

Supplementary Material

Efficient water splitting over a hybrid photocatalyst with (002) active facet and heterostructure

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1 Experiment

1.1 Equipment and apparatus

All chemicals were analytical, purchased from commercial sources and were utilized without any further purification. Pure water (18.2 MΩ cm, TOC < 3 ppb) was produced by Molecular Lab Water Purifier. IR spectra (2–4 wt% samples in KBr pellets) were recorded on a Bruker VERTEX 70v FT-IR spectrometer. Powder X-ray diffractions (XRD) were recorded on PANalytical X'Pert Pro Diffractometer using Cu–K radiation as the X-ray source. Elemental analyses of the catalysts were performed on a TJA ICP-atomic emission spectrometer (ICP-AES, IRIS Advantage ER/S). Photoluminescence (PL) spectra were performed on FLS920 fluorescence spectrometer (Edinburgh Instruments). X-Ray photoelectron spectra (XPS) were measured by ESCALAB250xi with X-ray monochromatisation, in which the binding energy was calibrated using peak C 1s at 284.8 eV. UV-vis absorption spectra were registered in a TU-1810 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) equipped with a photomultiplier tube detector. Diffuse reflectance spectra were measured using a PerkinElmer Lambda 950 UV-vis diffuse reflectance spectrophotometer. The surface morphology of the samples was characterized by a field emission scanning electron microscope (SEM, Carl Zeiss Ultra Plus, Germany) and transmission electron microscopy (TEM, FEI Tecnai G²TF20, America). The H₂ amount was detected by gas chromatography (GC) analysis.

1.2 Synthesis of six transition metal mono-substituted polyoxometalates

[Ni(H₂O)SiW₁₁O₃₉]⁶⁻ (SiW₁₁Ni), [SiW₁₁Mn(H₂O)O₃₉]⁵⁻ (SiW₁₁Mn), [SiW₁₁Co(H₂O)O₃₉]⁶⁻ (SiW₁₁Co), [SiW₁₁ZnH₂O₄₀]⁶⁻ (SiW₁₁Zn), [SiW₁₁Fe(H₂O)O₃₉]⁵⁻ (SiW₁₁Fe) and [Cu(H₂O)SiW₁₁O₃₉]⁶⁻ (SiW₁₁Cu) polyoxometalates were prepared according to the method proposed in the previous literature¹.

1.3 Synthesis of CdS/NiW

CdS/NiW was prepared by one-step hydrothermal reaction. 5 g of Cd(NO₃)₂·4H₂O, 3.7 g of CS(NH₂)₂ and different SiW₁₁Ni amount (0, 0.05, 0.1, 0.5, 0.75 mmol) were

dissolved in 60 mL ethylenediamine. After stirring for 1 h, the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and hydrothermally treated at 180 °C for 24 h. Cool to room temperature; the precipitates were collected by centrifugation and washed thoroughly with deionized water. The material used for photocatalytic test is the 0.5-CdS/NiW sample (CdS/NiW for clarity) unless otherwise stated. Other CdS/MW composites were synthesized by adding 0.5 mM of SiW_{11}M polyoxometalates (M = Mn, Co, Zn, Fe, Cu).

1.4 Synthesis of P-CdS@P-NiWO_x

P-CdS@P-NiWO_x was prepared via a pyrolysis-phosphidation method. 60 mg of CdS/NiW and different NaH_2PO_2 amount (180, 300, 420, 540 mg) were ground about 30 minutes to form a uniform distribution and placed into a quartz boat of the tube furnace. Subsequently, the samples were maintained at 300 °C for 2 h with a heating rate of 2 °C·min⁻¹ in a flowing Ar atmosphere. After cooling to room temperature, the obtained P-CdS was washed with deionized water and ethanol three times and dried in a 60 °C oven for overnight. The obtained samples were denoted as P-CdS@P-NiWO_x-1:3, P-CdS@P-NiWO_x-1:5, P-CdS@P-NiWO_x-1:7 and P-CdS@P-NiWO_x-1:9, respectively. And the suffixes indicate the phosphating ratios is the feeding mass ratios between CdS/NiW and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$. Typically, the material used for characterizations and photocatalytic tests were the P-CdS@P-NiWO_x-1:7 sample (P-CdS@P-NiWO_x for clarity) unless otherwise stated. Preparation of other P-CdS@P-MWO_x is exactly the same as that for P-CdS except that CdS/MW (M = Mn, Co, Zn, Fe, Cu) composites were used instead of CdS.

