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P-doped CdS integrated with multiphasic MoSe₂ nanosheets accomplishing prominent photocatalytic activity for hydrogen evolution

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Materials

Cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O, AR), thiourea (CS(NH₂)₂, AR), ethylenediamine (C₂H₈N₂, AR), Sodium hypophosphite (NaH₂PO₂, AR), Sodium molybdate dihydrate (Na₂MoO₄·2H₂O, AR), selenium (Se, AR), hydrazine hydrate (N₂H₄·H₂O, AR), sodium sulfite anhydrate (Na₂SO₃, AR), sodium sulfate (Na₂SO₄, AR) and lactic acid (C₃H₆O₃, AR) were purchased from Aladdin Co. Ltd. (Shanghai, China). Deionized (DI) water, absolute ethanol (CH₃CH₂OH, AR) and terpineol (C₁₀H₁₈O, AR) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All agents were used without further purifications.

Characterization

The composition of as-prepared photocatalysts was characterized by Powder X-ray diffraction (PXRD) performed on Ultima IV (Rigaku, Japan) using Cu K α irradiation (λ = 1.54058 Å). Optical absorption spectra (UV-vis DRS) were collected on a Shimadzu UV-2600 spectrometer using BaSO₄ as a reference. Raman spectra were operated on a Thermo Fisher with a 532 nm laser. The X-ray photoelectron spectroscopy (XPS) measurement was acquired by a Perkin-Elmer PHI 5000C ESCA. Scanning Electron Microscope (SEM) images were obtained on FEI Inspect F50. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were performed on a JEOL-JEM-2010 electron microscope. Energy dispersive Xray spectroscopy (EDS) and elemental mapping were acquired with an accelerating voltage of 20 kV. Zeta potentials of samples were obtained by a NanoBrook Omni (Brookhaven) zeta analyzer. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was performed on a PerkinElmer Optima 8000 for the chemical compositions of the samples. The samples with accurate quality was firstly transferred to a clean polytetrafluoroethylene (PTFE) beaker and dissolved in 4 mL aqua regia at room temperature for about 15min. After that, the samples were heated at 150 °C on the electrothermal digestion plate for 20 min until forming 1-2 mL transparent solution. Then, the solution was cooled down naturally in a fuming hood and transferred to a 10 mL volumetric flask. After diluted to a certain concentration solution, the samples were processed for testing. Brunauer-Emmett-Teller isotherm (BET) was collected by the TriStar II 3020 (Micromeritics Instrument Corporation). The samples were transferred to the bottom of empty tubes with the assistant of paper slots and the temperature was maintained at 100 °C for 10 h. After sufficiently cooling, backfill the gas. The degassing process was finished and the samples were weighed again. The BET data was then obtained with analysis bath temperature of -195.85 °C and the equilibration interval of 10 s. Photoluminescence (PL) spectra and time-resolved photoluminescence (TRPL) spectra were realized on Fluoromax-4 fluorescence spectrometer (Horiba) with an excitation wavelength of 360 nm.

The photoelectrochemical performance tests were conducted in a three-electrode system using the CHI660D electrochemical workstation. The solution with 0.5 M Na₂SO₄ was used as the electrolyte. The Pt electrode, Ag/AgCl electrode, and catalyst-coated Fluorine-doped tin oxide were acted as a counter electrode, electrode, and working electrode separately. The working electrode was prepared by the following procedures: 20 mg catalyst was placed in a mortar and grinded evenly with the presence of one drop terpineol; after that, the catalyst was dried at 60 °C for 30 min and coated 0.25 cm² in area on the Fluorine-doped tin oxide. The electrochemical impedance spectroscopy (EIS) were recorded at different frequency (0.1—100,000 Hz) and the AC voltage amplitude was controlled at 10 mV. Photocurrent measurement was conducted in 0.5 M Na₂SO₄ solution with a fixed potential 6.0 vs Ag/AgCl. And 300 W Xe lamp equipped with 420 nm filter acted as light source.

