A synergistic photothermal effects for enhanced hydrogen evolution of S-scheme CdS@H_{0.95}MoO₃ photocatalyst: Mechanistic insights and

theory calculations

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1. Experimental section

1.1 Experimental materials

Ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) and anhydrous ethanol (Etoh) were produced by Fuchen (Tianjin) Chemical Reagent Co., Ltd. Concentrated nitric acid (H_2NO_3) was obtained by National Pharmaceutical Group Chemical Reagent Co., Ltd. Cadmium nitrate tetrahydrate ($Cd(NO_3)_2\cdot 4H_2O$) was bought by Shanghai Mackin Biochemical Co., Ltd. The above reagents were used directly without secondary treatment.

1.2 Preparation of MoO₃

MoO₃ was synthesized using the solvothermal method. First, 1.5 mmol of ammonium molybdate was dissolved in 40 mL of deionized water. Then, 5 mL of concentrated nitric acid was added and the mixture was stirred on a magnetic stirrer for 30 minutes. The mixed solution was transferred to an autoclave lined with PTFE and placed in a blast-drying oven. It was held at 180°C for 17 hours and cooled to room temperature. The resulting white precipitate was collected by centrifugation and washed several times with anhydrous ethanol and deionized water. Finally, MoO₃ nanorods were obtained by freeze-drying for 8 hours.

1.3 Preparation of needle-like H_{0.5}MoO₃

 $H_{0.5}MoO_3$ was synthesized by reducing MoO₃ with anhydrous ethanol. 0.5 g of MoO₃ was dispersed in 50 mL of anhydrous ethanol and stirred vigorously for 30 minutes. And then the suspension was transferred to the 100 mL PTFE-lined autoclave and stored by heating to 140°C for 12 h. The solution was cooled naturally to room temperature, and the blue precipitate was collected by centrifugation, followed by repeated washing with anhydrous ethanol and deionized water several times. Finally, the blue $H_{0.5}MoO_3$ was obtained via freeze-drying for 8 h.

1.4 Preparation of CMx

CMx was synthesized by precipitating CdS nanoparticles onto the surface of $H_{0.5}MoO_3$. 0.1 g of prepared $H_{0.5}MoO_3$ and 10 mmol TAA were dispersed in the 50 mL anhydrous ethanol solution. After oil bath treatment, the obtained suspension was stirred at 50°C for 1 hour. Then, 0.5 mmol of cadmium nitrate was added to the above mixed solution (cadmium nitrate: TAA=1:20), and the reaction was continued for 12 hours under the same conditions. Subsequently, the reaction solution was cooled, centrifuged, and washed to obtain the precipitate. Finally, the solid powder got by freeze-drying the precipitate for 8 hours was designated CMx. For comparison, pure CdS was also synthesized using a preparation method similar to CMx, but without the addition of $H_{0.5}MoO_3$.

1.5 Preparation of L-CMx

25 mg CMx was dispersed in 50 mL of 10 vol.% lactic acid solution, and the mixed solution was stirred and evacuated for 20 min. Then, the suspension was irradiated ($\lambda \ge 420$ nm) with a xenon lamp for about 2 hours. When the color of the suspension changed from blue to brown, the precipitate was collected by centrifugation, washed repeatedly with anhydrous ethanol and deionized water several times, and finally freeze-dried for 8 h to obtain a blue-green powder named L-CMx. In order to reduce the speed of the transformation of CMx to L-CMx, the wavelength of irradiation was changed to $\lambda \ge 450$ nm to irradiate the suspension for 2 hours. Other conditions were not changed.

In addition, other preparation conditions were kept constant to change the preparation temperature of $H_{0.5}MoO_3$ to 120°C, 160°C and 180°C to obtain L-CMx-120, L-CMx-160 and L-CMx-180 composite samples. The preparation conditions, other than the oil bath temperatures for CMx preparation, were kept unchanged. The temperatures were varied between 20°C, 30°C, 40°C, 60°C, and 80°C to obtain L-CMx-20°C, L-CMx-30°C, L-CMx-40°C, L-CMx-60°C, and L-CMx-80°C composite samples. The preparation conditions were kept unchanged, and composite samples of

L-CMx-0.1, L-CMx-0.25, and L-CMx-0.75 were obtained by adjusting the cadmium nitrate feeding amount to 0.1 mmol, 0.25 mmol, and 0.75 mmol during the preparation of CMx. The preparation conditions remained unchanged, while the ratios of cadmium nitrate and TAA were adjusted to 1:12, 1:16, 1:24, and 1:28 to obtain L-CMx-1:12, L-CMx-1:16, L-CMx-1:24, and L-CMx-1:28 composite samples.