1.5 Photocatalytic water splitting test

To test the photocatalytic H₂ evolution of the as-prepared samples, 80 mg of catalyst was dispersed in 30 mL ultrapure water without using any sacrificial reagents or noble metals, or other additives under LED irradiation (Beijing Perfectlight, PLS-LED100B, 100 mW cm⁻², $\lambda = 420$ nm). The reaction system was vacuumed with Ar gas for 50 min to remove any residual air in solution. To

determine the amount of H₂ evolution, 50 μL of the evolved gas was collected and analyzed by a gas chromatograph (GC).

1.6 EPR measurement

Electron paramagnetic resonance (EPR) spectroscopy was used to detect $\cdot\text{O}_2^-$ radicals. 10 mg of P-CdS@P-MWO_x was dissolved in 2.5 mL of EtOH/water (v/v=9/1) mixture solution, then 0.1 mmol of 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) was added. Under LED light irradiation, the $\cdot\text{O}_2^-$ radicals were captured by DMPO.

1.7 Detection of H₂O₂

An iodometric method was used to assess the H₂O₂ evolution on UV-vis absorption spectrum. To prepare the standard solution for H₂O₂ detection, 809.7 mg of potassium iodide and 15.1 mg of ammonium molybdate tetrahydrate were added into 50 mL ultrapure water under continuous stirring. Afterward, 50 μL of standard solution was added into 5 mL of collected filtrate after irradiating 3 h.

1.8 Photoelectrochemical measurement

The photoelectrochemical measurements were investigated on a CHI 760D workstation (CH Instruments Co.) with a three-electrode setup under simulated solar light irradiation (AM 1.5G filter, 100 mW cm⁻², 300 W Xe lamp, Perfect Light). The fabricated photoanode, Pt plate and Ag/AgCl electrode (3.5 M KCl) were conducted as working electrode, counter electrode and reference electrode, respectively. Deionized water was used as the electrolyte and bubbled with Ar gas about 30 min for all photoelectrochemical tests. All measured potentials were converted to V vs. normal hydrogen electrode (NHE) ($E_{\text{NHE}} = E_{\text{Ag/AgCl}} + E^{\theta}_{\text{Ag/AgCl}}$; $E^{\theta}_{\text{Ag/AgCl}} = 0.1976 \text{ V}$).

2. Relative calculations

2.1 Determination of electron transfer number

The electron transfer number was determined via a rotating ring-disk electrodes (RRDE) testing system (RRDE-3A, ALS Co. Ltd). RRDE experiments were performed in Ar saturated 0.1 M KPi buffer (pH 7) (rotating speed: 1600 rpm; scan rate: 10 mV·s⁻¹).

A CHI 760D workstation (CH Instruments Co.) was implemented to record the data. The RRDE consists of a glassy carbon disk ($r_1 = 4$ mm), an insulator ring ($r_2 = 5$ mm), and a glassy carbon ring ($r_3 = 7$ mm).

