Supplementary Information

Understanding charge separation in CdS/Ce-UiO66-NH_2 heterojunctions for enhanced photocatalytic hydrogen evolution

*Wenqing Hou, Sam A. J. Hillman, Soranyel Gonzalez-Carrero, Shilin Yao, Huangtianzhi Zhu and James R. Durrant**

Contents | Pages

Table S1. Amounts of reagents used for synthesis of *x*CdS/Ce-UiO-NH_2 samples

Reagents	20% CdS	30% CdS	40% CdS	50% CdS	CdS
Ce-UiO-NH_2 (mg)	80	70	60	50	0
$Cd(CH_3COO)_2{\cdot}2H_2O$ (mg)	36.9	55.3	73.8	92.2	184.4
$Na_2S{\cdot}9H_2O$ (mg)	33.2	49.8	66.4	83.0	166

Table S2. Physical parameters and HER performance of different samples[a)]

Samples	A_{sp} (m^2 g^{-1})	V_{tp} (cm^3 g^{-1})	V_{mp} (cm^3 g^{-1})	d_p (nm)	V_{mp}/V_{tp}	d_{cds}	*EQE* (%)	*EQE*/A_{sp} (g m^{-2})*10^{-3}
Ce-UiO-NH_2	942	0.521	0.416	2.2	0.80	--	n.d.	n.d.
20%CdS/Ce-UiO-NH_2	548(763)	0.433(0.481)	0.141(0.335)	4.0	0.33	2.0	1.3	23.7
30%CdS/Ce-UiO-NH_2	385(674)	0.389(0.462)	0.135(0.294)	4.1	0.35	2.2	1.8	46.8
40%CdS/Ce-UiO-NH_2	339(584)	0.358(0.442)	0.130(0.254)	4.4	0.36	2.3	2.2	64.9
50%CdS/Ce-UiO-NH_2	261(495)	0.332(0.422)	0.108(0.212)	5.3	0.32	2.6	1.5	57.5
CdS	49	0.323	0.009	25.7	0.028	8.9	0.2	40.8

[a)] A_{sp}, surface area; V_{tp}, total pore volume; V_{mp}, micropore volume; d_p, average pore size; d_{cds}, CdS size from X-ray; *EQE*: external quantum efficiency. Bracket data are calculated from CdS content added in synthesis.

Table S3. Literature survey for H_2 production on different photoctalysts[a)]

Samples	Cat. (mg/mL)	Sacrificial agent	Light source	H_2 (μmol h^{-1} g^{-1})	*EQE* (%)	Ref.
CdS/Ce-UiO-NH_2	0.50	10% MeOH	4*3 W (LED/λ = 420 nm)	2064	2.2	This work
CdS/Ce-UiO-NH_2	0.50	Na_2S/Na_2SO_3	4*3 W (LED/λ = 420 nm)	4109	4.4	[1]
0.5% Pt/Ce-UiO-NH_2	0.50	Na_2S/Na_2SO_3	4*3 W (LED/λ = 420 nm)	244	0.2	[1]
Ce-UiO-NH_2	1.0	20% MeOH	150 W (Hg–Xe/AM 1.5G)	200	-	[2]
CdS/ZIF	0.87	-	100 W (LED/λ > 400 nm)	349	1.77	[3]
CdS/Zr-UiO-66-NH_2	0.06	CH_3CN/H_2O/LA	300 W (Xe/λ > 380 nm)	172	0.85(420 nm)	[4]
CdS/MIL-125-NH_2	0.20	Na_2S/Na_2SO_3	350 W (Xe/λ > 420 nm)	6620	-	[5]
CdS/g-C_3N_4	0.10	20% TEOA	300 W (Xe/λ > 400 nm)	216	-	[6]
CdS/UiO-66-$(SH)_2$	0.50	Na_2S/Na_2SO_3	225 W (Xe/420–780 nm)	15320	11.9	[7]
CdS_4/Zr-MOF-808	0.14	8% TEOA	300 W (Xe/400–800 nm)	10410	-	[8]
CdS/Ni-MOF	0.50	6% LA	300 W (Xe/λ > 420 nm)	2508	-	[9]
CdS/Zn(L_{For})-MOF	0.20	Na_2S/Na_2SO_3	300 W (Xe/λ > 420 nm)	26760	-	[10]

[a)] MeOH: methanol; LA: lactic acid; TEOA: triethanolamine; SH: 2,5-disulfanyl.