Photocatalytic activity measurements

The experiments for photocatalytic hydrogen evolution were executed in a Pyrex reaction glass container furnished with a 300 W Xe lamp. The reaction temperature was maintained at 25 °C by a circulating cooling water system. 10 mg of the as-fabricated catalyst was scattered in 80 mL aqueous solution containing 20 vol% lactic acid as the sacrificial reagent. The system was then completely deaerated by a vacuumed pump and purged with Ar before being exposed to the illumination of visible light ($\lambda \ge 420$ nm). The gases generated were evaluated via an online gas chromatograph with a TCD and Ar as the carrier gas. Control experiments were conducted in the same condition without photocatalysts. The AQE was calculated by Equation S1, the parameters of which included wavelength, intensity and area of irradiation. The experiments were conducted using various bandpass filters of 420 nm, 450 nm, 500 nm, and 550 nm and the irradiation area was controlled to be 23.74 cm⁻². The intensity was recorded on an optical power meter (CEL-NP2000-2) with an illumination area of 23.74 cm⁻².

AQE (%) = $\frac{\text{sum of electrons reacted}}{\text{sum of incident photons}} \times 100\%$

Density functional theory (DFT) calculation

All calculations were carried out in the Vienna Ab-initio Simulation Package (VASP) with the plane-wave pseudopotential. The Perdew-Burke-Ernzerhof (PBE) functional of generalized gradient approximation (GGA) was employed to illustrate the correlation potentials and exchanges. Van der Waals correction was taken into account in all calculations. The cutoff energy was 400 eV and the convergence threshold was 10⁻⁵ eV for self-consistent-field (SCF) iteration. The atom positions were controlled when the force of atoms was no more than 0.05 eV/Å.

The MoSe₂ is attributed to space group P2₁/m, which is consistent with that of 1T-MoS₂. The optimized experimental constants of hexagonal lattices are a = b = 3.291 Å, c = 6.875 Å. CdS is assigned to space group P63mc and the experimental constants of tetragonal lattices are a = b = 4.195 Å, c = 6.826 Å. The doping model P-CdS was constructed by the substitution of partial lattice S atoms by P atoms. The (100) facet of P_{1-x}CdSx was modeled by rectangular unit cells of which the surface unit cells was (2×2). The vacuum gap thickness was also considered. All structures images were attained by Visualization for Electronic and Structural Analysis (VESTA, revision 3.5.7) and P4VASP (revision 0.3.30).



Fig. S1 Zeta potentials of PCS and MS-T.



Fig. S2. Enlarged XRD patterns of (a) CdS with different content of doping P range from 23° to 31° and (b) XRD patterns of MS-T and MS-H nanosheets and their composites; (c) the magnified patterns of 8wt% MS-H/PCS.



Fig. S3. Raman spectra of (a)CdS and PCS, (b) MS-T and MS-H nanosheets.



Fig. S4 (a) The mapping images and (b) EDS result of PCS



Fig. S5. (a)(b) TEM and HRTEM images of CdS; (c) SEM, (d) TEM and (f) HRTEM images of MS-H nanosheets.



Fig. S6 High-resolution XPS for (a) Cd, (b) S of pure CdS and PCS, MoSe₂ for (c)Mo and (d) Se.



Fig. S7 The hydrogen evolution rates of (a) CdS with different content of doped-P and (b)PCS coupled with various dosage of cocatalyst MS-T; (c) contrasts for the H₂ rates of composites loaded with MS-T and MS-H nanosheets and (d) the H₂ rates of optimal composite in different wavelength.



Fig. S8 The cumulative amount of hydrogen evolved in four hours over lactic acid, (b) the H_2 rates of lactic acid in different wavelengths.



Fig. S9 The wavelength-dependent AQE for hydrogen evolution of pure PCS and 8wt% MS-T/PCS.



Fig. S10 (a)(b) HRTEM images and (c) the XRD pattern of 8wt% MS-T/PCS composite after cycling experiment.



Fig. S11 The band gaps of (a) CdS, (b) PCS and (c) MS-T nanosheets.



Fig. S12 N_2 adsorption-desorption isotherms of composites.



Fig.S13 The lifetime of CdS and MS-T.



Fig.S14 The optimized structures of PCS and MS-T (the Cd atom is magenta; the S atom is yellow; the P atom is grey; the Mo atom is green and the Se atom is grey).



Fig.S15 The energy changes of the slab cell for (a) P-CdS, (b) MS-T and (c) 8 wt% MS-T/PCS nanosheets calculated slab modules.



Fig.S16 Energy-level lineup diagrams for the PCS and the MS-T.