The number of transferred electron (n), H_2O_2 yield and Faradaic efficiency are calculated according to the following equations (1–3)²⁻⁴:

$$n = 4I_{\text{disk}} / (I_{\text{disk}} + I_{\text{ring}} / N) \quad (1)$$

$$H_2O_2 \text{ yeild (\%)} = 2I_{\text{ring}} / (N * I_{\text{disk}} + I_{\text{ring}}) \quad (2)$$

$$\text{Faradaic efficiency of } H_2O_2 \text{ (\%)} = 100 \times (i_r / N) / i_d \quad (3)$$

Where, I_{disk} and I_{ring} represent the disk and ring currents, respectively. N is the RRDE collection efficiency determined to be 0.353.

For preparing RRDE measurements, 1 mg of P-CdS@P-MWO_x sample and 20 μ L of 0.5% Nafion (DuPont) were uniformly dispersed in 1 mL of water/ethanol ($v/v=1/1$) mixture solution. Subsequently, the mixture was treated under ultrasonication for 1 h to get the homogeneous suspension. Whereafter, 10 μ L of suspension was drop-cast onto the disk electrode. Pt plate and Ag/AgCl electrode (3.5 M KCl) were used as counter and reference electrodes, respectively. 0.1 M KPi buffer (pH 7) was employed as the electrolyte after saturation with Ar gas for 30 min.

2.2 Quantum yield calculation for P-CdS@P-MWO_x system (reaction time is 3 h)

The quantum yield (Φ_{QY}) was measured for the photocatalytic water splitting under the following conditions: a quartz flask containing 30 mL pure water with 80 mg P-CdS@P-MWO_x was irradiated by a LED lamp (100 mW cm^{-2} ; $\lambda = 420 \text{ nm}$). The photon flux of the incident light was determined using a Ray virtual radiation actinometer (FU 100, silicon ray detector, light spectrum, 420 nm; sensitivity, 10–50 $\mu\text{V mmol}^{-1} \text{ m}^{-2} \text{ s}^{-1}$), affording a value of $88 \mu\text{mol m}^{-2} \text{ s}^{-1}$.

$$H_2 \text{ formation rate} = 0.00929 \mu\text{mol s}^{-1}$$

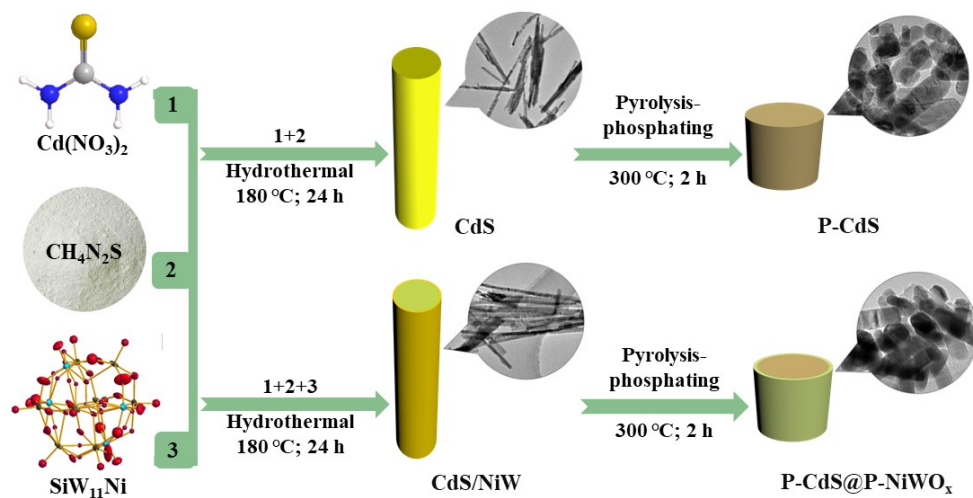
$$\text{Irradiation radius} = 1.5 \text{ cm} = 0.015 \text{ m}$$

$$\text{Photon flux} = \pi \times (0.015 \text{ m})^2 \times 88 \mu\text{mol m}^{-2} \text{ s}^{-1} = 0.0622 \mu\text{mol s}^{-1}$$

$$\Phi_{QY}(\%, \text{quantum yield}) = \frac{2 \times H_2 \text{ evolution rate}}{\text{photo flux}} \times 100\%$$

$$= \frac{2 \times 0.00929}{0.06220} \times 100\% = 29.9\%$$

3. Figures



Scheme S1 Schematic illustration for the formation process of CdS, P-CdS, CdS/NiW and P-CdS@P-NiWO_x photocatalyst.

