Supporting Information

S-vacancy-mediated efficient Z-scheme photocatalytic H_2 generation of ultrathin nanosheet-based 2D/2D intimate heterojunction

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Characterization results

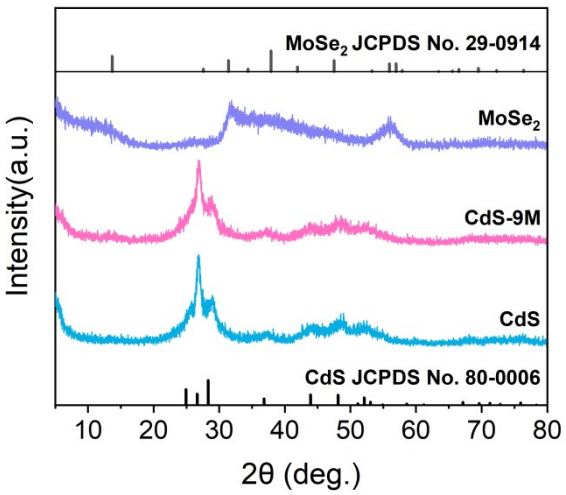

Figure S1. XRD patterns of $MoSe_2$, CdS, and CdS-9M composite.

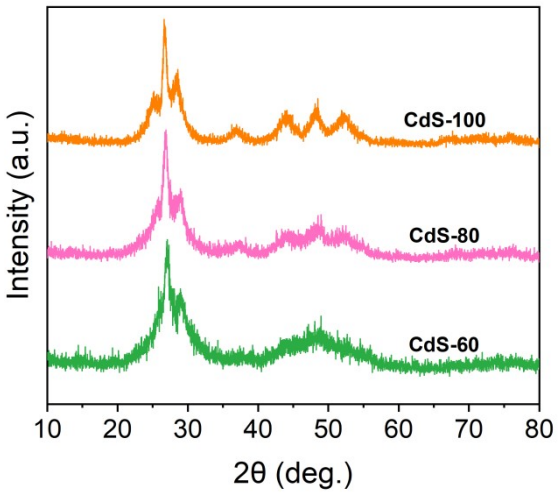

Figure S2. XRD patterns of CdS with varying synthesis temperatures.

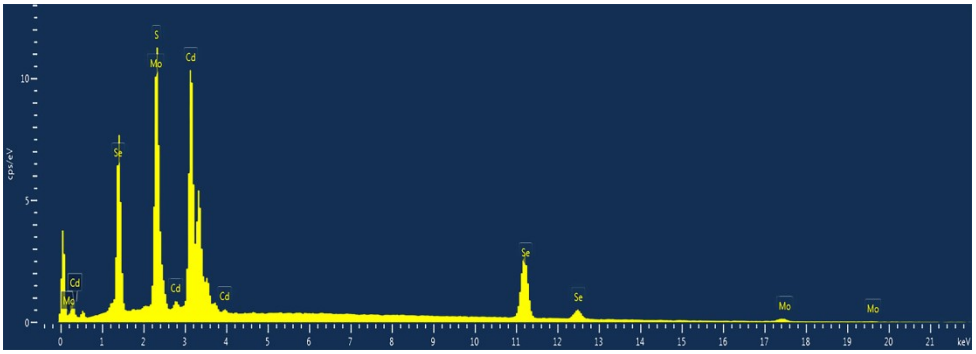

Figure S3. EDX spectrum of CdS-$MoSe_2$ heterojunction.

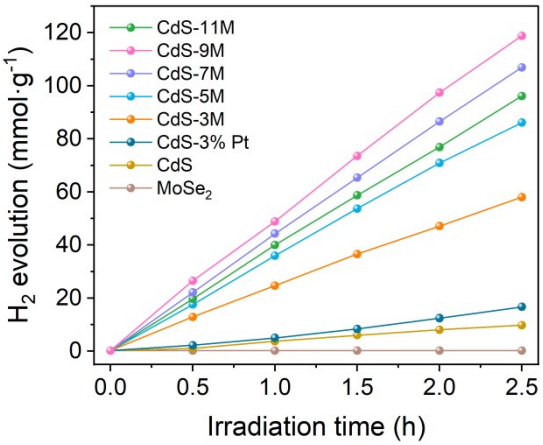

Figure S4. PHE activities of different samples.