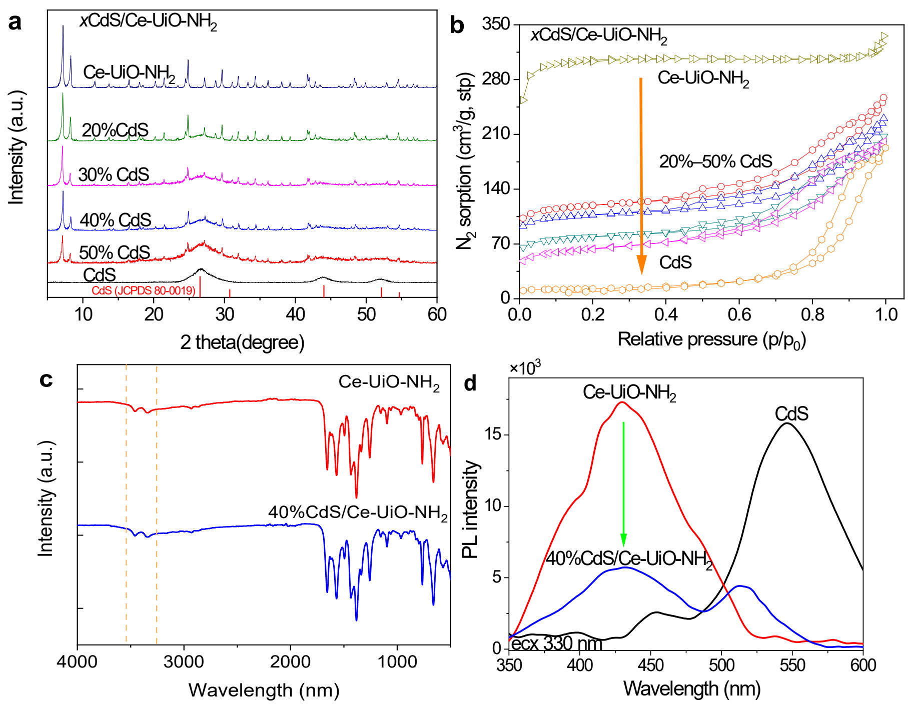

Fig. S1. (a) XRD patterns for *x*CdS/Ce-UiO-NH_2, where *x* was 0, 20, 30, 40, and 50 wt%, including the patterns for cubic CdS (JCPDS 80-0019) as reference (red columns at the bottom), (b) N_2 adsorption and desorption isotherms for *x*CdS/Ce-UiO-NH_2, (c) FT-IR spectra of Ce-UiO-NH_2 and 40%CdS/Ce-UiO-NH_2, and (d) the steady-state PL spectra for CdS, Ce-UiO-NH_2 and 40%CdS/Ce-UiO-NH_2.