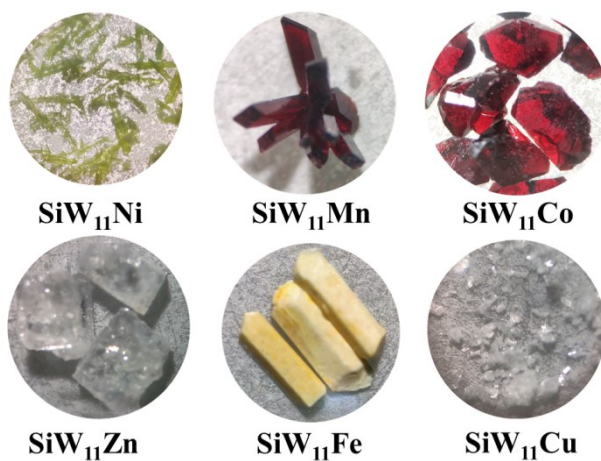


Fig. S1 Digital photos of SiW_{11}Ni , SiW_{11}Mn , SiW_{11}Co , SiW_{11}Zn , SiW_{11}Fe and SiW_{11}Cu under the electron microscope.

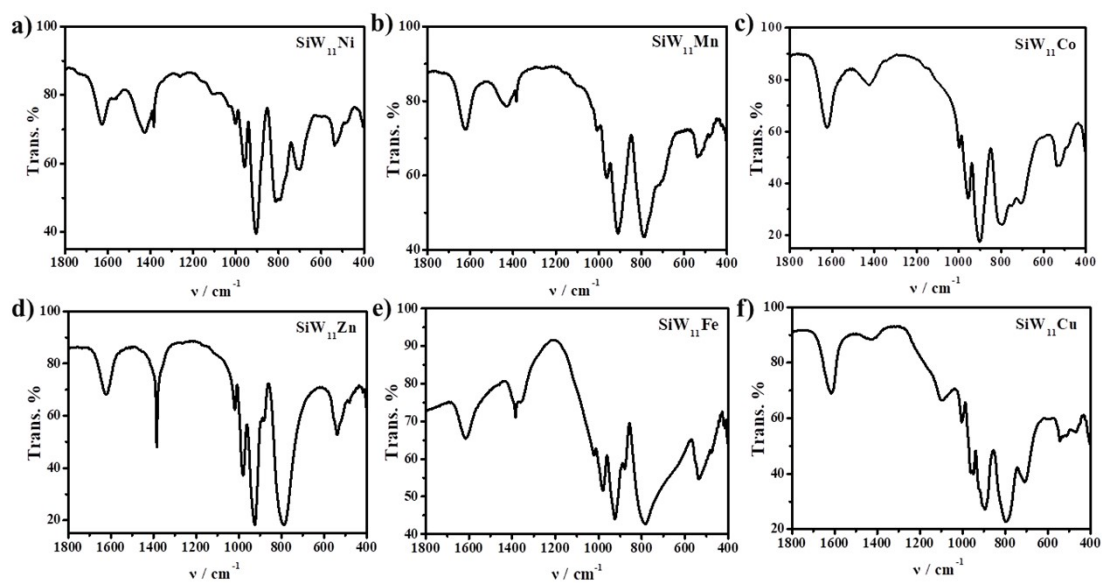


Fig. S2 FT-IR spectra of (a) SiW_{11}Ni , (b) SiW_{11}Mn , (c) SiW_{11}Co , (d) SiW_{11}Zn , (e) SiW_{11}Fe and (f) SiW_{11}Cu .