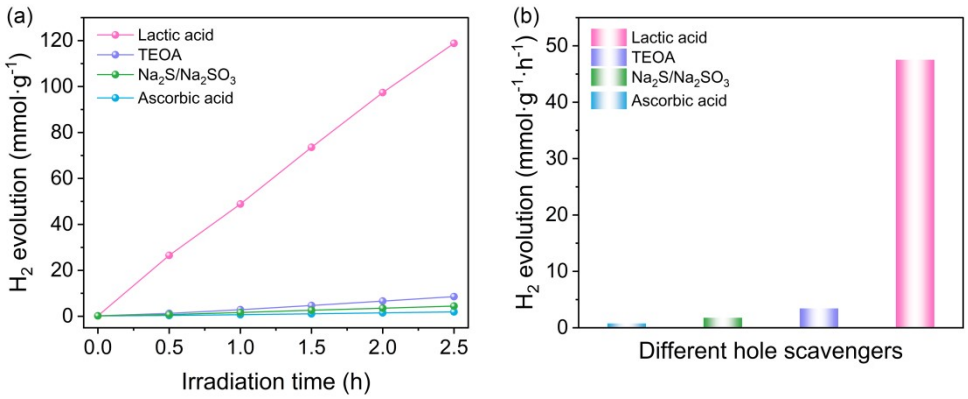

Figure S5. (a) PHE activities and (b) corresponding rates of CdS-9M measured with varying sacrificial agents.

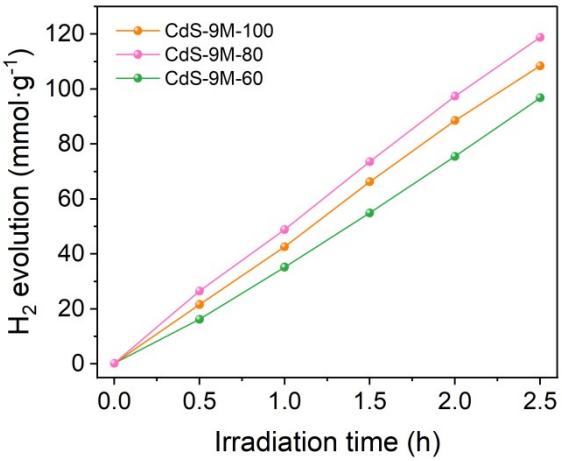

Figure S6. PHE activities of CdS-9M fabricated using CdS with different S_V contents.

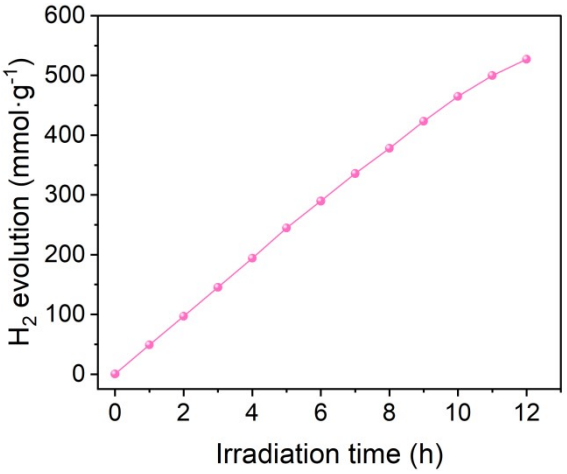

Figure S7. Long-term H_2 generation test of CdS-9M.

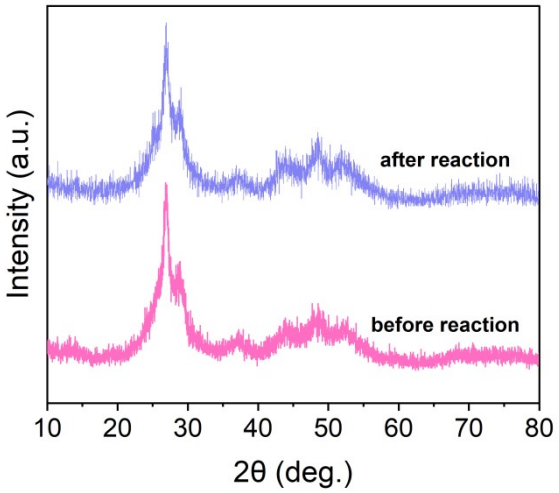

Figure S8. XRD patterns of CdS-9M before and after catalytic reaction.

