Supporting Information

Customizing Dumbbell-shaped Heterostructured Artificial Photosystems Steering Versatile Photoredox Catalysis

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Experimental Section

1. Materials

The following chemicals were used as received without further purification: All chemicals were used without further purification. Deionized water (DI H_2O, Millipore, 18.2 MΩ cm resistivity) was used for all experiments. Cadmium acetate ($C_4H_6CdO_4·2H_2O$), thioacetamide (CH_4N_2S), ethylenediamine (EDA), diethylenetriamine (DETA), sodium molybdate ($Na_2MoO_4·2H_2O$), silver nitrate ($AgNO_3$), Copper chloride ($CuCl_2·2H_2O$). Above-mentioned all materials were directly employed without further purification.

2. Preparation of CdS nanowires (NWs)

CdS nanowires were prepared by the solvothermal method. In a typical synthesis step, 2.8 g of cadmium acetate $C_4H_6CdO_4·2H_2O$ was dissolved in 50 mL of ethylenediamine. Then 1.4 g of CH_4N_2S was added to the solution and stirred again for about 1 h. After transferring to the reactor, it was kept at 160 ℃ for 18 h. The obtained precipitate was washed with distilled water and ethanol 3 times or more and finally dried in an oven at 60 ℃ overnight.[1]

3. Preparation of CdS/MoS_2 nanodumbbell binary nanocomposite

0.125 g of the previously synthesized cadmium sulfide was dispersed in 20 mL of diethylenetriamine and 4 mL of water. After 15 min of ultrasonic dispersion, sodium molybdate and thioacetamide were added. The resulting mixture was placed in an autoclave and reacted at 200 ℃ for 18 h. The amounts of molybdenum source and sulfur source were adjusted to obtain CM^1, CM^2, CM^3 and CM^4 binary photocatalysts at the ratios of 10 mg/40 mg, 20 mg/80 mg, 30 mg/120 mg, and 40 mg/160 mg, respectively.

4. Preparation of bare MoS_2

In a typical procedure, 20 mg sodium molybdate and 80 mg thioacetamide were added into a mixed solvent

containing 20 mL diethylenetriamine (DETA) and 4 mL DI water. After stirring for 1 h, the solution was transferred into 50 mL Teflon-lined autoclave, sealed and heated at 200 °C for 18 h, and then allowed to cool to room temperature naturally. The resulting precipitates were collected by centrifuging, washed with ethanol and DI water three times until the organic molecules were completely removed, and then dried under vacuum at 60 ℃ overnight.[2]

5. Preparation of CdS/MoS_2/Ag_2S nanodumbbells ternary heterostructure

The CdS/MoS_2/Ag_2S nanodumbbells heterostructures were synthesized through a cation exchange strategy using the CdS/MoS_2 (CM^2) nanodumbbells as the precursor. Specifically, 100 mg CM^2 nanodumbbell catalyst was dispersed in 100 mL deionized water under ultrasonic treatment. Then, 0.2 mL $AgNO_3$ aqueous solution (0.01 M) was added into the above suspension, vigorously stirred for 30 min, the samples precipitate and are centrifuged, washed and dried overnight at 60 ℃. The obtained sample is labeled as CMA.

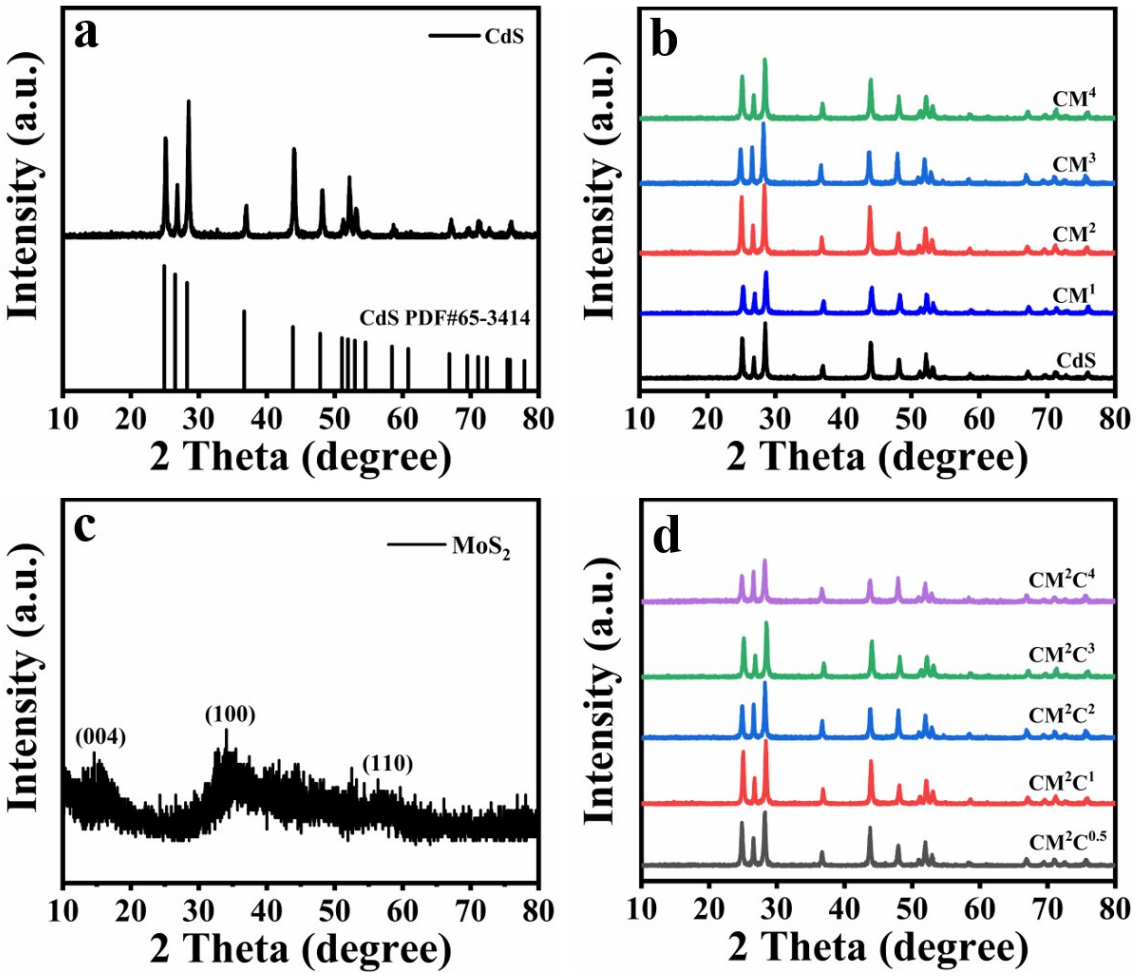

Figure S1. XRD patterns of (a) CdS, (b) CM^x (x=1, 2, 3, 4), (c) MoS_2, and (d) CM^2C^x (x=0.5, 1, 2, 3, 4).

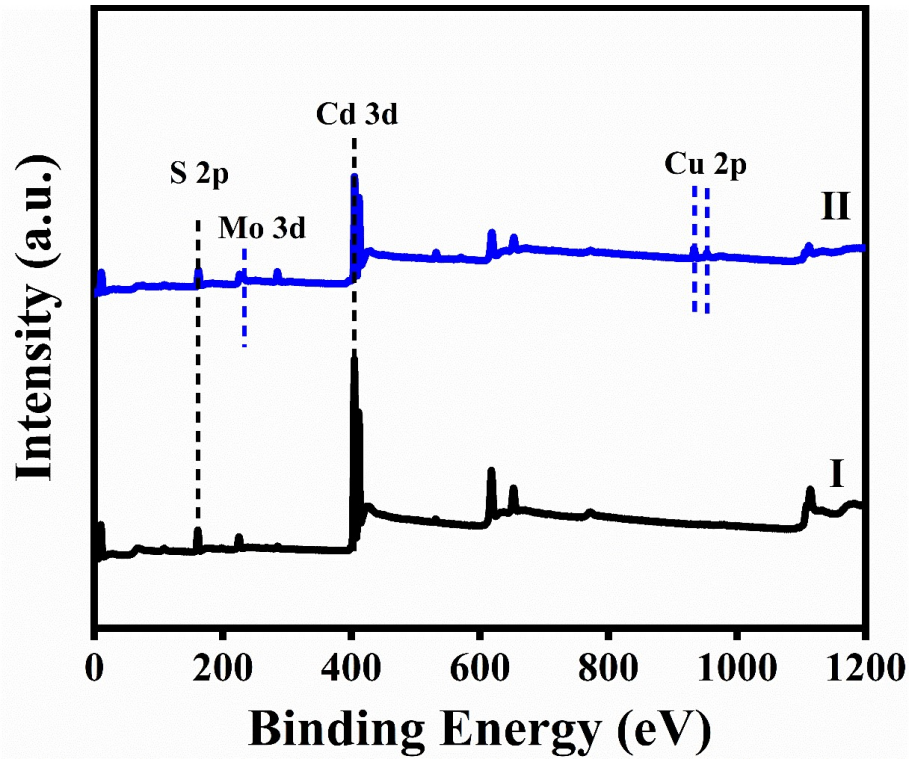

Figure S2. Survey spectrum of (I) CdS and (II) CM^2C^1.