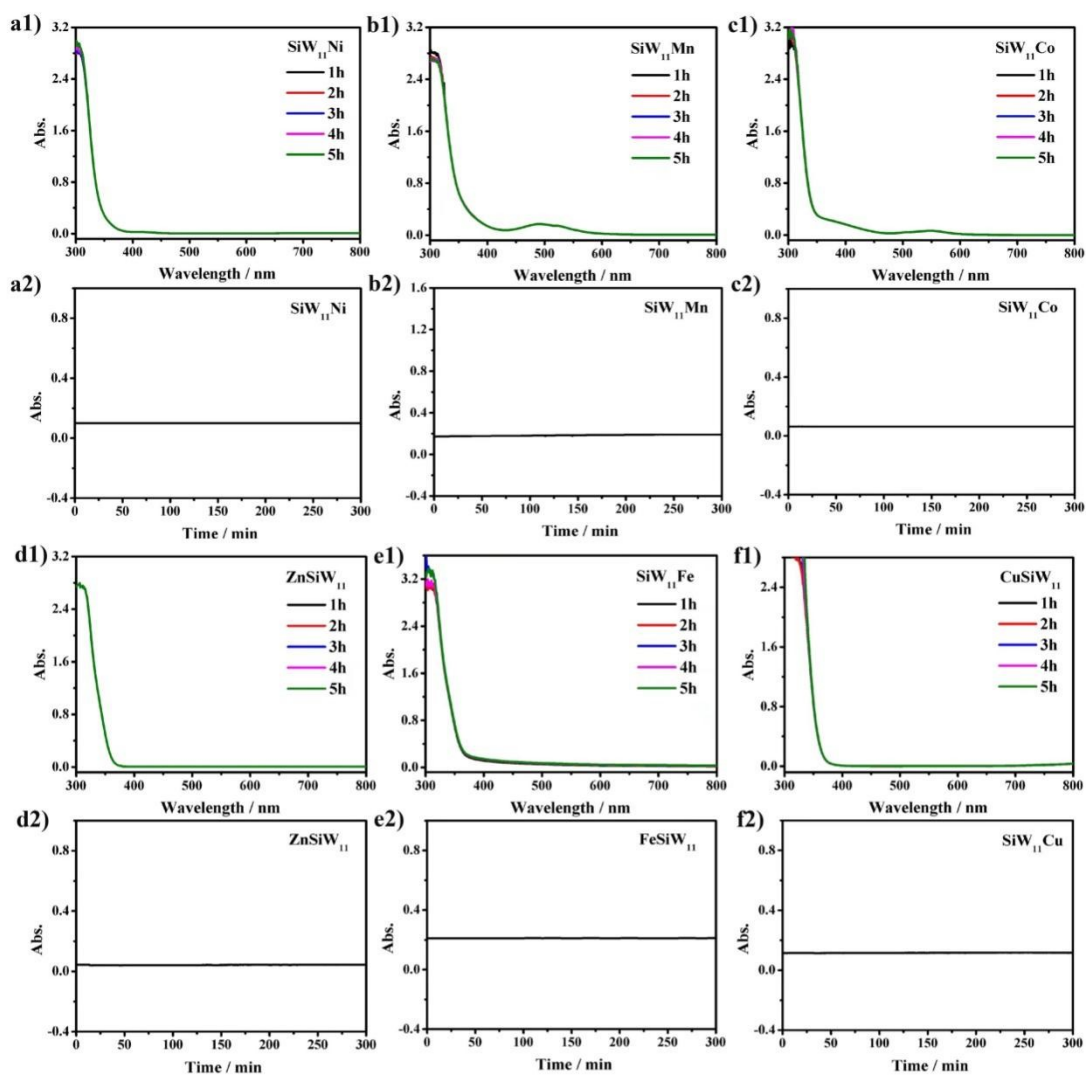


Fig. S3 Time-dependent UV-vis absorption spectra and time profile of UV-vis spectra in pure water over 5 h period with 1 mM different transition metal mono-substituted silicotungstate polyoxometalates: (a1, a2) SiW_{11}Ni , (b1, b2) SiW_{11}Mn , (c1, c2) SiW_{11}Co , (d1, d2) SiW_{11}Zn , (e1, e2) SiW_{11}Fe and (f1, f2) SiW_{11}Cu .