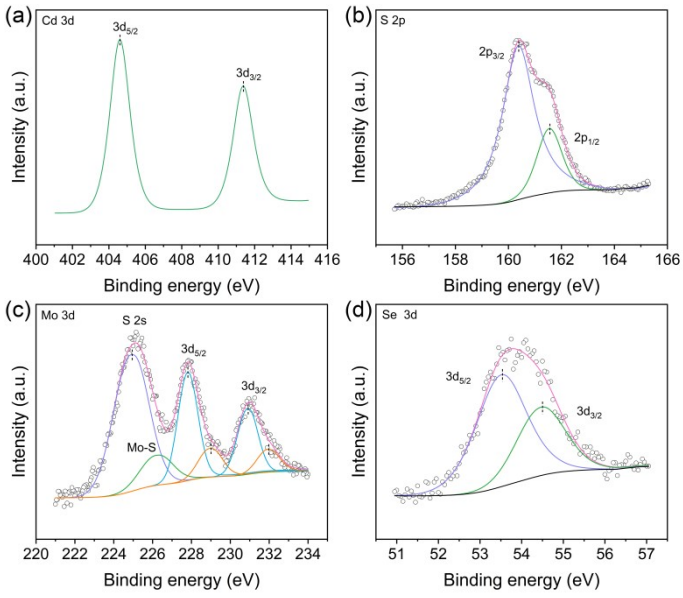

Figure S9. (a) Cd 3d, (b) S 2p, (c) Mo 3d, and (d) Se 3d XPS spectra of CdS-9M after H_2-evolving measurement.

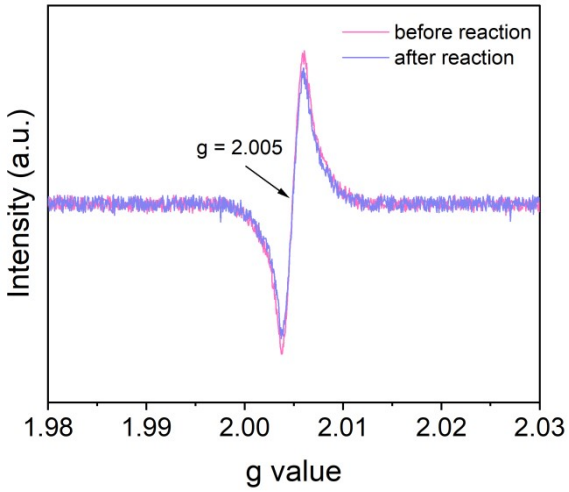

Figure S10. EPR spectra of CdS-9M before and after PHE test.

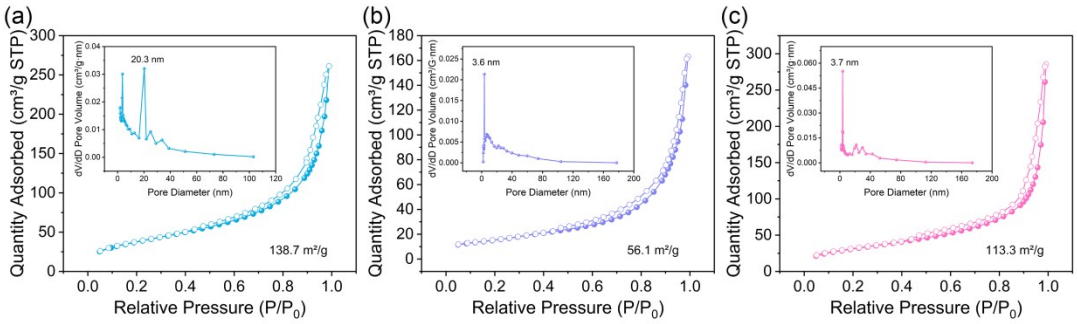

Figure S11. (a-c) N_2 adsorption-desorption isotherms and pore-size distributions (inset) of (a) CdS, (b) $MoSe_2$, and (c) CdS-9M.

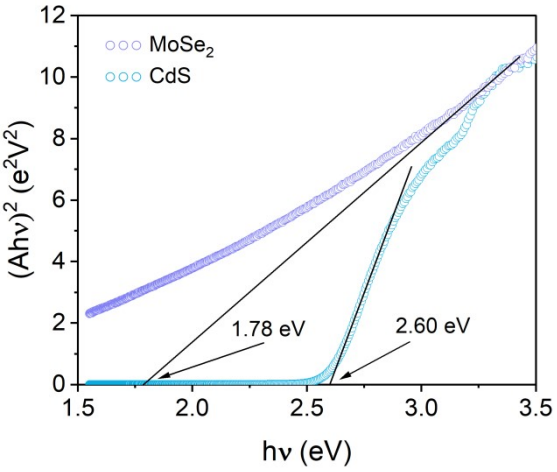

Figure S12. Tauc plots of CdS and $MoSe_2$.

