Electronic Supplementary Information

Construction of plasmonic $1T-WS_2/2H-WS_2/CdS$ heterostructures for enhanced solar driven hydrogen evolution

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Fig. S1. (a) PerfectLight Labsolar 6A and (b) PerfectLight PLS-SXE300/300UV.



Fig. S2. Optical images of (a) pure CdS nanorods, (b) $1T-WS_2/2H-WS_2/CdS$ heterostructures (WWC-1-6), and (c) pure WS₂ nanosheets.



Fig. S3. TG curves of pure CdS nanorods under N₂ atmosphere.



Fig. S4. XRD patterns of different $1T-WS_2/2H-WS_2/CdS$ heterostructures (WWC-3-6, WWC-1-6, WWC-3-2), CdS-W (CdS-W represents only calcination the mixture of CdS and $H_{28}N_6O_{41}W_{12}$ · H_2O after grinding), CdS-CN (CdS-CN represents only calcination the mixture of CdS and $C_2H_4N_4$ after grinding), and pure CdS nanorods.



Fig. S5. Raman spectra of different $1T-WS_2/2H-WS_2/CdS$ heterostructures (WWC-3-6, WWC-1-6, WWC-1-2), CdS-W (CdS-W represents only calcination the mixture of CdS and $H_{28}N_6O_{41}W_{12}$ · H_2O after grinding), CdS-CN (CdS-CN represents only calcination the mixture of CdS and $C_2H_4N_4$ after grinding), and pure CdS nanorods.



Fig. S6. Nitrogen sorption isotherms, BET surface areas, and pore volumes of pure WS₂ nanosheets.



Fig. S7. TEM and HRTEM images of pure CdS nanorods.



Fig. S8. TEM and the corresponding EDX mapping images of CdS-W heterostructures (CdS-W represents only calcination the mixture of CdS and $H_{28}N_6O_{41}W_{12}$ · H_2O after grinding).



Fig. S9. HRTEM images of pure WS₂ nanosheets.



Fig. S10. Comparison diagram of (a) Cd 3d, (b) S 2p, and (c) W 4f of $1T-WS_2/2H-WS_2/CdS$ heterostructures (WWC-3-6).



Fig. S11. Comparison diagram of (a) Cd 3d, (b) S 2p, and (c) W 4f of CdS-W heterostructures (CdS-W represents only calcination the mixture of CdS and $H_{28}N_6O_{41}W_{12}$ · H_2O after grinding).



Fig. S12. (a) N 1s and (b) C 1s XPS spectra of WWC-1-6 heterostructures.



Fig. S13. EPR spectra of $1T-WS_2/2H-WS_2/CdS$ heterostructures (WWC-1-6) and CdS-W (CdS-W represents only calcination the mixture of CdS and $H_{28}N_6O_{41}W_{12}$ · H_2O after grinding).



Fig. S14. Optical bandgaps of $1T-WS_2/2H-WS_2/CdS$ heterostructures (WWC-1-6) and pure CdS nanorods.



Fig. S15. (a) Ultraviolet-visible absorption spectrum and (b) optical bandgap of pure WS_2 nanosheets.



Fig. S16. H₂ evolution rates of (a) different catalysts and (b) 1T-WS₂/2H-WS₂/CdS heterostructures (WWC-3-1, WWC-3-2, WWC-3-4, WWCp-3-6, WWC-3-8).



Fig. S17. The highest temperature of photocatalytic system with (a) pure CdS and (b) WWC-1-6 as photocatalysts without cooling water.



Fig. S18. (a) XY direction, (b) XZ direction, (c) YZ direction, and (d) 3D modeling of FDTD simulation diagram of WS₂ nanosheets.



Fig. S19. (a) XZ direction, (b) XY direction, (c) YZ direction, and (d, e) 3D modeling of FDTD simulation diagram of CdS nanorods.



Fig. S20. (a) XZ direction, (b) XY direction, (c) YZ direction, and (d, e) 3D modeling of FDTD simulation diagram of $1T-WS_2/2H-WS_2/CdS$ heterostructures.



Fig. S21. Theoretically calculated bandgap of (a) CdS, (b) 2H-WS₂, and (c) 1T-WS₂.