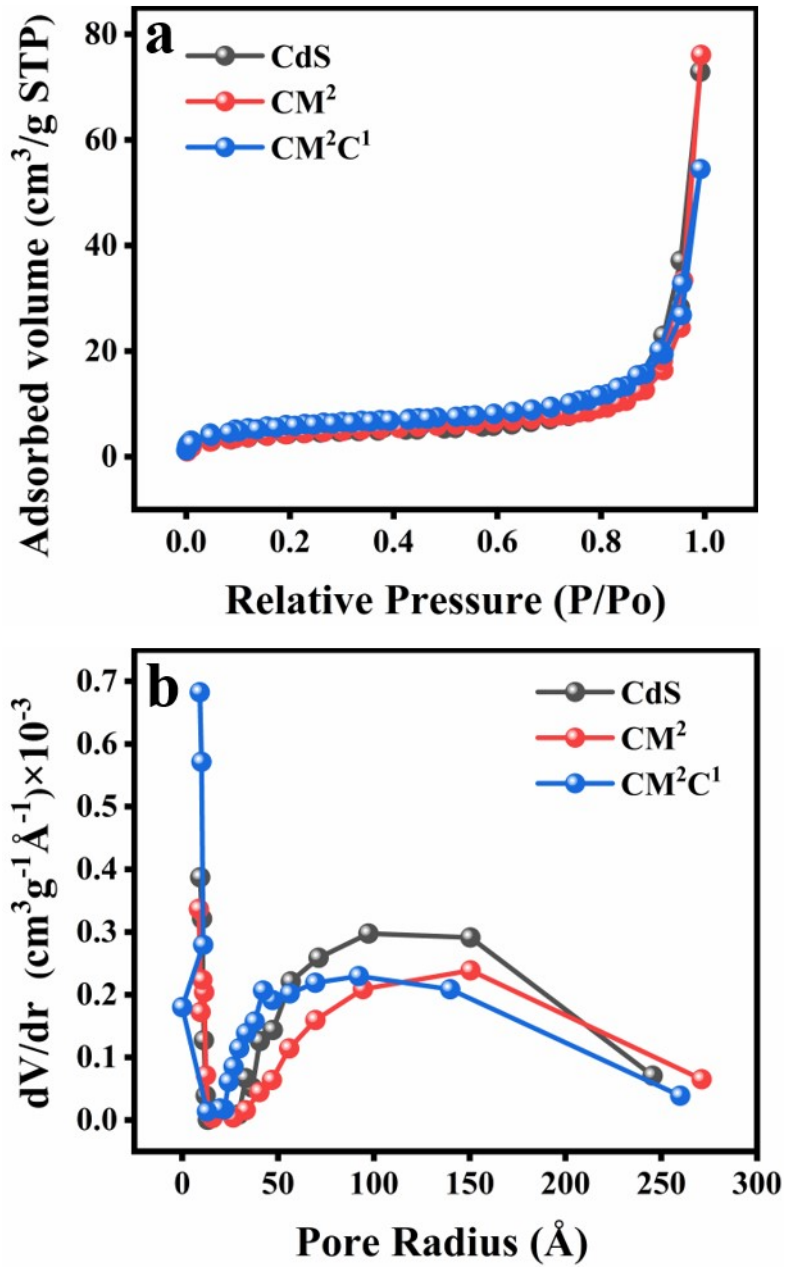

Figure S3. BET results of CdS, CM^2 and CM^2C^1.

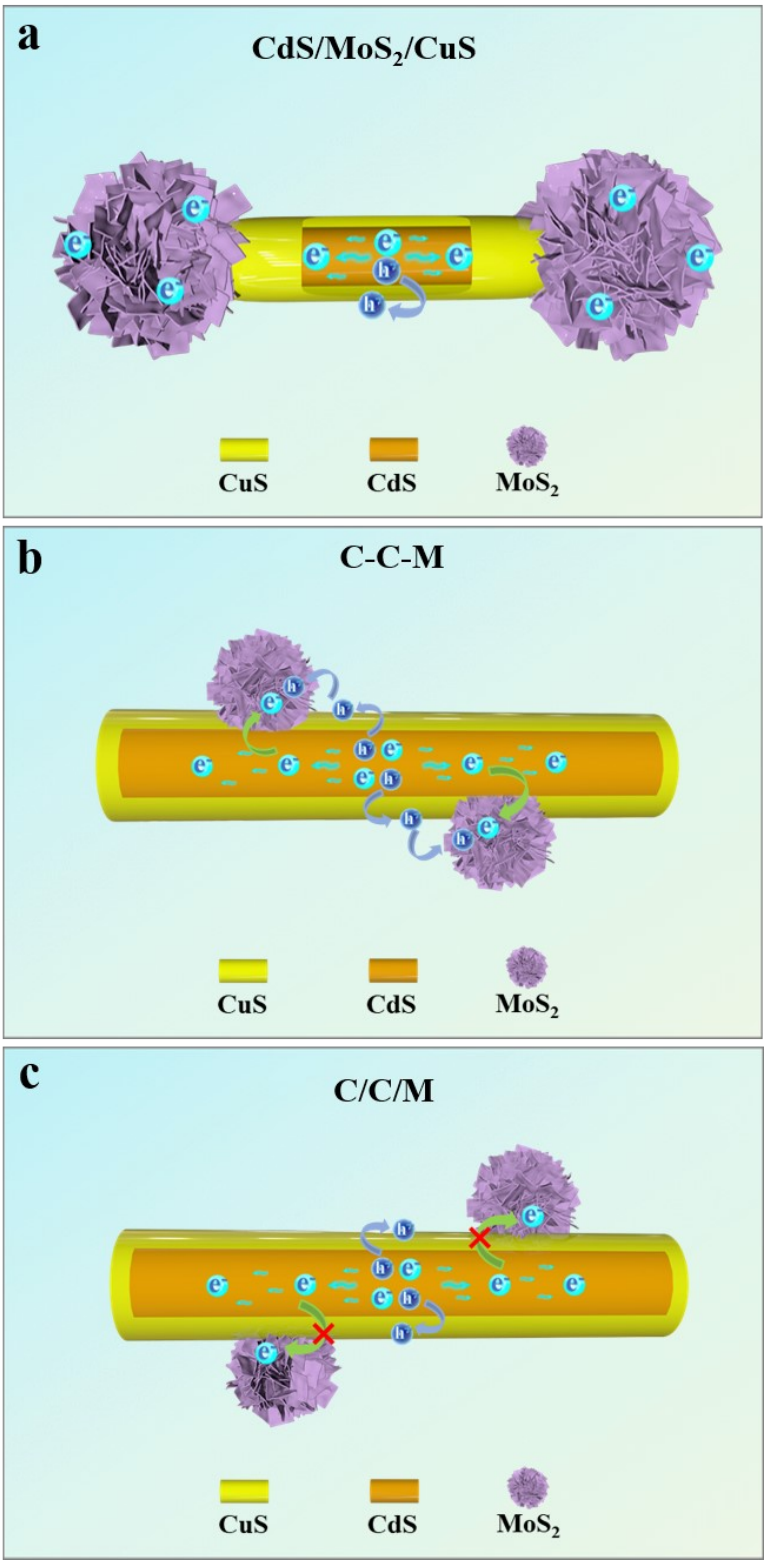

Figure S4. Schematic diagram of photoelectron transfer over the (a) $CdS/MoS_2/CuS$, (b) C-C-M and (c) C/C/M heterostructure.

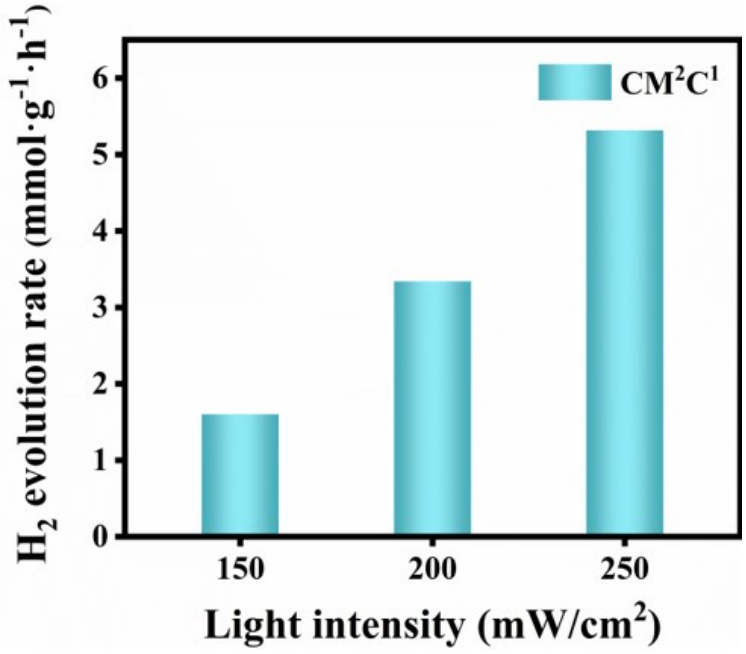

Figure S5. Photoactivities of CM^2C^1 under different light intensity.

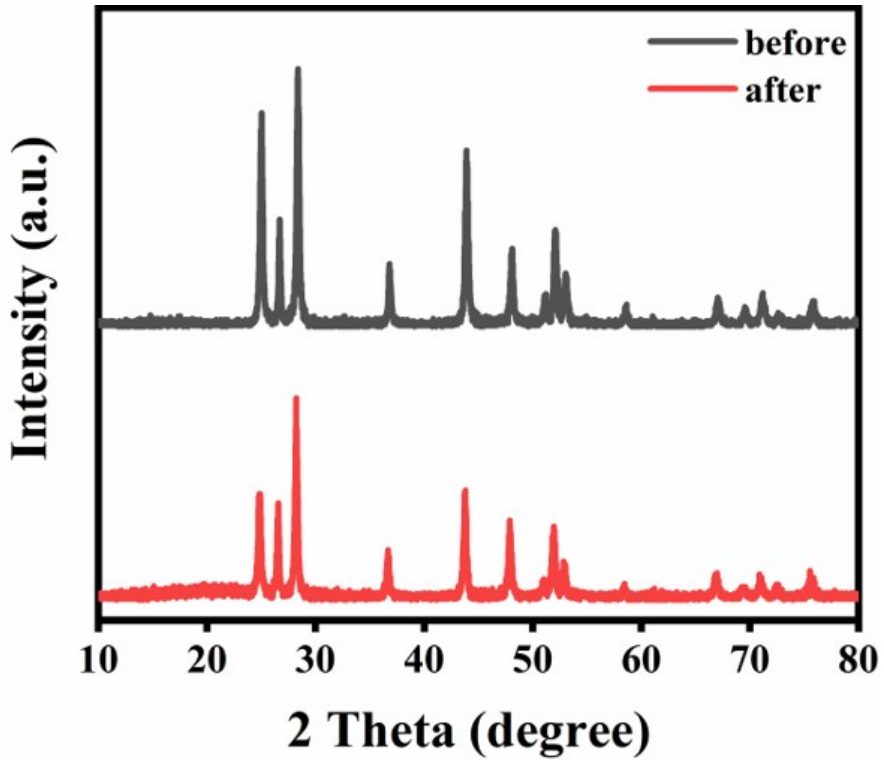

Figure S6. (a) XRD spectra of CM^2C^1 before and after cyclic reaction.