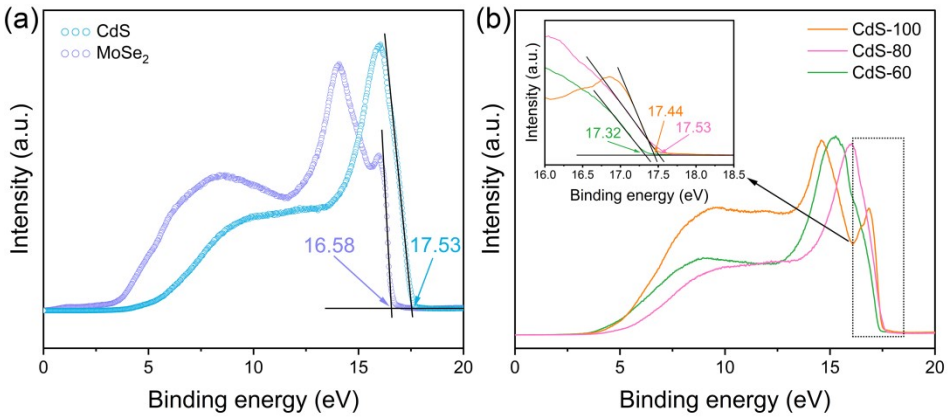

Figure S13. (a, b) UPS spectra of (a) CdS and $MoSe_2$ along with (b) CdS prepared with varying reaction temperatures.

The work function (Φ) of CdS and $MoSe_2$ was determined by the equation: Φ = 21.22 eV - E_{cutoff}, where 21.22 eV and E_{cutoff} represent the He(I) excitation energy and secondary cutoff binding energy, respectively.[1, 2] Based on the UPS spectra in Fig. S13a, the E_{cutoff} of CdS and $MoSe_2$ was recognized as 17.53 and 16.58 eV, thus their Φ can be calculated to be 3.69 and 4.64 eV, respectively. As a result, the Fermi level (E_f) of CdS and $MoSe_2$ was found as - 3.69 and - 4.64 eV, corresponding to - 0.81 and 0.14 V versus normal hydrogen electrode (vs. NHE), respectively.[3] Likewise, the E_f of CdS with differing synthesis temperatures could be discerned as - 0.60, - 0.72, and - 0.81 V vs. NHE for CdS-60, CdS-100, and CdS-80, respectively (Fig. S13b).

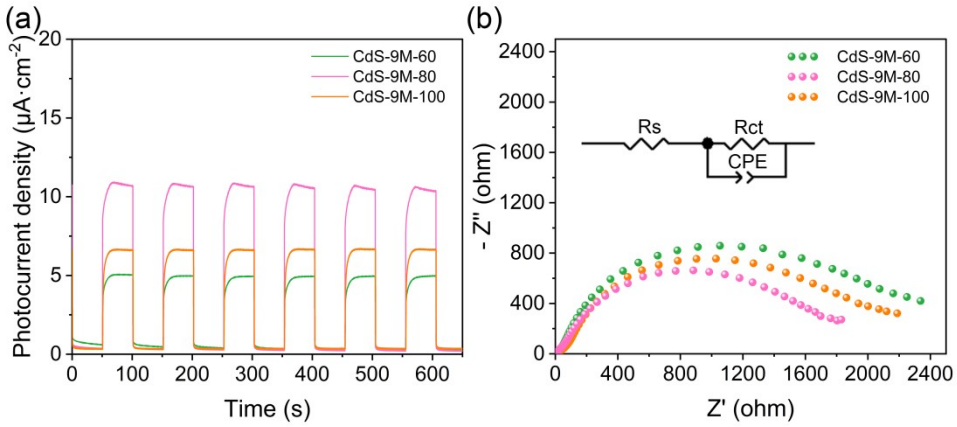

Figure S14. (a) Photocurrent densities and (b) EIS Nyquist curves of CdS-9M-60, CdS-9M-80, and CdS-9M-100.

