)	1.7	1.9	1.9	1.9	1.9	1.9

[a] is the size distribution from DLS; [b] is the diameter calculated according to the first excitonic peak at UV-vis spectra.

3. ICP-AES measurements

Table S2. The chemical composition of CdSe QDs characterized by ICP-AES.

Cd/Se ^a	n (Cd)	n (Se)	n (S)	Cd/Se	Cd%	Se%	S%
2	1.21	0.60	1.00	2.01	44.01	15.38	10.32
3	0.32	0.09	0.34	3.46	41.55	8.44	12.44
4	0.97	0.25	1.02	3.91	42.06	7.55	12.63
6	1.02	0.16	1.06	6.56	48.29	5.17	14.25
7	0.53	0.07	0.60	7.29	46.52	4.48	14.95
8	1.89	0.24	2.48	7.77	39.36	3.56	14.75

^aThe molar ratio of Cd and Se precursors applied for the synthesis of QDs with different surface stoichiometry.

4. XPS analysis

Table S3. Detailed XPS peak analysis data.

Surface Se %	peak		Binding Energy[eV]	FWHM	Area	%Conc.	
16.7	Cd 3d 5/2	1	404.75	1.45	130922.2	34.74	
		2	405.16	1.03	90365.8	23.98	
	Cd 3d 3/2	1	411.49	1.66	88660.7	23.53	
		2	411.91	1.03	66907.8	17.75	
	Se 3d 5/2	1	404.73	1.2	4442.7	30.67	
		2	53.58	1.16	4249.9	29.33	
	Se 3d 3/2	1	54.15	1.06	2961.8	20.44	
		2	54.9	1.54	2833.3	19.56	
	S 2p 3/2	1	159.66	2.17	12970.2	32.84	
		2	161.3	1.97	10723.9	27.16	
	S 2p 1/2	1	162.31	2.07	8646.8	21.90	
		2	163.84	4.51	7149.3	18.10	
	13.5	Cd 3d 5/2	1	404.73	1.35	141042	35.25
			2	405.3	1.16	95084.5	23.77
Cd 3d 3/2		1	411.41	1.38	99292.1	24.82	
		2	412	1.07	64677.9	16.17	
Se 3d 5/2		1	52.87	1.2	3519.7	33.93	
		2	53.68	1.17	2703.4	26.06	
Se 3d 3/2		1	54.3	1.3	2346.5	22.62	
		2	55.21	1.35	1802.3	17.38	
S 2p 3/2		1	159.95	2.89	12381.5	31.41	
		2	161.25	1.77	11269.7	28.59	
S 2p 1/2		1	162.39	1.63	8254.4	20.94	
		2	163.26	3.67	7513.1	19.06	
9.1		Cd 3d 5/2	1	404.79	1.29	126521.3	40.47

		2	405.42	1.11	94617.2	30.26
		1	411.51	1.34	84543.4	27.04
	Cd 3d 3/2	2	412	1.11	6979.8	2.23
		1	53.04	1.46	2772.7	32.88
	Se 3d 5/2	2	53.72	1.38	2287.4	27.12
		1	54.62	1.35	1848.4	21.92
	Se 3d 3/2	2	55.62	1.35	1524.9	18.08
		1	160.9	3.74	15847.5	40.79
	S 2p 3/2	2	161.39	2.15	7465.2	19.21
		1	162.39	2.44	10564.99	27.19
	S 2p 1/2	2	163.11	3.34	4976.8	12.81
		1	404.69	1.66	157959.7	30.95
	Cd 3d 5/2	2	405.26	1.14	140438.8	27.52
		1	411.46	1.78	117039.9	22.93
	Cd 3d 3/2	2	411.98	1.15	94926.2	18.60
		1	52.9	1.28	2367.9	35.16
	Se 3d 5/2	2	53.5	1.21	1673.3	24.84
4.9		1	54.02	0.94	1578.6	23.44
	Se 3d 3/2	2	54.95	1.4	1115.6	16.56
		1	160.43	2.56	16643.6	35.91
	S 2p 3/2	2	161.22	1.4	12363.2	26.68
		1	162.1	1.24	9095.7	19.63
	S 2p 1/2	2	162.94	1.56	8242.1	17.78
		1	404.69	1.37	109060.6	23.44
	Cd 3d 5/2	2	405.21	1.08	164984	35.46
		1	411.51	1.41	99061.5	21.29
3.4	Cd 3d 3/2	2	411.98	1.03	92149.7	19.81
		1	53.12	1.44	2210.3	36.59
	Se 3d 5/2	2	53.52	0.94	1640.4	27.15