Table S1. ICP-OES characterization of PCS sam	ples
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Samples	Real P content (wt%)
2.5 wt% PCS	0.43
5 wt% PCS	0.81
10 wt% PCS	1.05
15 wt% PCS	1.38
20 wt% PCS	2.16

Sample	Wavelength (nm)	420	450	500	550
8wt%	Evolved H ₂ (mmol g ⁻¹ h ⁻¹)	166.85	99.23	37.58	0
	AQE (%)	47.92	34.18	13.98	0
PCS	Evolved H ₂ (mmol g ⁻¹ h ⁻¹)	4.32	1.93	0.55	0
	AQE (%)	1.24	0.66	0.20	0

Table S2. The AQE values of PCS and 8wt% MS-T/PCS at different wavelengths.

Table S3. The fitting R_{ct} values for the different samples

Samples	R _{ct} (kΩ)
CdS	666.98
PCS	316.62
8wt% MS-T/PCS	273.95

Based on the fitted results of TRPL spectra, the average decay lifetime (τ_{Av}) of all samples was calculated according to Equation S2:

$$\tau_{Av} = \tau_1 A_1 + \tau_2 A_2 + \tau_3 A_3$$

Where, τ_{Av} is the average decay lifetime, τ_1 and A_1 , τ_2 and A_2 as well as τ_3 and A_3 are the fitted lifetime and corresponding proportion, respectively. The electrons transfer rate was calculated by Equation S3 and S4:

$$k_{ET} = k_F(PCS) - k_F(8 \text{ wt\% MS} - T/PCS) = \frac{1}{\tau_{Av}(PCS)} - \frac{1}{\tau_{Av}(8 \text{ wt\% MS} - T/PCS)}$$

$$\eta_{\rm ET} = 1 - \frac{\tau_{\rm Av}(\rm PCS)}{\tau_{\rm Av}(8 \text{ wt\% MS} - T/\rm PCS)}$$

Where $\tau_{Av}(PCS)$ and $\tau_{Av}(8 \text{ wt\% MS} - T/PCS)$ are the average lifetime of PCS and 8 wt% MS-T/PCS, respectively.

Table S4. The data obtained from time-resolved PL decay spectra fitted curves of CdS, PCS and8wt% MS-T/PCS.

Sample	T ₁ (ns)	T ₂ (ns)	T₃ (ns)	A ₁ (%)	A ₂ (%)	A ₃ (%)	Av (ns)	k _{ET} (10 ⁷ s ⁻¹)	η _{ΕΤ} (%)
MS-T	0.05	0.26	6.76	95.32	4.12	0.56	0.10	-	-
CdS	0.86	6.05	17.31	27.33	53.56	19.11	6.78	-	-

PCS	0.92	6.28s	18.56	27.65	53.93	18.42	7.06	-	-
8wt%	1.04	8.57	20.48	30.57	55.34	14.09	7.95	1.59	11.19

Photocatalyst	Sacrificial agonts	Light source	Maximum rate	Poforonco	
Filococatalyst	Sacificial agents	Light source	(mmol g ⁻¹ h ⁻¹)	Reference	
MS-T/PCS	20 vol% lactic acid	λ≥420nm	166.85	This work	
1T/2H MoSe ₂ /CdS	10 vol% lactic acid	λ >420nm	93.4	1	
ZnO–CdS–NiO _x	Na_2S/Na_2SO_3	simulated sunlight	84.834	2	
CoP/CdS	10 vol% lactic acid	λ >400nm	104.947	3	
NiCoP/CdS/NiCoPi	10 vol% lactic acid	λ >420nm	80.8	4	
MoSe ₂ /CdS-CdSe	10 vol% lactic acid	λ >420nm	24.34	5	
Cd _{0.5} Zn _{0.5} S/CoO	Na_2S/Na_2SO_3	λ >420nm	178	6	
NH ₂ -MIL-125(Ti)@	20 vol% mothonal) >100nm	2 267	7	
ZnIn ₂ S ₄ /CdS		λ >4001111	2.307		
WO ₃ /CdS/WS ₂	14 vol% lactic acid	λ >420nm	14.34	8	
$Pt/CdS/NaNbO_3$	10 vol% lactic acid	λ >420nm	29.297	9	
Exfoliated Mo ₂ C/CdS	20 vol% lactic acid	λ≥420nm	7.7	10	
Cu _{2-x} S/CdS/Bi ₂ S ₃	20 vol% methonal	λ ≥ 420nm	8.012	11	
Pt-CdS/g-C ₃ N ₄ / MnO _x	Pure water	λ >400nm	0.9244	12	
CdS@Cd _{0.5} Zn _{0.5} S@ ZnS-Ni(OH) ₂	Na_2S/Na_2SO_3	λ≥420nm	86.79	13	
$Cd_{0.6}Zn_{0.4}S$	Na_2S/Na_2SO_3	λ ≥ 420nm	42.66	14	
Cd_4S_5	Na_2S/Na_2SO_3	λ ≥ 420nm	29.44	15	
CdS/ZnS	Na_2S/Na_2SO_3	λ ≥ 350nm	24.1	16	
Ni ₂ SP/CdS	Na ₂ S/Na ₂ SO ₃	λ ≥ 420nm	18.96	17	

