Supporting Information

Enhanced photocatalytic H_2 evolution: Optimized atomic hydrogen desorption via free-electron transfer in sulfur-rich $MoWS_{2+x}$ on vacancy-engineered CdS crystals

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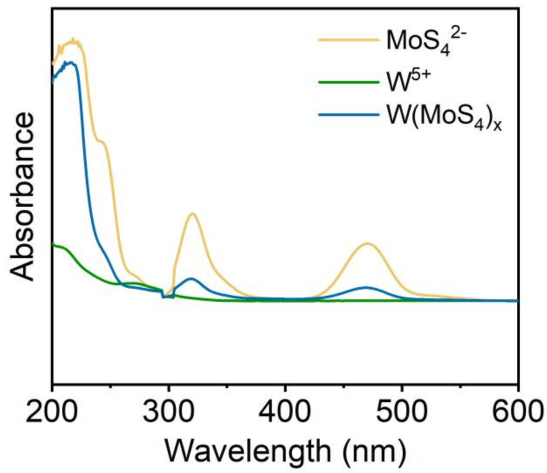
Table of Contents

(a)



(b)

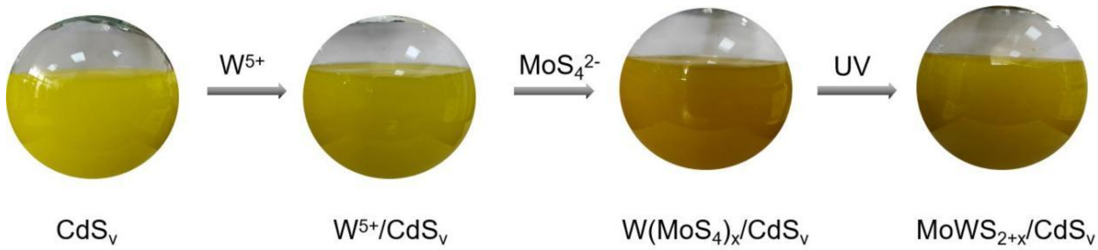


Figure S1. (a) UV-visible absorption spectrum of MoS_4^{2-}, W^{5+} and $W(MoS_4)_x$ solutions. (b) the corresponding photographs for the color change of CdS_v, W^{5+}/CdS_v, $W(MoS_4)_x/CdS_v$, and $MoWS_{2+x}$/ CdS_v suspensions.

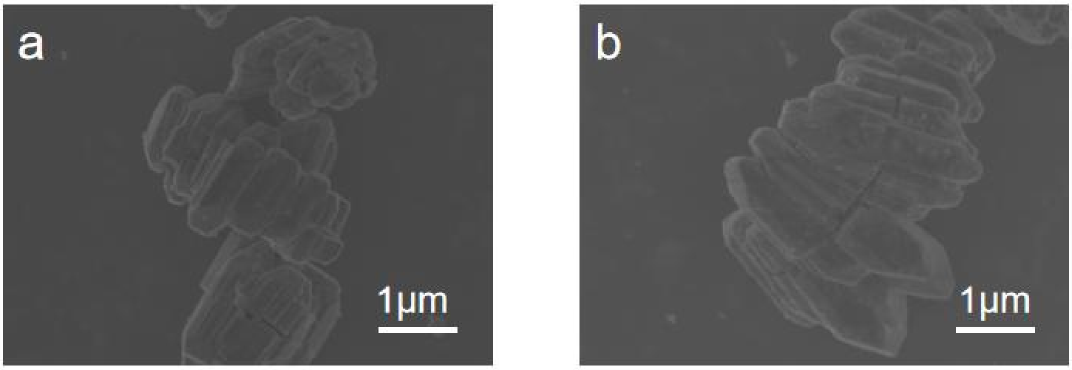


Figure S2. SEM image of (a) CdS_v and (b) MoS_{2+x}/CdS_v.