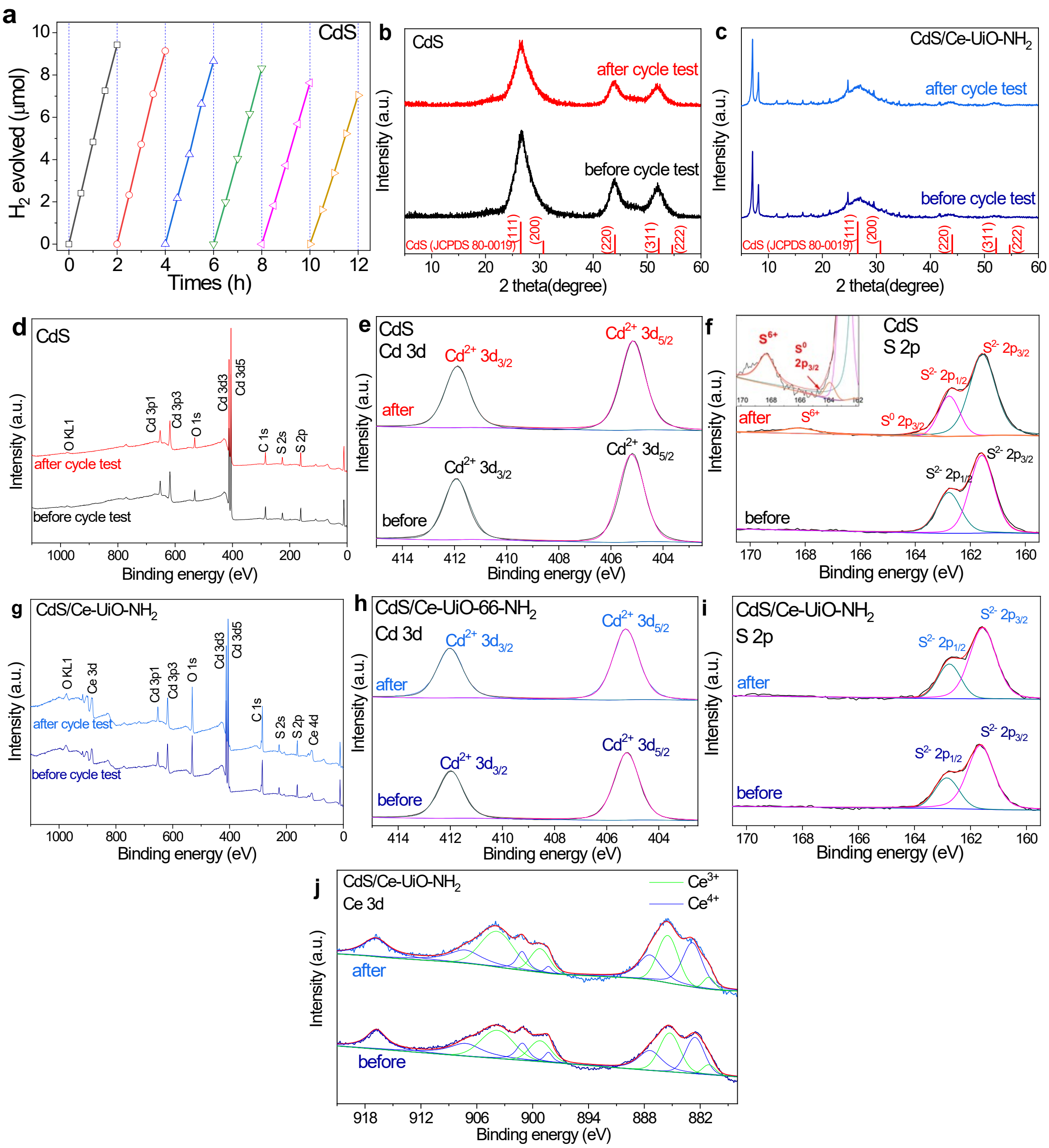

Fig. S2 (a) 6 sequential 2 h H_2 evolution tests for CdS, (b−c) XRD patterns, and (d−j) XPS spectra for CdS and 40%CdS/Ce-UiO-NH_2, before and after cycle HER test for 12 h.