		1	54.12	0.65	1213.2	20.08
	Se 3d 3/2	2	54.64	0.66	977.3	16.18
		1	160.86	2.18	11550.2	25.98
	S 2p 3/2	2	161.54	1.34	16603	37.34
		1	162.17	1.07	7700.1	17.32
	S 2p 1/2	2	162.96	1.27	8612.2	19.37
		1	404.55	1.08	80369.9	23.39
	Cd 3d 5/2	2	405.09	1.12	123935	36.07
		1	411.27	1.05	57237.9	16.66
	Cd 3d 3/2	2	411.84	1.05	82070.7	23.88
		1	53.02	1.15	1645.4	35.85
	Se 3d 5/2	2	53.86	0.82	1006.3	21.93
2.1		1	54.39	1.27	1170.2	25.50
	Se 3d 3/2	2	54.98	1.5	767.3	16.72
		1	160.97	2.1	11668.2	30.72
	S 2p 3/2	2	161.63	1.5	11120.2	29.28
		1	162.36	1.38	7778.8	20.48
	S 2p 1/2	2	163.11	1.63	7413.4	19.52

Note: raw XPS data was fitted with Gaussian functions as shown in Figure 3 in the main text. In each sample, peak 1 indicated signals from inner atoms of Cd, S or Se (also represented by the blue dash fitting curves in Figure 3), while peak 2 represented contributions to signals from surface atoms (the red dash fitting curves).

Table S4. The amount of Ni species incorporated into QDs after irradiation determined by XPS.

Surface Se %	Atomic (%)						wt.(%)
	O1s	C1s	Cd3d	Ni2p	S2p	Se3d	
16.7	16.4	46.8	15.3	1.9	15.0	4.5	0.7
13.5	19.0	44.3	16.9	2.2	15.1	2.6	0.7
9.1	20.8	46.8	15.1	1.8	13.2	2.2	0.7
4.9	18.3	51.5	14.8	1.2	13.1	1.0	0.8
3.4	20.2	47.1	15.5	2.1	13.5	1.6	0.7
2.1	19.8	46.0	15.7	2.6	14.5	1.4	0.7

5. Band gap (E_g) calculation

The band gap (E_g) of QDs could be calculated from the band-gap emission (λ_{peak}) of the corresponding sample using equation (S2)². Corresponding band gap of CdSe QDs with different surface stoichiometry can be determined as **Table S5**.

$$E_g = \frac{1240}{\lambda_{\text{peak}}} \quad (\text{S2})$$

Table S5. The band gap of CdSe QDs

Surface Se%	16.7%	13.5%	9.1%	4.9%	3.4%	2.1%
λ_{peak} (nm)	448	449	452	467	466	468
E_g (eV)	2.8	2.8	2.7	2.7	2.7	2.7

In our experiments, the band-edge emission (λ_{peak}) of CdSe QDs with different surface stoichiometry was determined using equation S2, the corresponding results are shown in **Figure 7a** and **Table S5**.

6. Introduction of different ligands and cocatalysts for solar H₂ evolution.

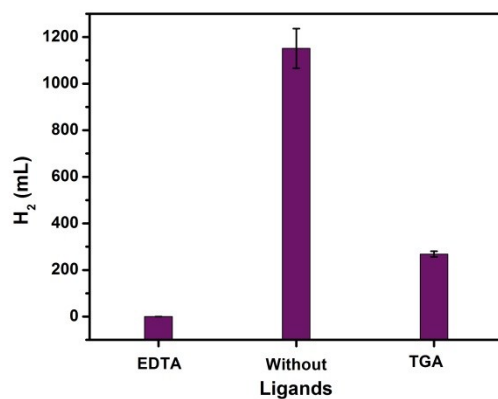


Figure S2. Ligand effect on the H₂ evolution of CdSe QDs with lowest surface Se under 3 h visible-light illumination. EDTA: ethylenediaminetetraacetic acid; TGA: thioglycolic acid.