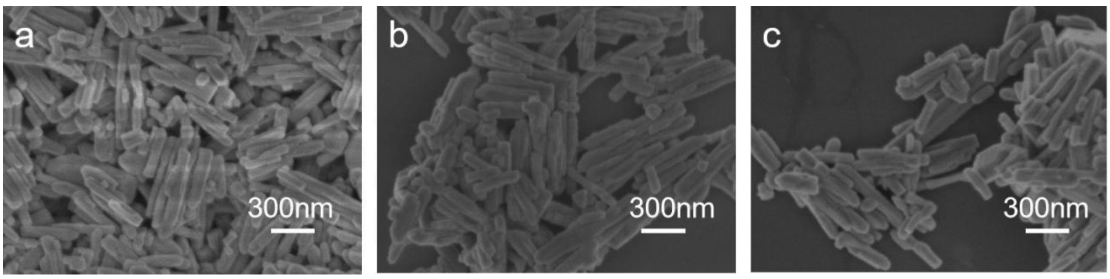


Figure S3. SEM image of (a) CdS, (b) MoS_{2+x}/CdS and (c) $MoWS_{2+x}/CdS$.

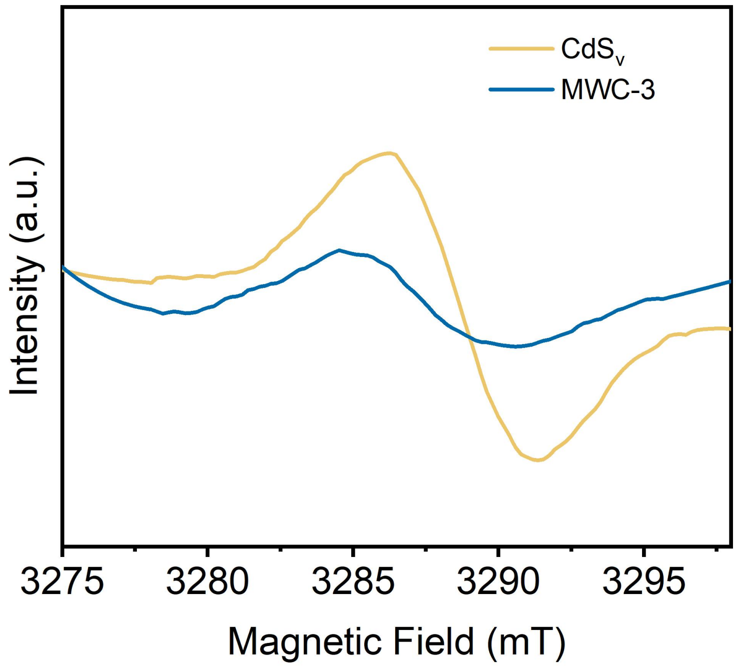


Figure S4. EPR spectra of CdS_v and MWC-3.

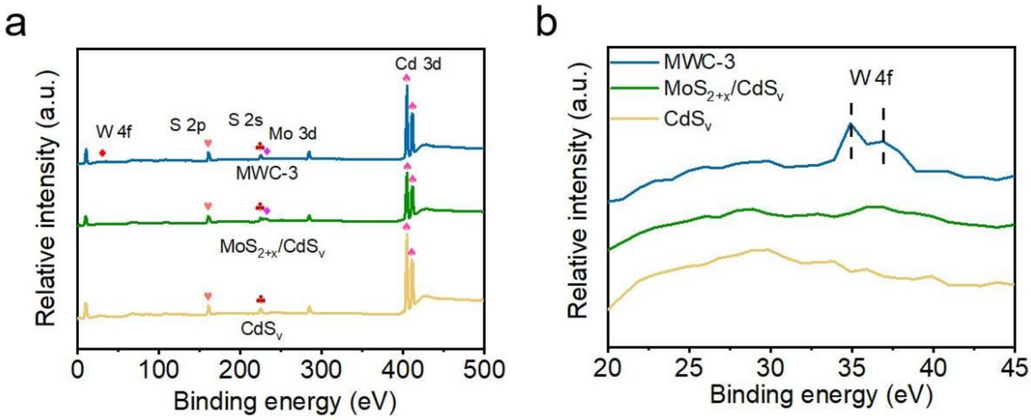


Figure S5. (a) XPS survey spectra of Cd 3d, S 2p, Mo 3d, W 4f and S 2s. (b) A magnified view of W 4f in the XPS survey spectrum.