1.6 Preparation of H_{0.95}MoO₃

Disperse 100 mg of L-CMx in 20 mL of deionized water. Then, 10 mL of concentrated nitric acid was added and stirred for 30 minutes. The mixture was centrifuged to collect the blue precipitate, which was washed repeatedly with anhydrous ethanol and deionized water. Finally, it was freeze-dried for 8 hours to obtain $H_{0.95}MoO_3$.

1.7 Characterization

The surface morphology of nanomaterials was observed using a cold field emission scanning electron microscope (Regulus 8220) manufactured by Hitachi, Japan. High-resolution transmission electron micrographs (TEM), transmission electron micrographs (HRTEM), selected-area electron diffraction maps (SAED), and elemental mapping maps were obtained using a field-emission transmission electron microscope (Talos 200X) manufactured by FEI, USA. The material was subjected to X-ray crystal diffraction analysis using a Rigaku Ultima IV X-ray diffractometer from Japan. Additionally, full and fine XPS spectra were collected using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer from the United States. Ultraviolet-visible absorption spectra (UV-Vis) and ultraviolet-visible-near-infrared absorption spectra (UV-Vis-NIR) were obtained using spectrophotometers UV-1800 and UV-3600 manufactured by Shimadzu, Japan. A three-electrode system was employed, comprising an Ag/AgCl electrode as the reference electrode and a platinum sheet electrode as the counter electrode. The samples were coated on indium tin oxide (ITO) conductive glass with an area of 1 cm² as the working electrode. The transient photocurrent spectra (PC), electrochemical impedance curves (EIS) and Mott-Schottky curves were obtained from the electrochemical testing of different materials on a CHI 760E electrochemical workstation (Shanghai Chenhua, China).

1.8 Photocatalytic hydrogen precipitation performance testing

10 mg L-CMx was dispersed in 50 mL of 10 vol% lactic acid solution, and the mixed solution was transferred to a 150 mL reactor connected to a glass system used for photocatalytic hydrogen production test (CEL-PAEM-D6, CEAULIGHT, Beijing). A vacuum pump was taken to remove the air from the glass system prior to the photocatalytic experiments and maintain an airtight negative pressure environment. A 300 W xenon lamp (PLS-SXE300) was used as the light source ($\lambda \ge 420$ nm) to irradiate the reactor for the photocatalytic hydrogen production experiments. Distance of light source from sample 15 cm. The generated gas was analyzed by online gas chromatography (GC7920-7F2A). And sample was taken at an average hourly interval within four hours of the reaction to calculate the average rate of hydrogen evolution in the catalyst.

The apparent quantum yield (AQY) of L-CMx was estimated by adjusting the incident light wavelengths to 400 nm, 450 nm, and 500 nm through the filter under the condition of the light area of about 9.82 cm², and the AQY was calculated as follows: $2 \times Number of evolved by drogen moleculas$

$$AQY = \frac{2 \times Number of volvea hydrogen molecules}{Number of incident photons} \times 100\%$$

1.9 DFT calculation method

All spin-polarized density functional theory (DFT) calculations were performed using the Perdew-Burke-Ernzerhof (PBE) ^[S1] formulation in the generalized gradient approximation (GGA) using first principles ^[S2, S3]. The projection-augmented wave (PAW) potential ^[S4, S5] was chosen to describe the ionic nuclei, and valence electrons were accounted for using a plane-wave basis set with a kinetic energy cutoff of 450 eV. Kohn-Sham orbital partial occupancies were allowed using the Gaussian smearing method and a width of 0.05 eV. If the energy change was less than 10⁻⁵ eV, the electronic energy was considered self-consistent. If the energy change was less than 0.02 eV Å⁻¹, the geometry optimization was considered convergent. To eliminate the artificial interactions between the periodic images, the 18 Å vacuum layer was usually added to the surface. The DFT+D3 method with empirical correction in the Grimme scheme [S6, S7] was used to describe the weak interaction. To account for the strong correlation effects of the transition metal in the structure, the spin-dependent GGA plus Hubbard correction U method [S8, S9] was used for all calculations, and the effective Ueff parameters are 4 eV for Mo. For these calculations, the Dipole correction has been taken into account.