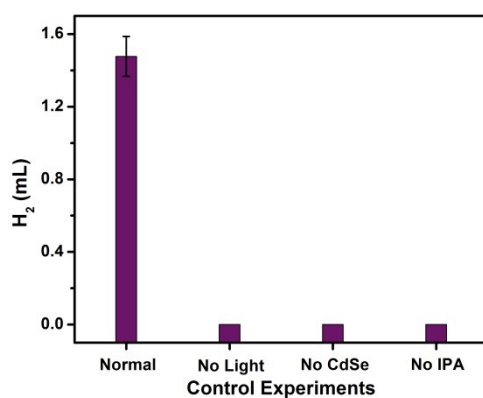


Figure S3 Control experiments of solar H₂ evolution under dark, and in the absence of sacrificial reagent or QDs.

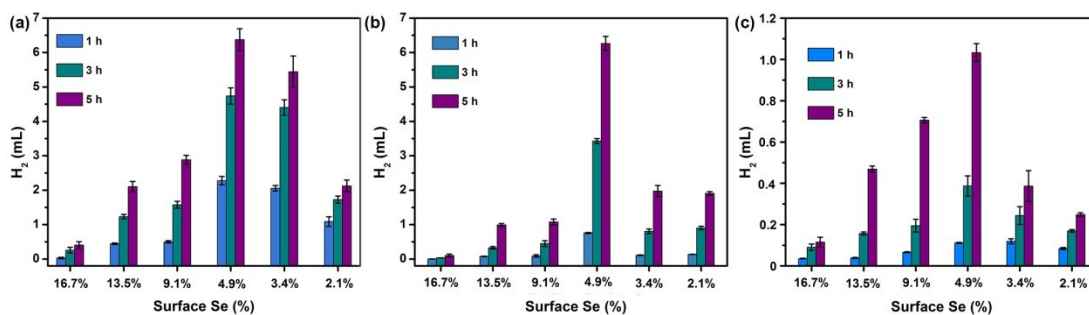


Figure S4. Photocatalytic hydrogen evolution of CdSe QDs with different surface Se ratio using (a) Pt-nanoparticles, (b) CoCl₂ salt and (c) Cobalt complex as the cocatalysts.

7. Diffuse transmission spectrum

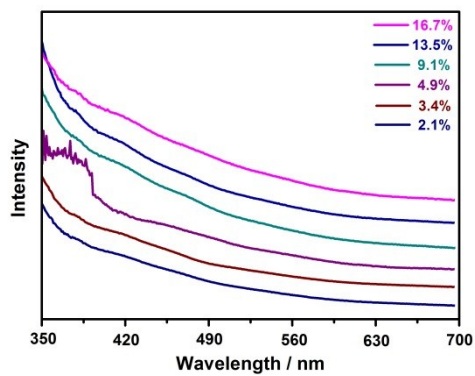


Figure S5. Diffuse Transmission spectra of CdSe QDs with different surface Se% loaded on the substrate of mesoporous NiO/FTO. Detailed information of QD-photocathode fabrication can be found in our previous reports^{3,4}.