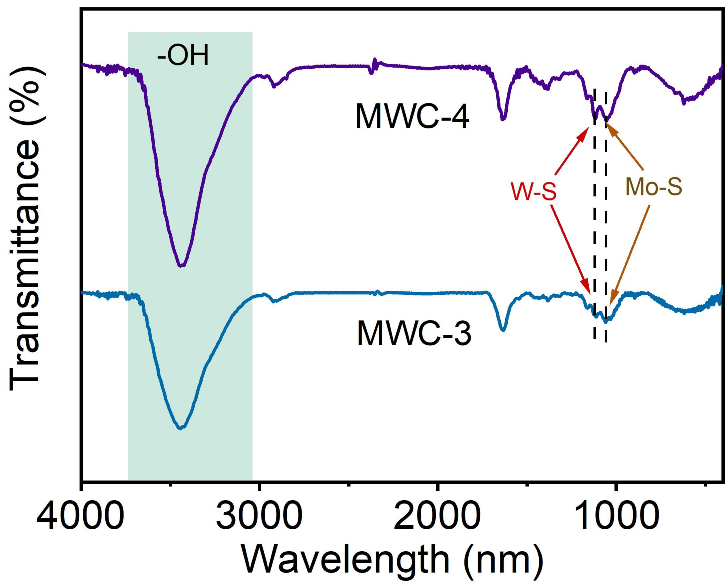


Figure S6. Fourier transform infrared spectroscopy of MWC-3 and MWC-4.

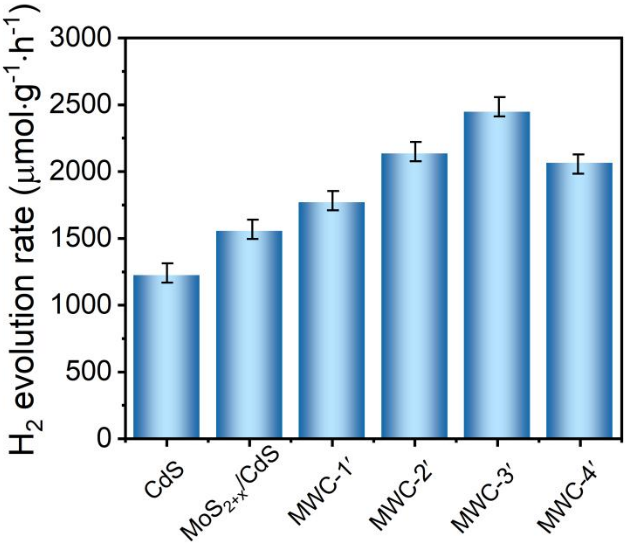


Figure S7. Hydrogen evolution rates of CdS, MoS_{2+x}/CdS and MWC-x' samples.