Figure S1. (a) SAED pattern of CMx. (b) High-angle annular dark field image of CMx and elements mapping of Mo, O, Cd, and S.



Figure S2. (a) XPS survey spectra of MoO_{3-x}, CdS, CMx and L-CMx. (b) Cd 3d, and (c) S 2p spectra of CdS, CMx and L-CMx.



Figure S3. Raman spectra of different samples.



Figure S4. (a) UV-Vis curves of different samples; (b) UV-Vis curves of $H_{0.5}MoO_3$ and $H_{0.95}MoO_3$.



Figure S5. (a) XRD patterns of CMx series samples prepared under oil bath at 30°C, 40°C, 50°C, 60°C and 80°C, respectively. (b) XRD plots of different samples of MoO_{3-x} heated by ethanol as the solvent for 18 h at 100°C, 120°C, 140°C, 160°C and 180°C, respectively.



Figure S6. Photocatalytic hydrogen evolution rates under different catalyst dosages.



Figure S7. XPS nuclear level spectra of (a) Mo 3d, (b) O 1s, (c) Cd 3d and (d) S 2p.



Figure S8. XRD spectra before and after cycling test.



Figure S9. SEM images after round robin testing.



Before

After

Figure S10. Comparison pictures of the reaction solution before and after the reaction (After light treatment, CMx composits have been transformed into L-CMx).



Figure S11. Optimized geometries of (a) CdS(002) and (b) $H_{0.95}MoO_3(400)$.



Figure S12. Work functions of (a) CdS (002) and (b) $H_{0.95}MoO_3$ (400) plane.

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Samples	$E_{VB} (eV)$	$E_{CB} (eV)$	$E_{g}(eV)$
CdS	1.52	-0.94	2.46
MoO ₃	3.38	0.17	3.21
$H_{0.5}MoO_3$	3.04	0.30	2.74
$H_{0.95}MoO_3$	2.73	0.43	2.30

Table S1. E_{VB} , E_{CB} , and E_g values for CdS, MoO₃, $H_{0.5}MoO_3$ and $H_{0.95}MoO_3$.

		5			
Photocatalysts	Heterojunc- tion Scheme	Light Source	Sacrificial reagents	Hydrogen evolution rates (mmol g ⁻¹ h ⁻¹)	Refs
L-CMx	S-scheme	λ≥420 nm	Lactic acid (10 vol.%)	20.90	This work
Cu _{0.5} Cd _{0.5} S/MoO _{3-x}	Z-scheme	$\lambda \geqslant 420 \text{ nm}$	0.35 M Na ₂ S 0.25 M Na ₂ SO ₃	19.28	[S10]
MoO _{3-x} /Mn _{0.3} Cd _{0.7} S	S-scheme	$\lambda \ge 420 \text{ nm}$	Lactic acid (10 vol.%)	2.24	[S11]
MoO ₃ @Mo-ZIS	S-scheme	$\lambda \geqslant 400 \text{ nm}$	Triethanolamine (10 vol.%)	5.50	[S12]
CdS@MoS ₂ /Ti ₃ C ₂	_	$\lambda \ge 420 \text{ nm}$	Lactic acid (10 vol.%)	14.88	[S13]
H _{0.53} WO ₃ /CdS	Z-scheme	$\lambda \ge 420 \text{ nm}$	Lactic acid (10 vol.%)	2.94	[S14]
CdS/GaZnON	type-II	$\lambda \ge 420 \text{ nm}$	0.35 M Na ₂ S 0.25 M Na ₂ SO ₃	14.76	[S15]
ZnIn ₂ S ₄ /CdS	Z-scheme	$\lambda \ge 420 \text{ nm}$	0.35 M Na ₂ S 0.25 M Na ₂ SO ₃	7.44	[S16]
CdS-MoO ₂	S-scheme	$\lambda \ge 420 \text{ nm}$	Lactic acid (10 vol.%)	4.77	[S17]
MoO _{3-x} /PCN	Z-scheme	$\lambda \ge 420 \text{ nm}$	10 vol% Triethanolamine	2.3	[S18]
CdS/MoO _{3-x}	S-scheme	$\lambda \geqslant 420 \text{ nm}$	Lactic acid (10 vol.%)	7.44	[S19]

 Table S2. Comparison of photocatalytic hydrogen precipitation performance of different

catalytic materials.

usting.					
Concentration (mg L ⁻¹)					
0.7706					
1.0207					
0.2632					

 Table S3. ICP analysis of the reaction solution after removing the catalyst following five cycles of testing

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