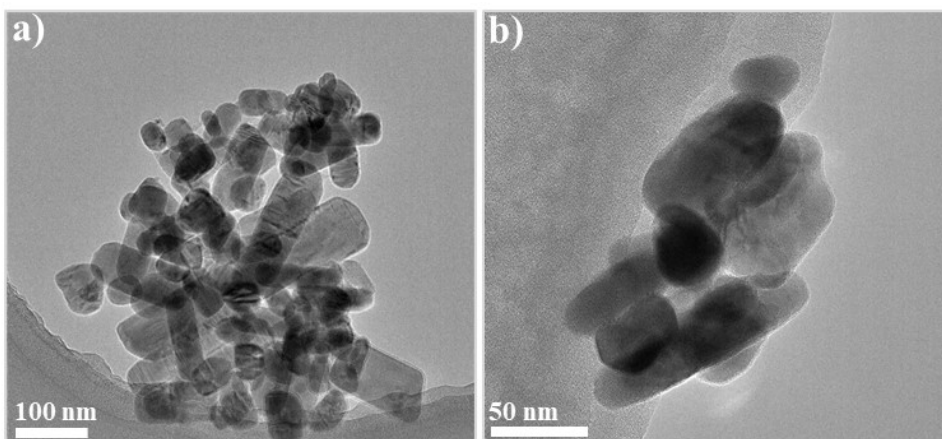


Fig. S4 (a, b) TEM images of pristine P-CdS.

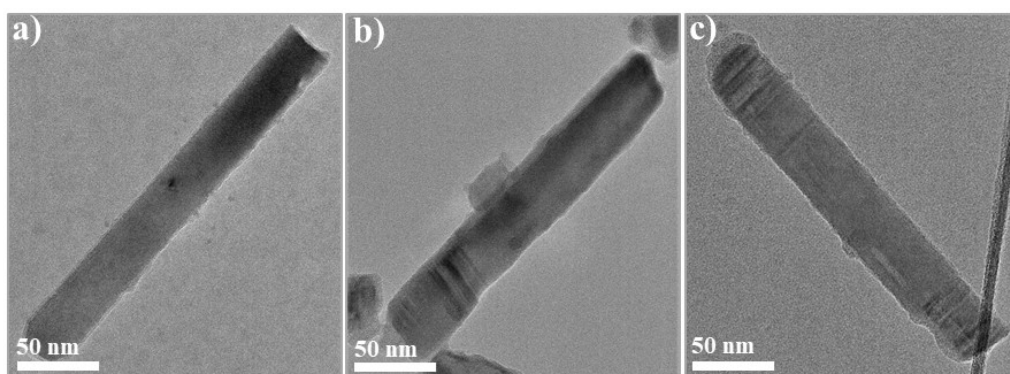


Fig. S5 TEM images of P-CdS@P-NiWO_x prepared at different phosphating ratios with NaH₂PO₂·H₂O as phosphorus source. The phosphating ratios is the feeding mass ratios between CdS/NiW and NaH₂PO₂·H₂O. (a) P-CdS@P-NiWO_x-1:3; (b) P-CdS@P-NiWO_x-1:5; (c) P-CdS@P-NiWO_x-1:9.