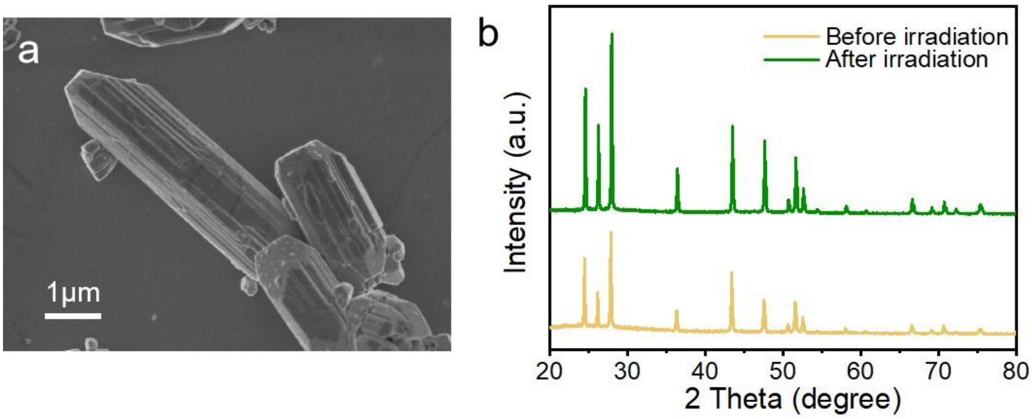


Figure S8. SEM images of MWC-3 (a) after 2 h irradiation ($\lambda \geq 420$ nm). (b) XRD patterns of MWC-3 before and after 2 h irradiation.

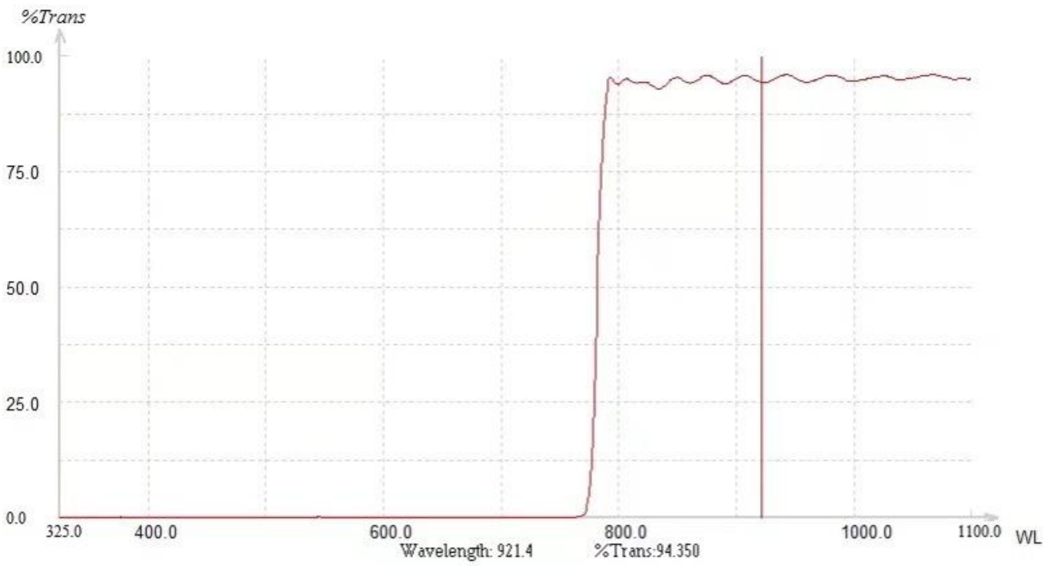


Figure S9. The raw data from absorption test of the NIR filter.

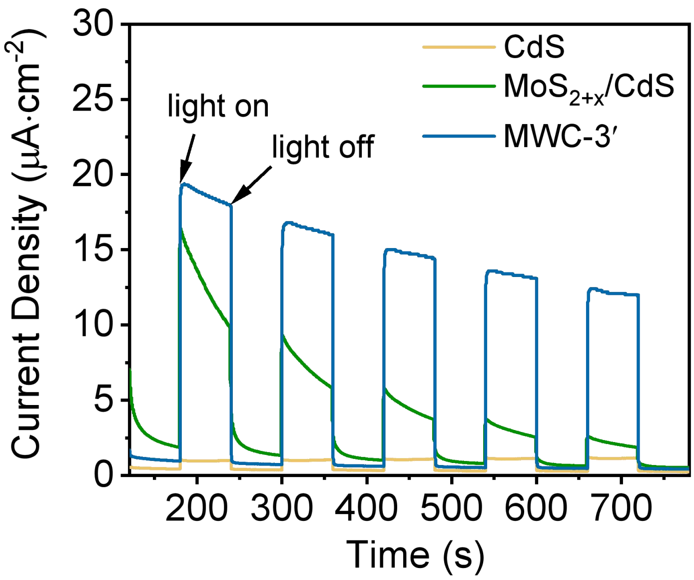


Figure S10. Photocurrent curves of CdS, MoS_{2+x}/CdS and MWC-3'.