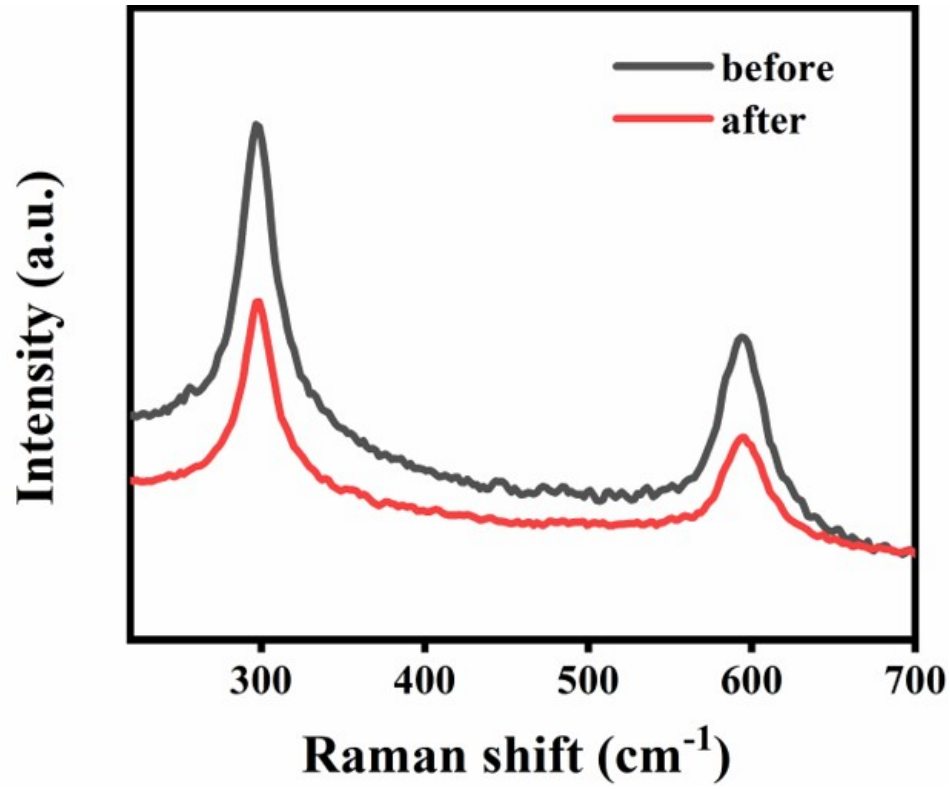

Figure S7. (a) Raman spectra of CM^2C^1 before and after cyclic reaction.

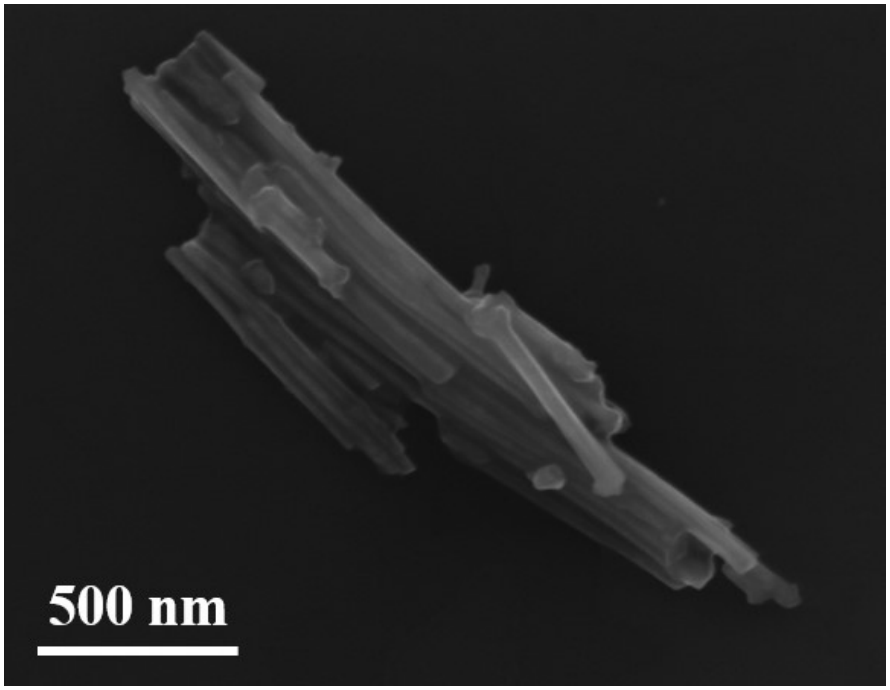

Figure S8. (a) SEM spectra of CM^2C^1 after cyclic reaction.

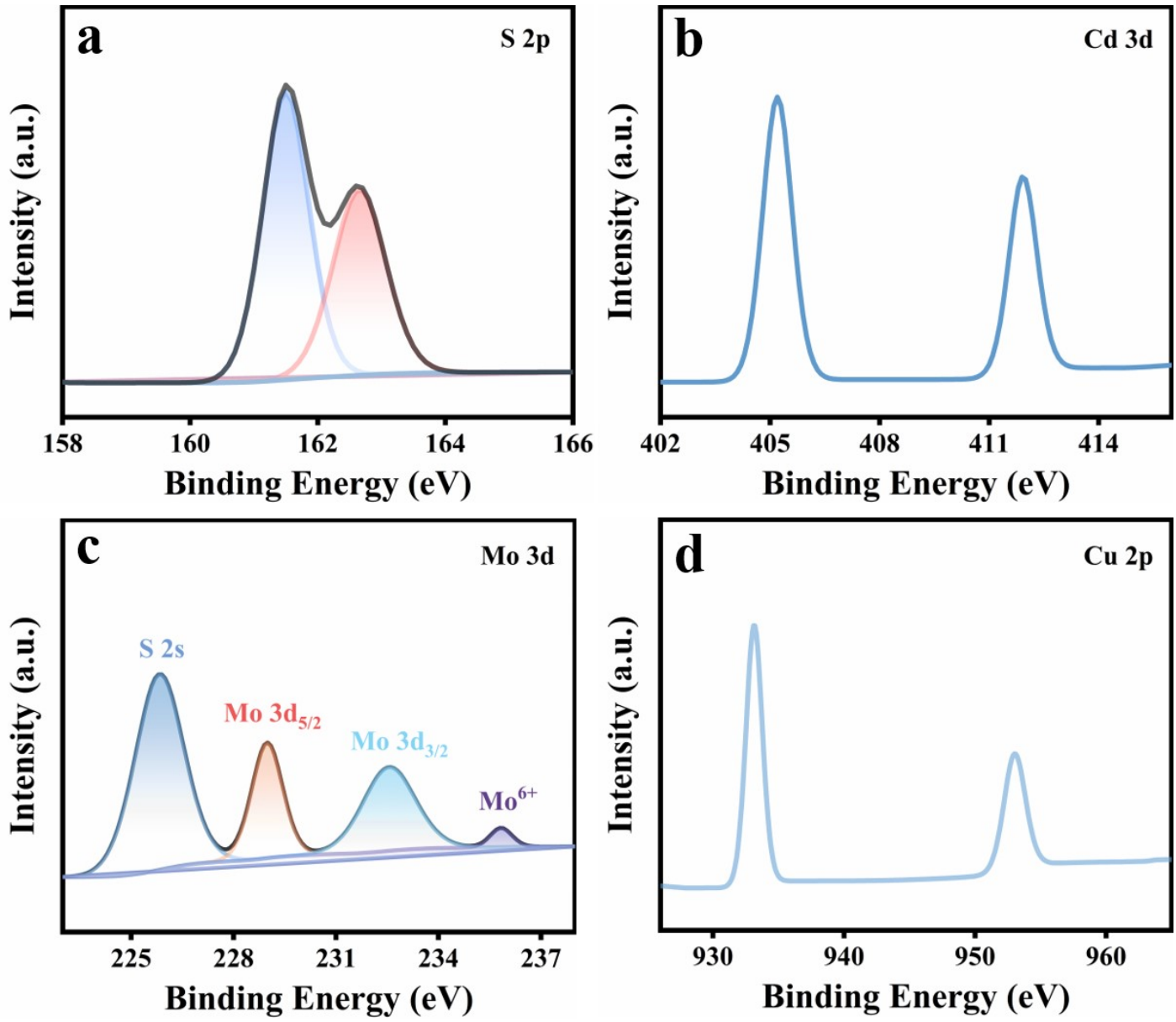

Figure S9. High-resolution (a) S 2p, (b) Cd 3d, (c) Mo 3d and (d) Cu 2p spectra of CM^2C^1 after cyclic reaction.