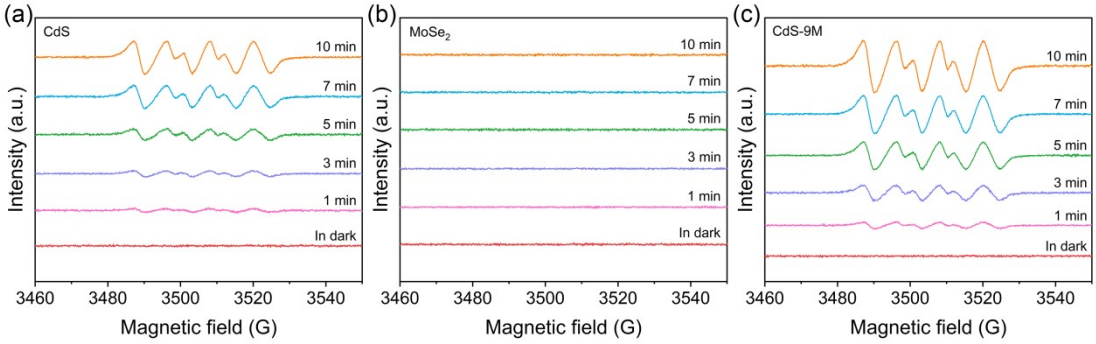

Figure S15. (a-c) Irradiation time-dependent EPR signals of DMPO-·O_2^- adducts produced by (a) CdS, (b) $MoSe_2$, and (c) CdS-$MoSe_2$ composite. All figures were plotted with the identical abscissa and ordinate ranges.

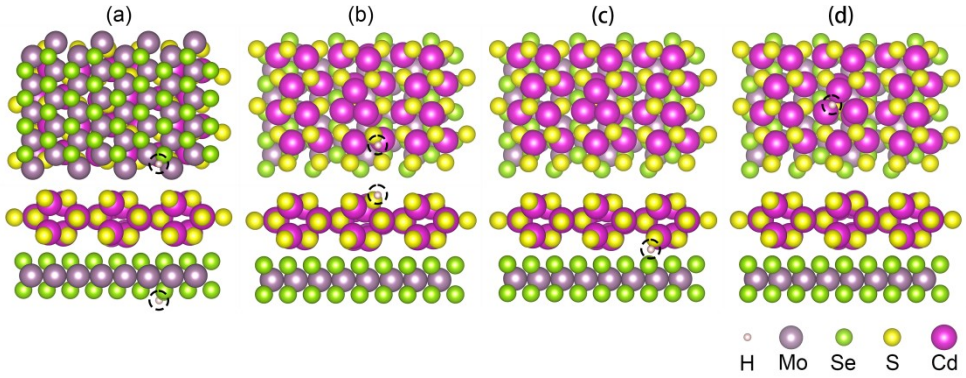

Figure S16. Optimized structural models of hydrogen adsorption on (a) Se site, (b) S site, (c) interface site, and (d) S_V site of CdS-$MoSe_2$ heterojunction. The adsorbed hydrogen atoms were indicated by black dashed circles.

Table S1. Summarized PHE data of our CdS-$MoSe_2$ heterojunction and CdS-based photocatalysts reported in literatures.

Photocatalyst	**Hole scavenger (aqueous solution)**	**Light source (Xe lamp)**	**Maximum rate ($mmol \cdot h^{-1} \cdot g^{-1}$)**	**AQY (420 nm)**	**Reference**
CdS-$MoSe_2$	Lactic acid	$\lambda \geq 400$ nm	47.52	18.2% 22.9% (400 nm)	This work
CdS-MoS_2-CoO_x	TEOA	UV-vis	7.4	7.6%	[4]
Cd/CdS	Na_2S/Na_2SO_3	$\lambda > 420$ nm	10.6	12.1%	[5]