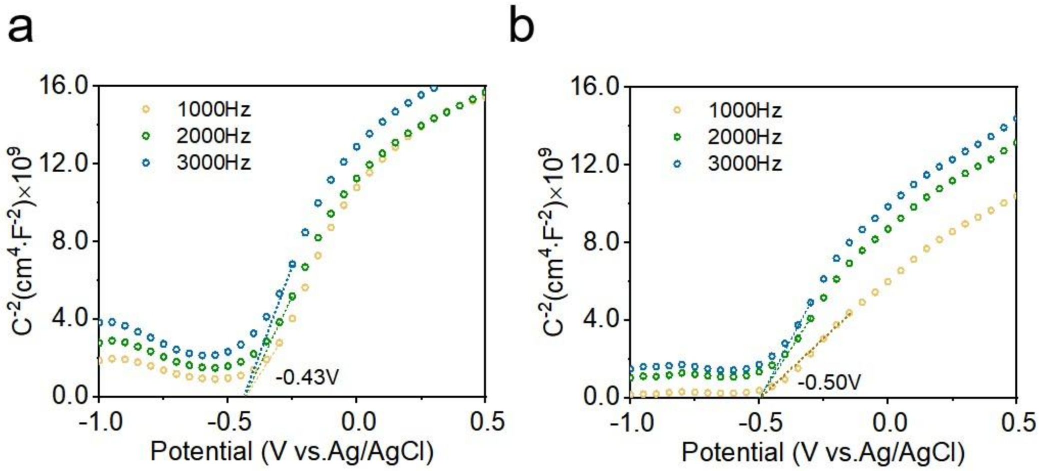


Figure S11. Mott-Schottky plots of (a) CdS_v and (b) MoS_{2+x}/CdS_v in 0.5 M Na_2SO_4 tested at 1000 Hz, 2000 Hz and 3000 Hz, respectively.