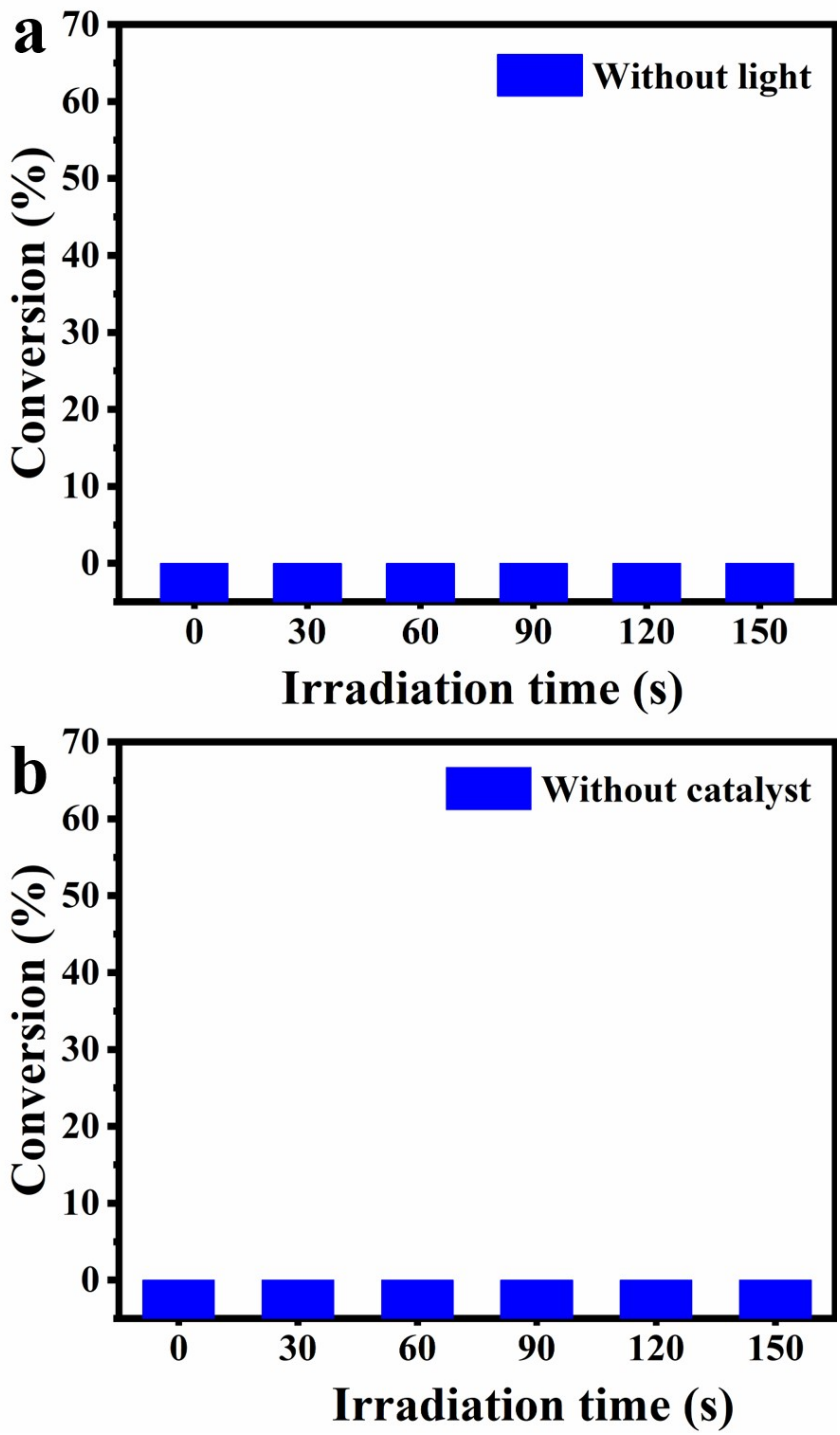

Figure S10. Blank experiments for photocatalytic reduction of 4-NA (a) without catalyst or (b) light irradiation.

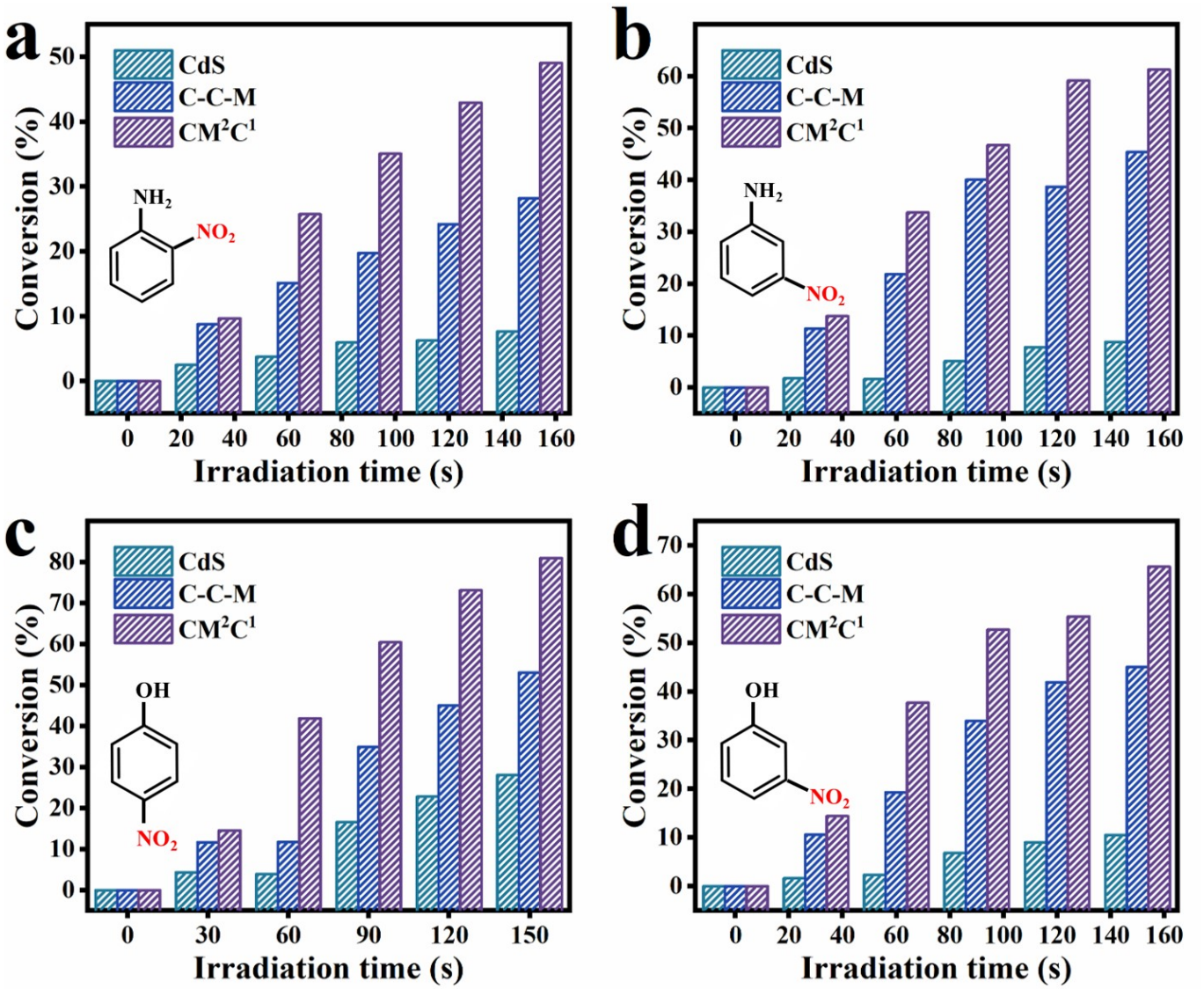

Figure S11. Photoactivities of CdS, C-C-M, and CM^2C^1 towards the photoreduction of (a) 2-NA, (b) 3-NA, (c) 4-NP and (d) 3-NP.

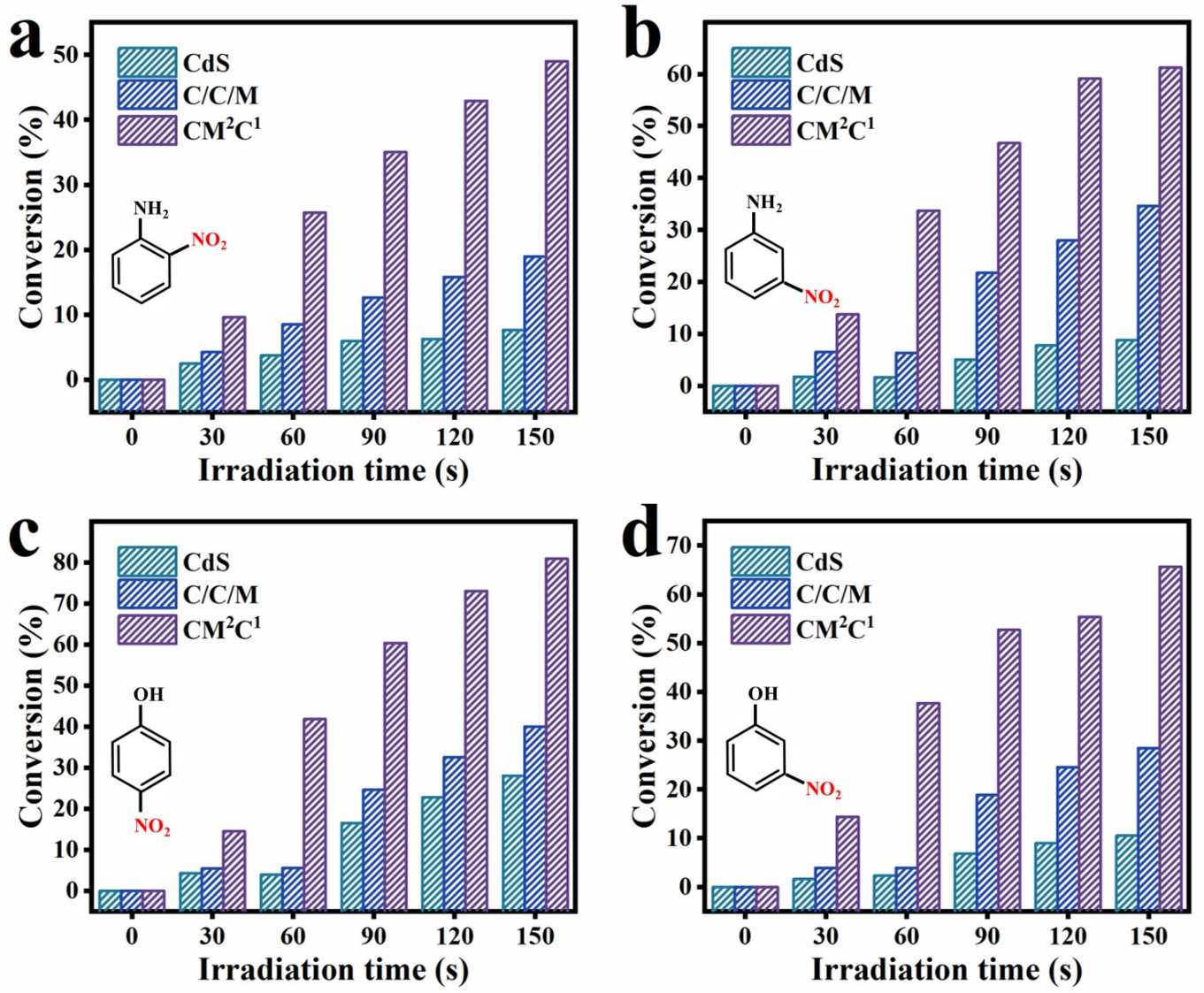

Figure S12. Photoactivities of CdS, C/C/M, and CM^2C^1 towards photoreduction of (a) 2-NA, (b) 3-NA, (c) 4-NP and (d) 3-NP.