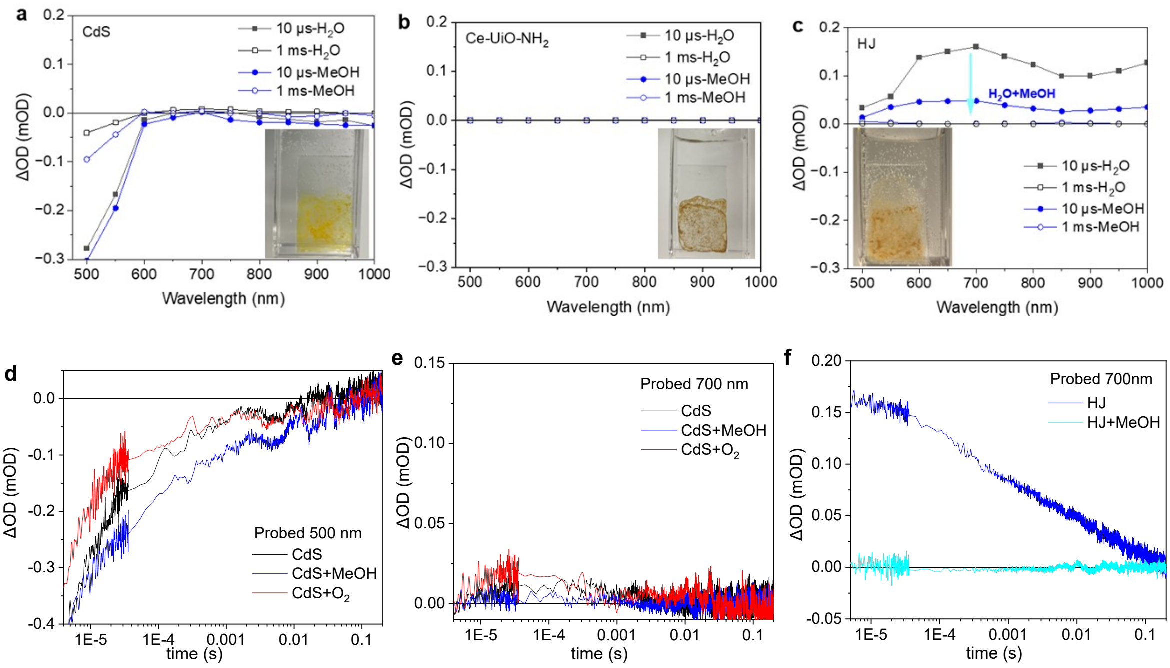

Fig. S3 (a–c) Transient absorption spectra at different time delays of CdS, Ce-UiO-NH_2 and 40%CdS/Ce-UiO-NH_2 in water. Decay dynamics of (d) CdS probed at 500 nm, (e) CdS probed at 700 nm in Ar-purified DI water, 10 vol% MeOH solution and O_2-bubbled water. (f) HJ probed at 700 nm in Ar-purified DI water with and without 10 vol% MeOH. All samples were excited at 420 nm (840 μJ cm^{-2}).

References.

1 W. Hou, C. Chen, Y. Wang and Y. Xu, *Catal. Sci. Technol.*, 2022, **12**, 4012–4019.

2 S. Dai, E. Montero-Lanzuela, A. Tissot, H. G. Baldoví, H. García, S. Navalón and C. Serre, *Chem. Sci.*, 2023, **14**, 3451–3461.

3 L. Shiuan Ng, T. Raja Mogan, J.-K. Lee, H. Li, C.-L. Ken Lee and H. Kwee Lee, *Angew. Chem. Int. Ed.*, 2023, **62**, e202313695.

4 H.-Q. Xu, S. Yang, X. Ma, J. Huang and H.-L. Jiang, *ACS Catal.*, 2018, **8**, 11615–11621.

5 X. Zhang, Z. Chen, Y. Luo, X. Han, Q. Jiang, T. Zhou, H. Yang and J. Hu, *J Hazard. Mater.*, 2021, **405**, 124128.

6 C. Ji, C. Du, J. D. Steinkruger, C. Zhou and S. Yang, *Mater. Lett.*, 2019, **240**, 128–131.

7 S. Mao, Y. Zou, G. Sun, L. Zeng, Z. Wang, D. Ma, Y. Guo, Y. Cheng, C. Wang and J.-W. Shi, *J Colloid Interface Sci.*, 2021, **581**, 1–10.

8 A. Ghosh, S. Karmakar, F. A. Rahimi, R. S. Roy, S. Nath, U. K. Gautam and T. K. Maji, *ACS Appl. Mater. Interfaces*, 2022, **14**, 25220–25231.

9 J. Guo, Y. Liang, L. Liu, J. Hu, H. Wang, W. An and W. Cui, *Appl. Surf. Sci.*, 2020, **522**, 146356.

10 L.-X. Chi, N. D. Clarisse, S. Yang, W.-L. Bao, M. Xiao, Y.-P. Zhao, J.-T. Wang, Q. Chen and Z.-H. Zhang, *J. Solid State Chem.*, 2023, **324**, 124117.