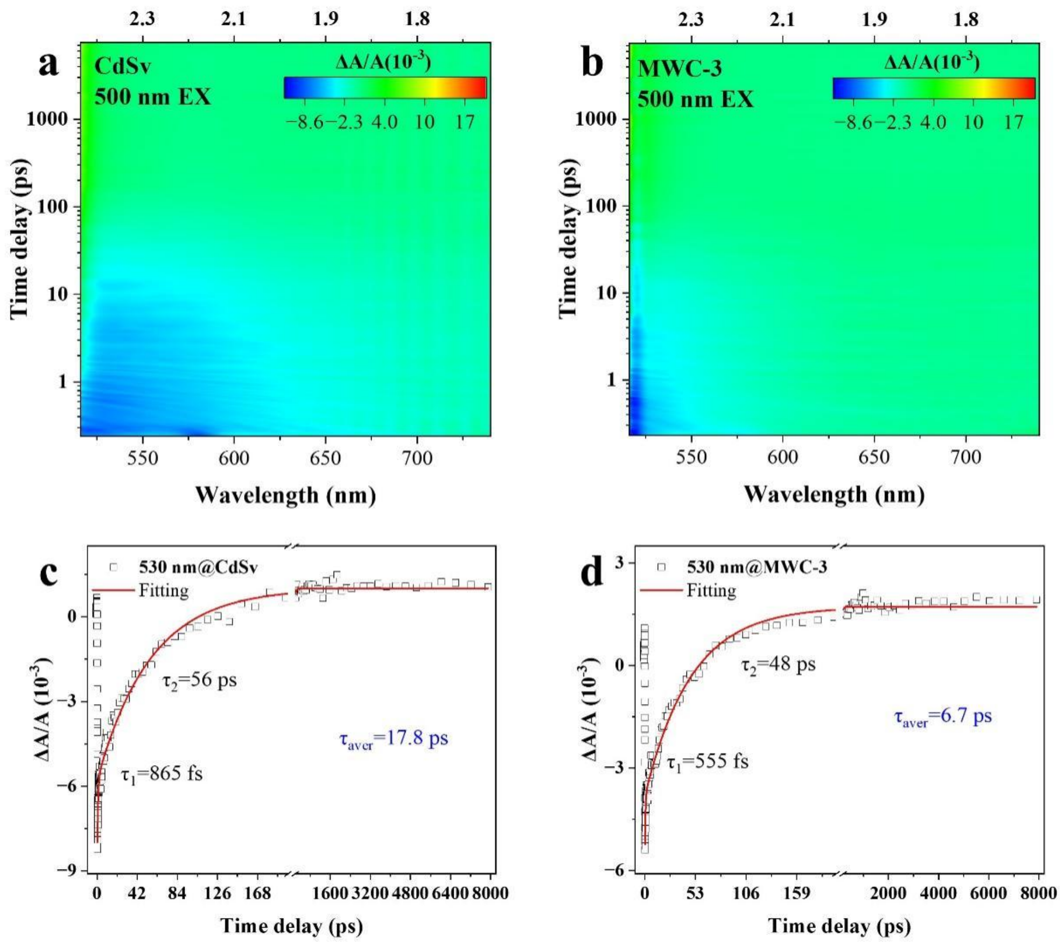


Fig. S12. Fs-TA measurements after 500 nm excitation with fluence of 2.2 μJ/pulse at visible region: (a, b) The contour maps of samples upon 500 nm excitation, (c, d) the kinetic fitting at 530 nm for corresponding samples.

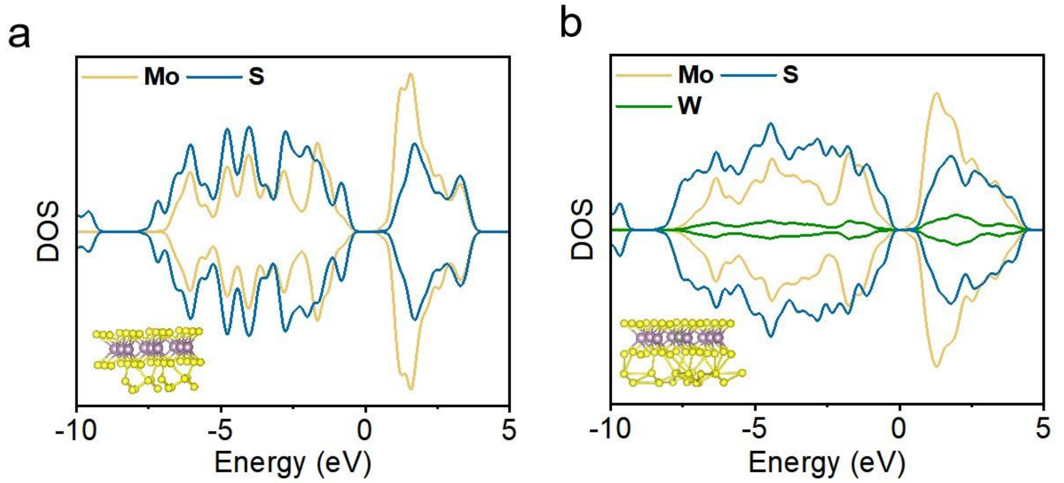


Figure S13. Density of states (DOS) diagram for (a) MoS_{2+x} and (b) $MoWS_{2+x}$ (Illustrations for the respective computational models).

Table S1. Calculated quantum yields at different wavelengths.

λ (nm)	*A (cm^2)*	*E ($mW \cdot cm^{-2}$)*	*Chromatographic indication*	R_{H_2}(*$\mu mol \cdot h^{-1}$*)	*QE*
390-400	2	12.5	1.6043	19.637	19.13%
420-430	2	19.8	2.0608	25.2238	14.40%
440-450	2	27.3	2.9018	35.5184	14.04%
480-485	2	16.2	1.8426	22.553	13.77%
500-510	2	13.2	1.1017	13.4848	9.70%

Table S2. Composition (wt %) of the various samples based on the ICP-AES results.