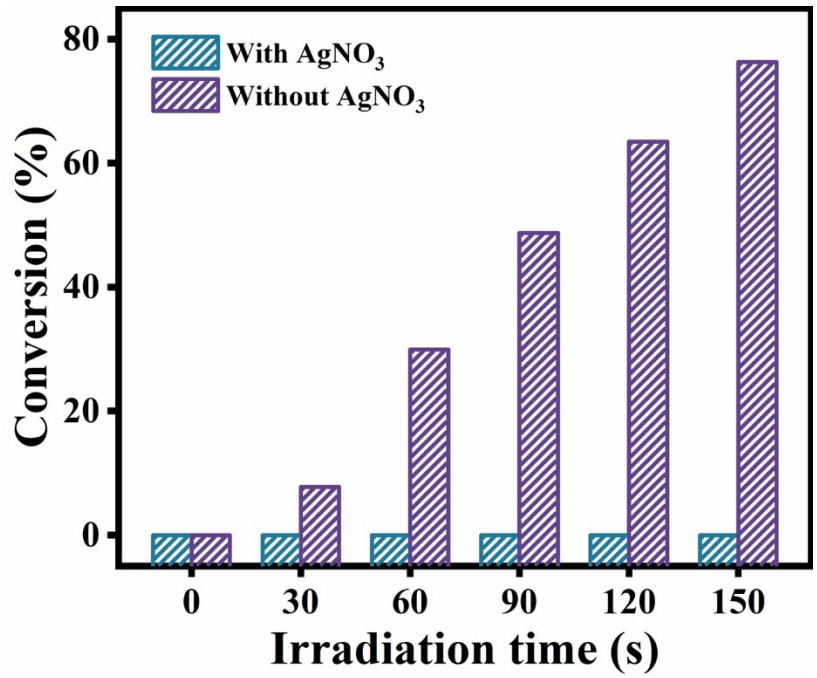

Figure S13. Photoactivities of CM^2C^1 towards photoreduction of 4-NA with and without adding $AgNO_3$ as the electron scavenger.

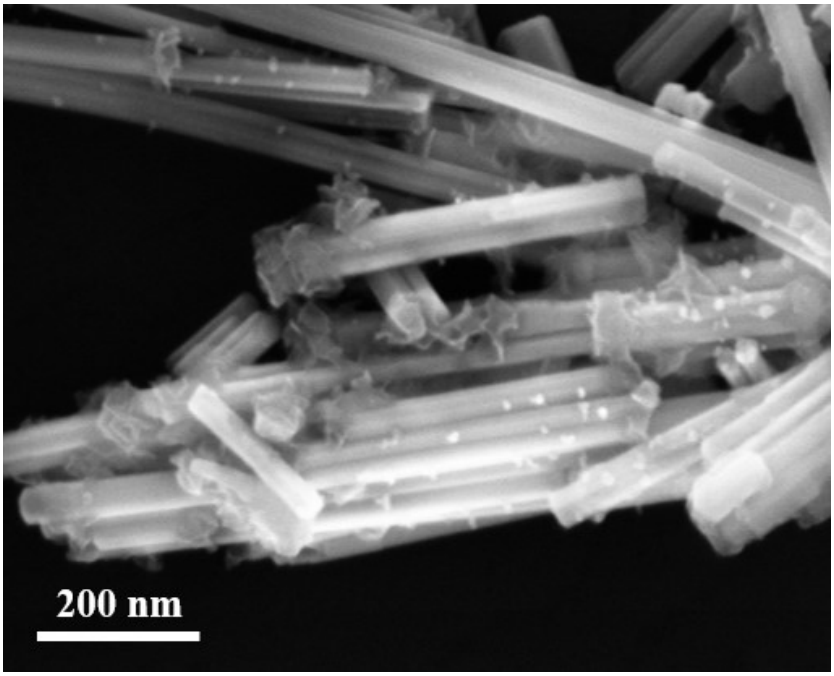

Figure S14. SEM image of CMA.

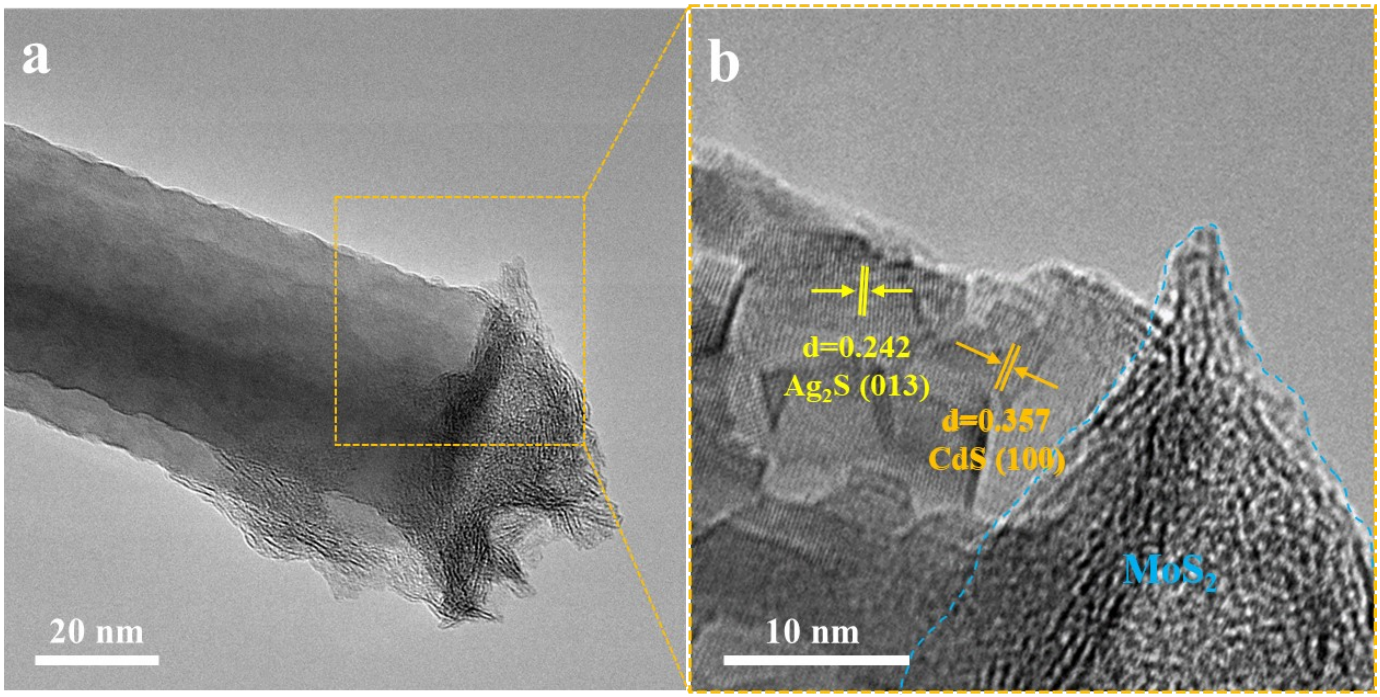

Figure S15. (a) TEM and (b) HRTEM image of CMA.