8. PEC measurements

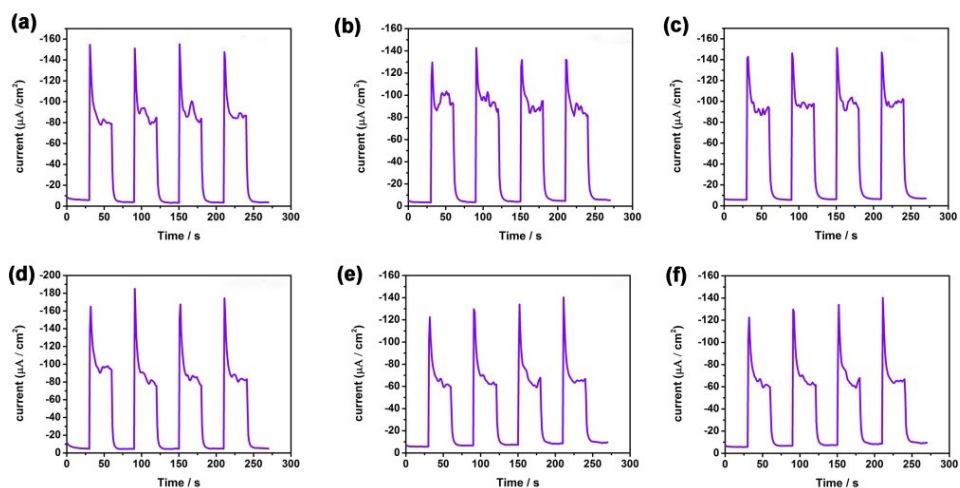


Figure S6. The photocurrent responses of QD-based photocathode using CdSe QDs with different surface Se ratio: (a) 16.7%; (b) 13.5%; (c) 9.1%; (d) 4.9%; (e) 3.4%, and (f) 2.1%, respectively.

9. Spectroscopic analysis

The PL quenching of CdSe QDs is described by using equation S3, in which A is the degree of PL Quenching of CdSe QDs by addition same amount of IPA, I_0 and I_1 represent the intensity of PL of CdSe QDs in the absence and presence of IPA, respectively.

$$A = I_0 / I_1 - 1 \quad (S3)$$

$$I_{trap} = \frac{PL_{tse}}{PL_{nbe} + PL_{tse}} \quad (S4)$$

The ratio of trap-state emission is defined as equation S4, in which I_{trap} is the relative intensity, PL_{nbe} is the intensity of PL of near-band-edge emission, and PL_{tse} is the intensity of PL of trap-state emission.

The calculation of the rate constant of electron transfer from QDs to cocatalysts is determined by using equation S5:

$$K_{ET} = (1/\tau_1 - 1/\tau_0) / C_{Ni(II)} \quad (S5)$$

Where τ_0 is the emission lifetime of CdSe QDs in the absence of external cocatalysts and τ_1 is the emission lifetime of CdSe QDs in the presence of Ni^{2+} salt ($2.1 \times 10^{-4} \text{ mol L}^{-1}$), see corresponding experimental results in **Figure S7**.

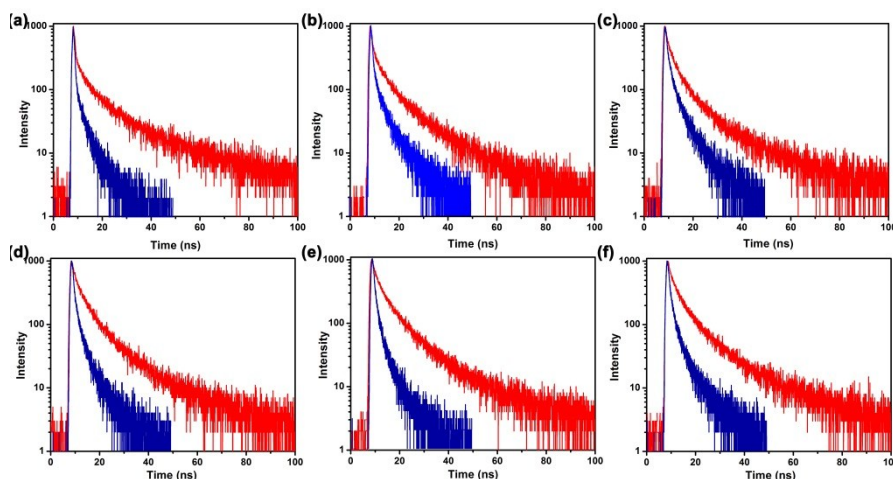


Figure S7. Time-resolved luminescent decay of CdSe QDs with different surface Se ratio (405 nm laser excitation). The red line represents PL decay of CdSe QDs in the absence of external cocatalysts and the blue line represents PL decay of CdSe QDs in the presence of Ni^{2+} salt: (a) 16.7%; (b) 13.5%; (c) 9.1%; (d) 4.9%; (e) 3.4 %, and (f) 2.1%, respectively.

10. Reference

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