The mass ratio	H ₂₈ N ₆ O ₄₁ W ₁₂ ·H ₂ O	$C_2H_4N_4$	sample designations	
	0.01 g	0.01 g	WWC-1-1	
	0.02 g	0.02 g	WWC-1-2	
1:1	0.04 g	0.04 g	WWC-1-4	
	0.06 g	0.06 g	WWC-1-6	
	0.08 g	0.08 g	WWC-1-8	
	0.01 g	0.03 g	WWC-3-1	
	0.02 g	0.06 g	WWC-3-2	
1:3	0.04 g	0.12 g	WWC-3-4	
	0.06 g	0.18 g	WWC-3-6	
	0.08 g	0.24 g	WWC-3-8	

Table S1. Specific dosage and the corresponding sample designations.

Table S2. Quantitative analyses of the fitted XPS peaks of 1T-WS₂ and 2H-WS₂.

	2H phase	Peaks BE (eV)	35.02	32.66
		Area	10787.43	13683.78
VV VVC-1-0	1T phase	Peaks BE (eV)	34.18	31.95
		Area	6930.8	8791.84
	2H phase	Peaks BE (eV)	35.12	32.98
		Area	11220.54	14265.61
VV VVC-5-0	1T phase	Peaks BE (eV)	34.09	31.87
		Area	2844.80	3573.97

For WWC-1-6:

$$[1T]\% = \frac{[1T]}{[1T] + [2H]} \times 100\% = \frac{15722.64}{15722.64 + 24471.21} \times 100\% = 39.12\%$$

For WWC-3-6: $[1T]\% = \frac{[1T]}{[1T] + [2H]} \times 100\% = \frac{6418.77}{6418.77 + 25486.15} \times 100\% = 20.11\%$

Photocatalysts	H ₂ (mmol/g/h)	Illumination	Sacrificial agent	Ref.
CdS/g-C ₃ N ₄	0.392	3 W LED	20% CH₃OH	1
		(full spectrum)		
CdS/TiO ₂	1.5	300 W Xe lamp	0.5 M Na ₂ S and	2
		(>420 nm)	0.5 M Na ₂ SO ₃	
CdS/Ti ₃ C ₂	2.407	300 W Xe lamp	10 wt% lactic acid	3
		(>420 nm)	solution	
CdS/g-C ₃ N ₄	4.15	300 W Xe lamp	$0.35 \text{ M} \text{ Na}_2\text{S} \text{ and}$	4
		(>400 nm)	0.25 M Na ₂ SO ₃	
CdS/Ti ³⁺ /N-TiO ₂	1.118	300 W Xe lamp	$0.35 \text{ M} \text{ Na}_2\text{S} \text{ and}$	5
		(>420 nm)	0.25 M Na ₂ SO ₃	
CdS/Cu ₂ O/g-C ₃ N ₄	1.84	300 W Xe lamp	20% CH ₃ OH	6
		(AM 1.5G)		
NiS/CdS	2.18	300 W Xe lamp	$0.35 \text{ M} \text{ Na}_2\text{S} \text{ and}$	7
		(>420 nm)	0.25 M Na ₂ SO ₃	
NiS/CdS	0.15	300 W Xe lamp	10 wt% lactic acid	8
		(>420 nm)	solution	
CdS/g-C ₃ N ₄ /CuS	1.15	300 W Xe lamp	$0.35 \text{ M} \text{ Na}_2\text{S} \text{ and}$	9
		(>420 nm)	0.25 M Na ₂ SO ₃	
CdS/Co-MoS _x	0.54	300 W Xe lamp	10 wt% lactic acid	10
		(>420 nm)	solution	
1T-WS ₂ /2H-	4.67	300 W Xe lamp	0.35 M Na ₂ S and	This
WS ₂ /CdS		(>420 nm)	0.25 M Na ₂ SO ₃	work

Table S3. Photocatalytic hydrogen production performance of photocatalystsreported in literatures.

Table S4. Carrier densities of pure CdS and 1T-WS2/2H-WS2/CdS heterostructures(WWC-1-6 and WWC-3-6).

Samples	Carrier density cm ⁻³
pure CdS	7.16×10 ¹⁸
WWC-1-6	1.78×10 ¹⁹
WWC-3-6	1.45×10 ¹⁹

Table S5. Time-resolved PL decay curve parameters obtained by double-exponential

function simulation.					
Samples	τ ₁ (ns)	τ_2 (ns)	A1 (%)	A ₂ (%)	τ _{av} (ns)
pure CdS	1.12	10.13	66.22	33.78	4.16
pure WS_2	1.52	17.61	64.52	35.48	7.23
WWC-1-6	1.38	12.13	63.93	36.07	5.25

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