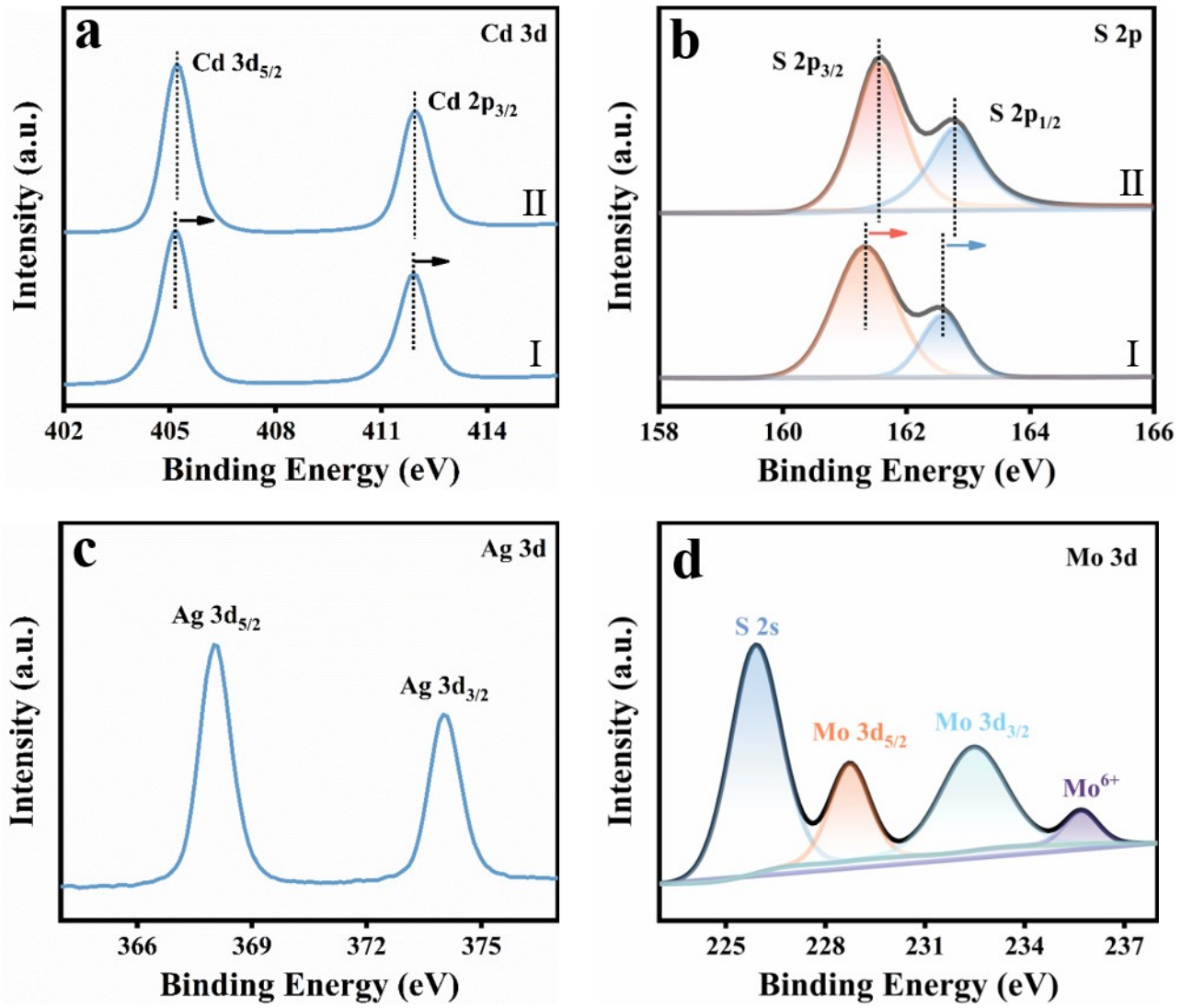

Figure S16. High-resolution (a) Cd 3d, (b) S 2p of (I) CdS and (II) CMA; high-resolution (h) Ag 3d and (i) Mo 3d of CMA.

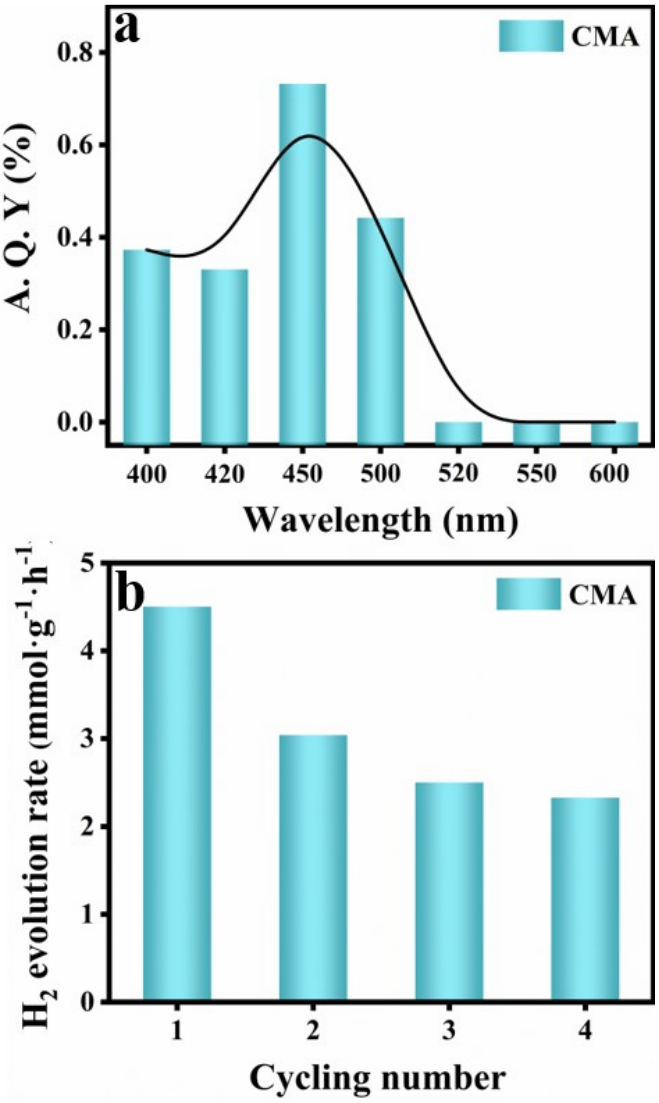

Figure S17. (a) A.Q.Y result of CMA under monochromatic light irradiation; (b) photostability of CMA.

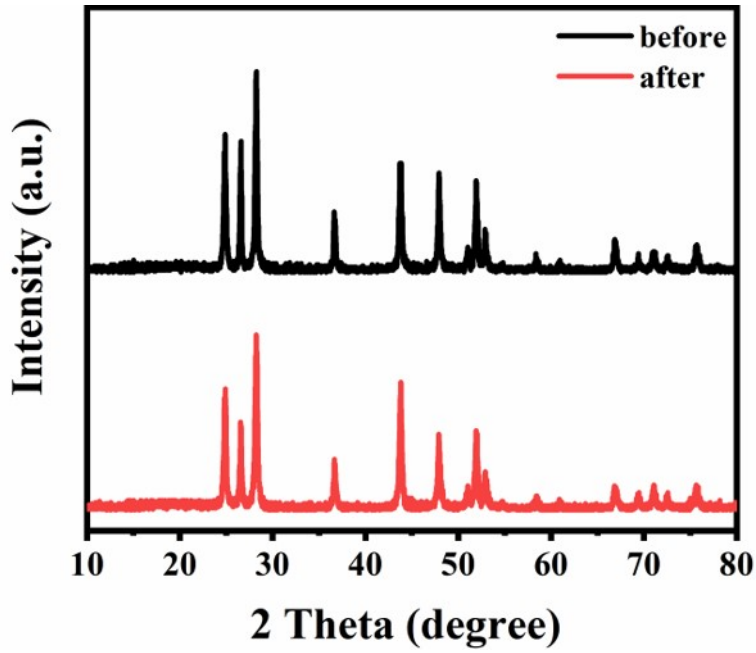

Figure S18. (a) XRD spectra of CMA before and after cyclic reaction.

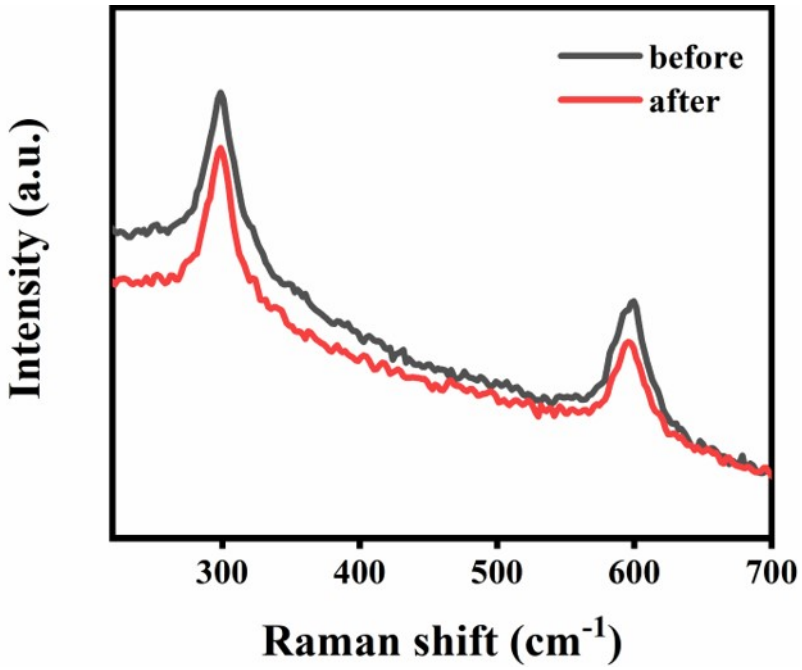

Figure S19. (a) Raman spectra of CMA before and after cyclic reaction.