Samples	S (at.%)	Mo (at.%)	W (at.%)	S/(Mo+W)
$MoWS_{2+x}/TiO_2$	8.64	0.019	0.039	> 2

Table S3. Comparison of H_2 evolution activity between molybdenum disulfide cocatalysts and cadmium sulfide based composite photocatalysts.

Photocatalysts	Light source	Incident light	Photocatalytic performance	AQY	Ref.
CdS/Mo-VC	300 W Xe light	λ≥420 nm	H_2 rate: 2267 μmol·g^{-1}·h^{-1}	4.3% (420 nm)	[1]
$MoWS_{2+x}/TiO_2$	4 LED light	λ≥365 nm	H_2 rate: 4620.8 μmol·g^{-1}·h^{-1}	22.2% (365 nm)	[2]
TiO_2/Au@MoS_{2+x}	4 LED light	λ≥365 nm	H_2 rate: 7858.1 μmol·g^{-1}·h^{-1}	38.1% (365 nm)	[3]
NiCd/CdS	300 W Xe light	λ>410 nm	H_2 rate: 11570 μmol·g^{-1}·h^{-1}	/	[4]
$RuMoS_{2+x}/TiO_2$	4 LED light	λ≥365 nm	H_2 rate: 2649.3 μmol·g^{-1}·h^{-1}	10.73% (365 nm)	[5]
ZnO/CdS/MoS_2	300 W Xe light	λ≥420 nm	H_2 rate: 10247.4 μmol·g^{-1}·h^{-1}	/	[6]
CdS-MoS_2-CoO_x	300 W Xe light	λ≥420 nm	H_2 rate: 7400 μmol·g^{-1}·h^{-1}	7.6% (420nm)	[7]
$MoSe_2$/CdS	300 W Xe light	λ≥420 nm	H_2 rate: 4700 μmol·g^{-1}·h^{-1}	15.6% (450 nm)	[8]
CdS/MoC	300 W Xe light	λ≥420 nm	H_2 rate: 224.5 μmol·g^{-1}·h^{-1}	7.6% (420 nm)	[9]
$MoWS_{2+x}/CdS_v$	300 W Xe light	λ≥420 nm	H_2 rate: 9166.13 μmol·g^{-1}·h^{-1}	19.13% (390 nm)	This work

Table S4. The calculated carrier density of CdS_v, MoS_{2+x}/CdS_v, MWC-3 at 1000 Hz, 2000 Hz and 3000 Hz, respectively.

Frequency	Carrier Density (cm^{-3})		
	CdS_v	**MoS_{2+x}/CdS_v**	**MWC-3**
1000Hz	5.73×10^{21}	7.63×10^{21}	9.11×10^{21}
2000Hz	4.28×10^{21}	4.66×10^{21}	6.73×10^{21}
3000Hz	3.85×10^{21}	4.13×10^{21}	5.12×10^{21}

Table S5. Kinetic fitting parameters for MWC-3 and CdS_v at 1273 nm upon 410 nm excitation.

Sample	**λ (nm)**	**τ_1/ps**	**A_1 (%)**	**τ_2/ps**	**A_2 (%)**	**τ_{aver}/ps**
MWC-3	1273	12.1	86.2	77.6	13.8	21.2
CdSv	1273	10.1	59.7	104.5	40.3	48.2

Table S6. Kinetic fitting parameters for MWC-3 and CdS_v at 1273 nm wavelengths upon 500 nm excitation.

Sample	**λ (nm)**	**τ_1/ps**	**A_1 (%)**	**τ_2/ps**	**A_2 (%)**	**τ_{aver}/ps**
MWC-3	1273	4.1	59.5	106	40.5	45.4
CdSv	1273	NA	NA	NA	NA	NA*

Note: NA* means that there is no absorption peak at 1273 nm for the corresponding sample, so it is not applicable (NA).

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