CdS/NiCoAl-LDH	Na_2S/Na_2SO_3	$\lambda > 420$ nm	2.1	-	[6]
CdS/WN	Lactic acid	$\lambda > 420$ nm	24.13	18.59 %	[7]
Cu-Ni/CdS	Na_2S/Na_2SO_3	$\lambda \geq 420$ nm	28.19	10.8%	[8]
CdS@MoS_2/Ti_3C_2	Lactic acid	$\lambda \geq 420$ nm	14.88	-	[9]
Ni-CdS	Na_2S/Na_2SO_3	$\lambda > 420$ nm	20.28	13.62%	[10]
CdS/NiS	Na_2S/Na_2SO_3	$\lambda > 420$ nm	2.18	-	[11]
CdS/Pt/$NaTaO_3$	Lactic acid	$\lambda > 420$ nm	19.8	7.9% (350 nm)	[12]
CdS/Co_3S_4	Lactic acid	$\lambda \geq 420$ nm	23.45	18.5%	[13]
CdS/ZnS/Bi_2Se_3	Na_2S/Na_2SO_3	AM 1.5	7.13	8.13%	[14]
Pt, Au/CdS	TEOA	$\lambda > 380$ nm	6.71	3.72% (380 nm)	[15]
graphdiyne/Ni-doped CdS	Lactic acid	$\lambda \geq 420$ nm	13.33	4.76%	[16]
$NaZn_2(OH)(MoO_4)_2 \cdot H_2O$/CdS	Na_2S/Na_2SO_3	UV-vis	17.44	9.3% (475 nm)	[17]
CdS/Pt@NU-1000	Lactic acid	$\lambda \geq 420$ nm	3.6	-	[18]
NiS@N-doped carbon/CdS	TEOA	300 nm > λ > 1100 nm	6.1	0.66% (365 nm)	[19]
CdS/MoB MBene	Lactic acid	$\lambda \geq 420$ nm	16.89	32.9%	[20]
$ZnIn_2S_4$/CdS	Na_2S/Na_2SO_3	$\lambda \geq 400$ nm	5.68	6.1% (400 nm)	[21]
NiS_xSe_{2-x}/phase junction CdS	Na_2S/Na_2SO_3	$\lambda \geq 400$ nm	11.43	15.3%	[22]
Mo_2C/CdS	Lactic acid	$\lambda \geq 420$ nm	19.94	13.6%	[23]
CeO_2@CdS	Lactic acid	$\lambda \geq 400$ nm	8.36	56.5%	[24]
F-TiO_2/CdS	Na_2S/Na_2SO_3	UV-vis	1.70	4.3%	[25]
CdS-CuS-NiOOH	Na_2S/Na_2SO_3	$\lambda > 420$ nm	11.36	14.4%	[26]
Au/$ZnWO_4$/CdS	Na_2S/Na_2SO_3	420 nm > λ > 800 nm	5.48	2.62% (450 nm)	[27]
CdS-MXene/MoS_2	Lactic acid	$\lambda > 420$ nm	38.5	34.6%	[28]
$Cu_{2-x}S$/CdS	Na_2S/Na_2SO_3	$\lambda \geq 420$ nm	5.75	0.80%	[29]
$CoZnS_x$/CdS	Lactic acid	$\lambda \geq 420$ nm	21.0	-	[30]
Zn_2MnO_4/CdS	Na_2S/Na_2SO_3	UV-vis	22.42	4.15% (365 nm)	[31]
CdNCN-CdS	Na_2S/Na_2SO_3	$\lambda \geq 420$ nm	14.7	20.50% (400 nm)	[32]
Pd single atoms/hollow CdS	Lactic acid	$\lambda > 420$ nm	22.23	14.9%	[33]

Table S2. Fitting parameters for the EIS Nyquist curves of CdS, $MoSe_2$, and CdS-9M composites prepared using CdS with varying formation temperatures. (Rs: series resistance, Rct: charge transfer resistance, CPE: constant phase angle element)

Sample	Rs (Ω)	Rct (Ω)	CPE-T (F)	CPT-P
CdS	24.09	2592	1.50×10^{-4}	0.842
$MoSe_2$	38.06	4369	1.89×10^{-4}	0.836
CdS-9M-60	22.11	2344	2.20×10^{-4}	0.814
CdS-9M-80	27.41	1791	1.65×10^{-4}	0.807
CdS-9M-100	43.35	2148	2.07×10^{-4}	0.786

Table S3. XPS peak binding energies of CdS, $MoSe_2$, and CdS-9M with and without in-situ light irradiation.

XPS species	$MoSe_2$	CdS	CdS-9M	light-irradiated CdS-9M
Mo-S	-	-	226.2 eV	226.4 eV
Mo^{4+}	228.3-231.4 eV	-	228.0-231.1 eV	228.1-231.2 eV
Mo^{5+}	229.4-232.4 eV	-	228.9-231.9 eV	229.1-232.1 eV
Se^{2-}	53.9-54.8 eV	-	53.6-54.5 eV	53.7-54.6 eV
Cd^{2+}	-	404.3-411.0 eV	404.7-411.4 eV	404.5-411.2 eV
S^{2-}	-	160.0-161.2 eV	160.4-161.6 eV	160.3-161.5 eV

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