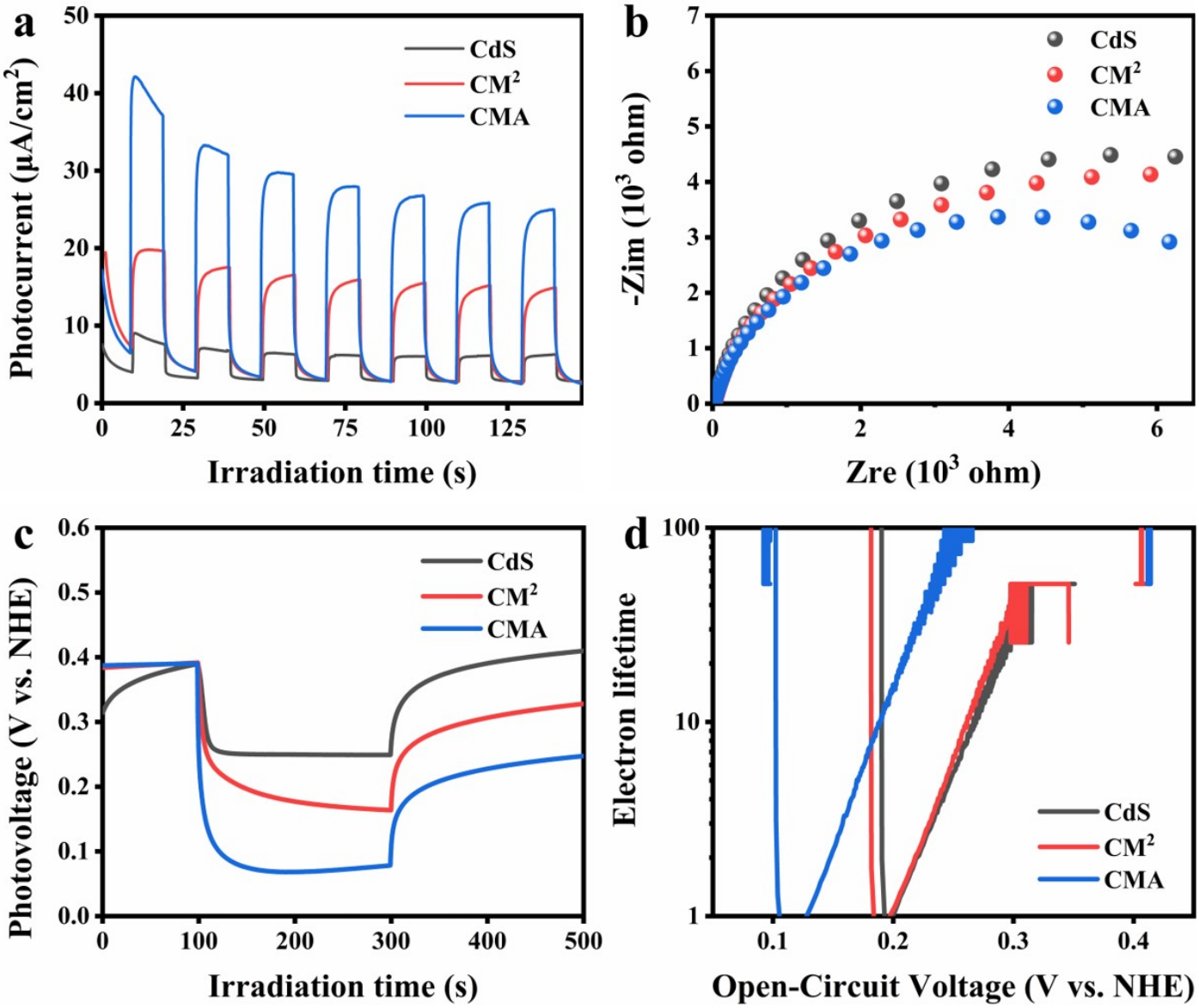

Figure S20. (a) I-t, (b) EIS (c) OCVD and (d) electron lifetime of CdS, CM^2 and CMA under visible light (λ > 420 nm) irradiation.

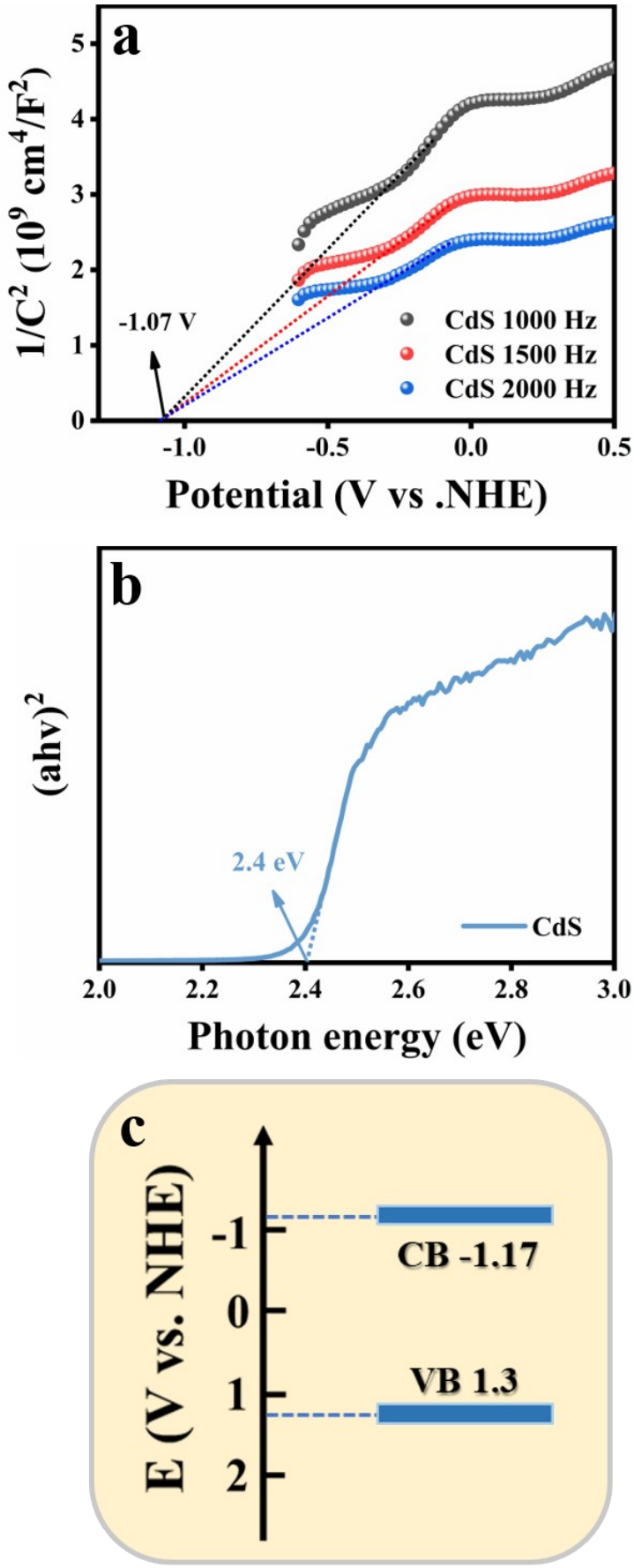

Figure S21. (a) M-S results, (b) bandgap determination, and (c) diagram showing the energy levels of CdS.

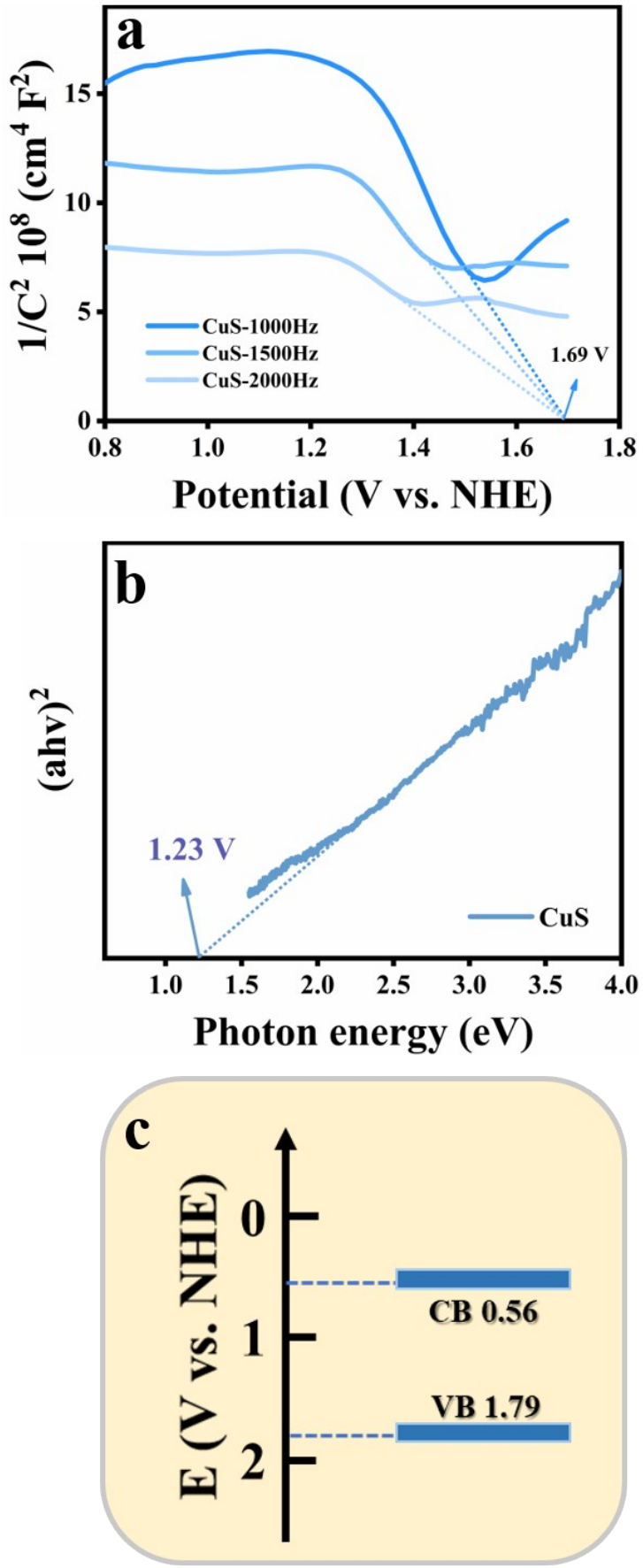

Figure S22. (a) M-S results, (b) bandgap determination, and (c) diagram showing the energy levels of CuS.

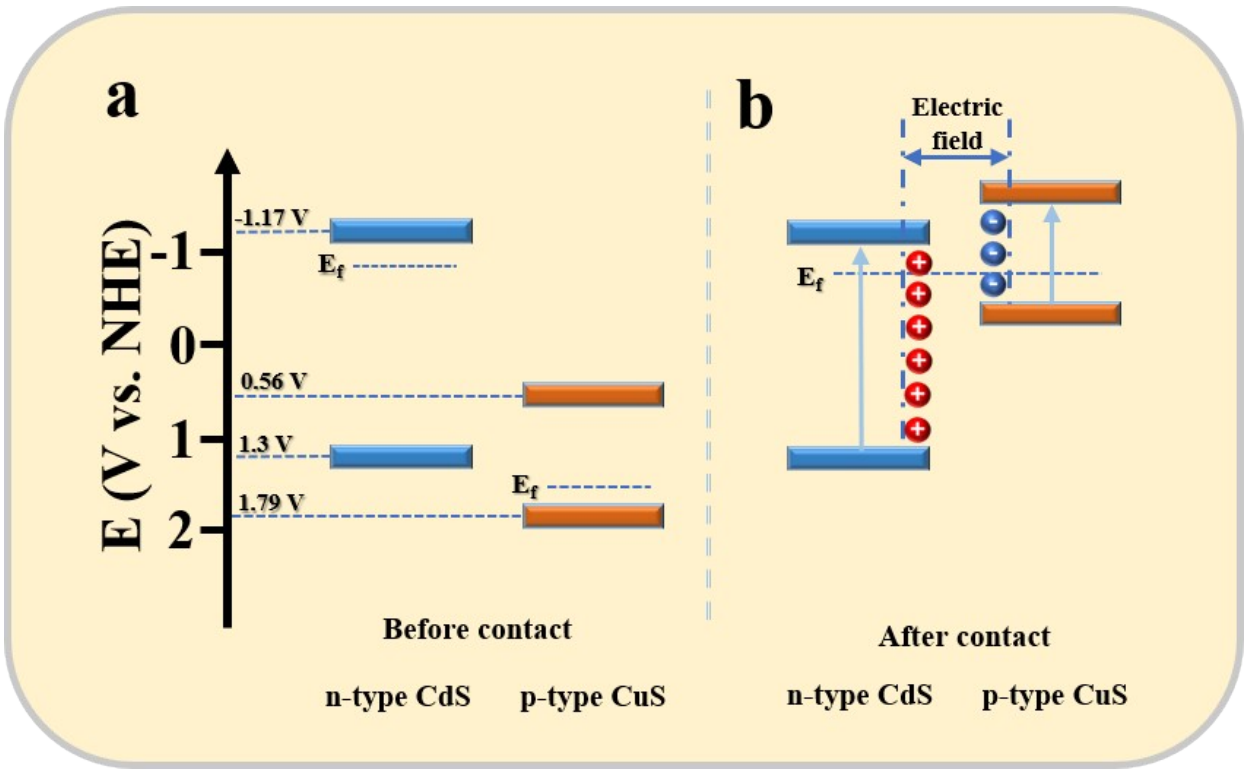

Figure S23. Energy band diagram of CdS/CuS heterostructure before and after contact.