Table S5. Comparison for hydrogen evolution performances among CdS-based photocatalysts.

Reference:

- 1 N. Li, J. Wu, Y. Lu, Z. Zhao, H. Zhang, X. Li, Y.-Z. Zheng and X. Tao, *Appl. Catal., B*, 2018, **238**, 27-37.
- D. You, C. Xu, X. Wang, J. Wang, W. Su, R. Wang, T. Chen, R. Wang and Z. Shi, *J. Mater. Chem.* A, 2020, 8, 3726-3734.
- 3 Q. Sun, Z. Yu, R. Jiang, Y. Hou, L. Sun, L. Qian, F. Li, M. Li, Q. Ran and H. Zhang, *Nanoscale*, 2020, **12**, 19203-19212.
- 4 Y. Zhao, Y. Lu, L. Chen, X. Wei, J. Zhu and Y. Zheng, *ACS Appl. Mater. Interfaces*, 2020, **12**, 46073-46083.
- 5 Y. Liu, Y. Li, Y. Lin, S. Yang, Q. Zhang and F. Peng, *Chem. Eng. J.*, 2020, **383**, 123133.
- 6 H. Zhao, L. Guo, C. Xing, H. Liu and X. Li, J. Mater. Chem. A, 2020, 8, 1955-1965.
- 7 S. Zhang, M. Du, Z. Xing, Z. Li, K. Pan and W. Zhou, *Appl. Catal., B*, 2020, **262**, 118202.
- 8 C. Xue, P. Zhang, G. Shao and G. Yang, *Chem. Eng. J.*, 2020, **398**, 125602.
- 9 F. Yang, Q. Zhang, J. Zhang, L. Zhang, M. Cao and W.-L. Dai, Appl. Catal., B, 2020, 278,

119290.

- 10 D. Ruan, M. Fujitsuka and T. Majima, *Appl. Catal., B*, 2020, **264**, 118541.
- 11 M. Guo, T. Zhao, Z. Xing, Y. Qiu, K. Pan, Z. Li, S. Yang and W. Zhou, ACS Appl. Mater. Interfaces, 2020, **12**, 40328-40338.
- 12 X. Zhou, Y. Fang, X. Cai, S. Zhang, S. Yang, H. Wang, X. Zhong and Y. Fang, *ACS Appl. Mater. Interfaces*, 2020, **12**, 20579-20588.
- 13 Q. Ruan, X. Ma, Y. Li, J. Wu, Z. Wang, Y. Geng, W. Wang, H. Lin and L. Wang, *Nanoscale*, 2020, **12**, 20522-20535.
- 14 H.-B. Huang, Z.-B. Fang, K. Yu, J. Lü and R. Cao, J. Mater. Chem. A, 2020, **8**, 3882-3891.
- 15 Y.-M. Xie, X.-H. Liu, R. Zhang, H. Liu, J. Mao, C.-K. Dong and X.-W. Du, *J. Mater. Chem. A*, 2020, **8**, 3586-3589.
- Y. Lin, Q. Zhang, Y. Li, Y. Liu, K. Xu, J. Huang, X. Zhou and F. Peng, ACS Sustainable Chem. Eng., 2020, 8, 4537-4546.
- 17 D. Ren, Z. Liang, Y. H. Ng, P. Zhang, Q. Xiang and X. Li, *Chem. Eng. J.*, 2020, **390**, 124496.