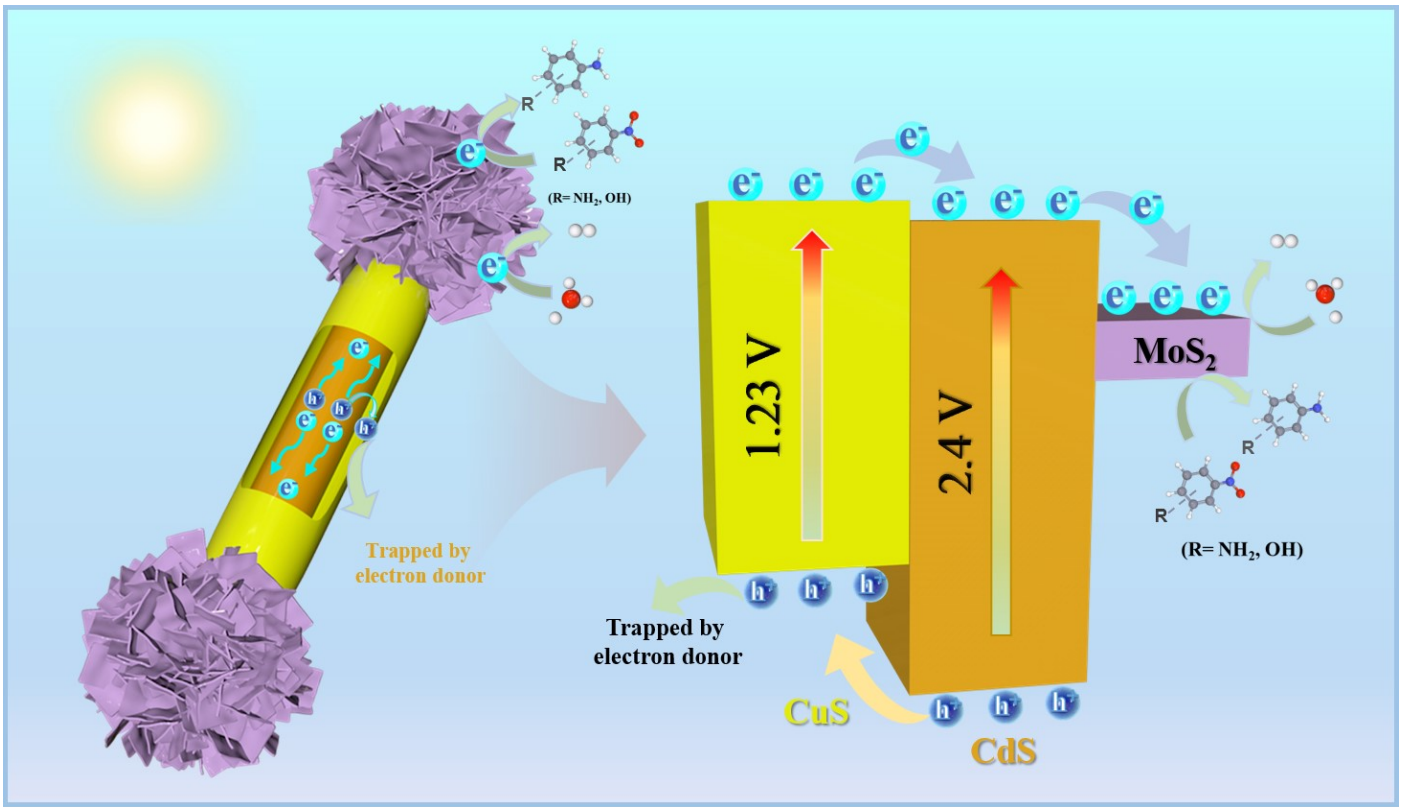

Figure S24. Schematic illustration of the photocatalytic mechanism of CdS/MoS_2/CuS heterostructure.

Table S1. Peak position with corresponding functional groups for CM^2C^1 and CdS.

Peak position (cm^{-1})	***CM^2C^1***	***CdS***
3435	N-H stretching vibration	N-H stretching vibration[3]
1637	O-H deformation vibration	O-H deformation vibration[4]
2927＆2848	-CH_2- stretching vibration	-CH_2- stretching vibration[5]

Table S2. Chemical bond species for different photoelectrodes.

Element	*CdS (eV)*	*CM²C¹*	*Chemical Bond Specie*
S $2p_{1/2}$	162.6	162.65	S^{2-}[2, 6]
S $2p_{3/2}$	161.37	161.5	S^{2-}[2, 6]
Cd $3d_{3/2}$	411.89	411.95	Cd^{2+}[7]
Cd $3d_{5/2}$	405.16	405.21	Cd^{2+}[7]
Cu $2p_{1/2}$	/	953.05	Cu^{2+}[8]
Cu $2p_{3/2}$	/	933.16	Cu^{2+}[8]
Mo $3d_{5/2}$	/	228.93	Mo^{4+}[9]
Mo $3d_{3/2}$	/	232.27	Mo^{4+}[9]
Mo $3d_{3/2}$	/	235.88	Mo^{6+}[10]
S 2s	/	225.87	S^{2-}[1]

Table S3. Specific surface area, pore volume and pore size of CdS, CM^2 and CM^2C^1.

Samples	*SBET (m^2/g)[a]*	*Total pore volume (cm^3/g)[b]*	*Average pore size (nm)[c]*
CdS	***14.47***	***0.11***	***11.03***
CM^2	***14.79***	***0.11***	***8.12***
CM^2C^1	***20.00***	***0.08***	***10.49***

Table S4. Comparison on the photocatalytic activity of this work with the previously reported CdS-based Photocatalytic systems.

Number	*Materials*	*Sphere*	*Light source*	*Sacrificial reagent*	*Activity (μmol/g/h)*	*Reference*
This work	$CdS/MoS_2/CuS$	dumbbell-shaped	Visible light (λ > 420 nm)	0.25 M Na_2S and 0.35 M Na_2SO_3	4075	/
1	CdS/CoOx	core-shell nanorods	Visible light (λ > 420 nm)	0.35 M Na_2S and 0.25 M Na_2SO_3	3500	Appl. Catal. B Environ. Energy, 2018, 234, 109-116.
2	5.0%-Ag_2S/CdS	nanowires	Visible light (λ > 420 nm)	2 vol% lactic acids	777	RSC Adv., 2021, 11, 28211-28222.
3	1% CSs/CdS	spheres	Visible light (λ > 420 nm)	0.5 M Na_2S and 0.5 M Na_2SO_3	3887	Catal. Today, 2017, 281, 662-668.
4	NiPx/MoS_2/NiS/CdS	nanowires	Visible light (λ > 400 nm)	5 g/L glucose	297	J. Am. Ceram. Soc., 2021, 104, 5307-5316.
5	g-C_3N_4/CdS/NiS	nanorods	Visible light (λ > 420 nm)	10% triethanolamine	2563	J. Mater. Chem. A, 2015, 3, 18244-18255.
6	NiS/CdS/h-TiO_2	nanosheets	Visible light (λ > 420 nm)	0.35 M Na_2S and 0.25 M Na_2SO_3	2149	Appl. Surf. Sci., 2019, 476, 378-386.
7	2%Ni_2P/CdS NRs	nanorods	Visible light (λ > 400 nm)	Na_2S and Na_2SO_3	2602	Catalysts, 2022, 12, 417.
8	3DOM TiO_2-Au-CdS	nanoparticles	Visible light (λ > 400 nm)	0.1 M Na_2S and 0.1 M Na_2SO_3	3500	Nano Energy, 2018, 47, 266-274.
9	CdS/Ni-MOF (40)	spheres	Visible light (λ > 420 nm)	6% lactic acid	2508	Appl. Surf. Sci., 2020, 522, 146356.
10	CdS–Ag_2S	Hierarchically nanostructured	Visible light (λ > 420 nm)	10% triethanolamine	380	Appl. Surf. Sci., 2019, 470, 196–204.

Table S5. Chemical bond species for different photoelectrodes.

Element	*CdS (eV)*	*CMA*	*Chemical Bond Specie*
S $2p_{1/2}$	162.6	162.79	S^{2-}[2, 6]
S $2p_{3/2}$	161.37	161.57	S^{2-}[2, 6]
Cd $3d_{3/2}$	411.89	411.94	Cd^{2+}[7]
Cd $3d_{5/2}$	405.16	405.21	Cd^{2+}[7]
Ag $2p_{3/2}$	/	374.03	Cu^{2+}[11]
Ag $2p_{5/2}$	/	368.04	Cu^{2+}[11]
Mo $3d_{5/2}$	/	228.93	Mo^{4+}[9]
Mo $3d_{3/2}$	/	232.27	Mo^{4+}[9]
Mo $3d_{3/2}$	/	235.88	Mo^{6+}[10]
S 2s	/	225.87	S^{2-}[1]

References

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