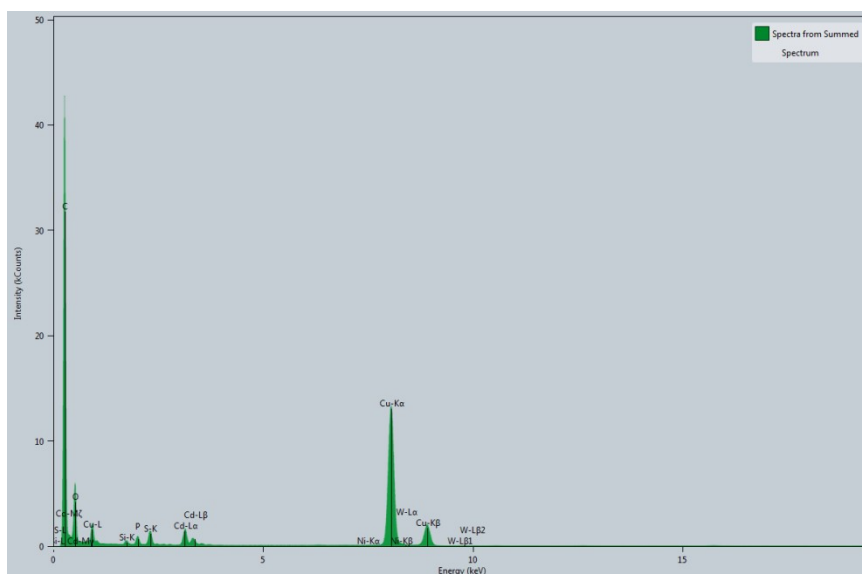


Fig. S6 The EDS spectrum of P-CdS@P-NiWO_x.

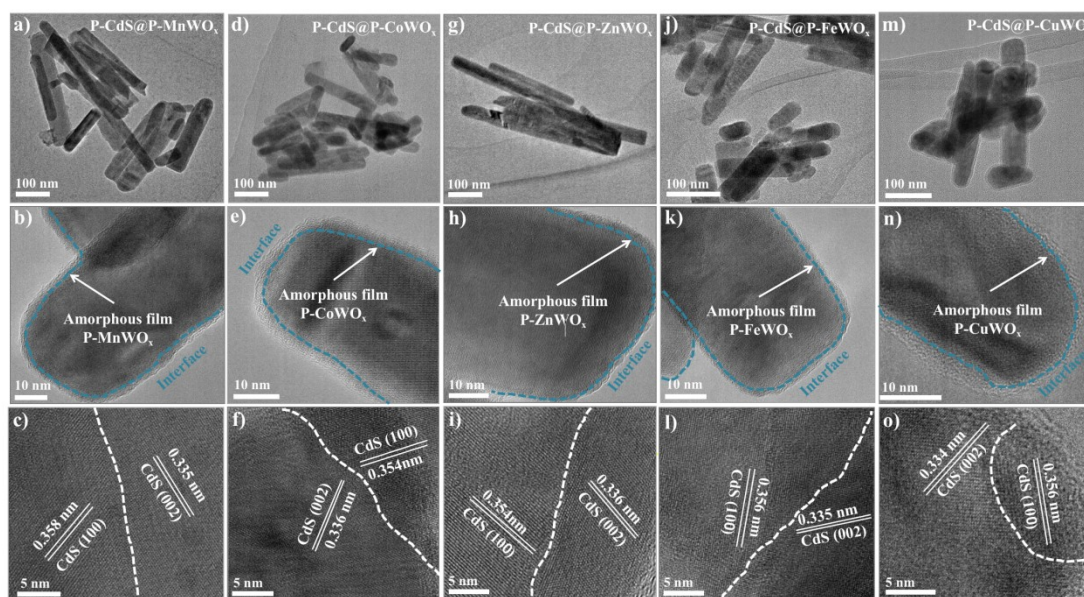


Fig. S7 Structural characterization of P-CdS@P-MWO_x derived from other transition metal SiW₁₁M polyoxometalates. (a) TEM and (b-c) HRTEM images of P-CdS@P-MnWO_x, (d) TEM and (e-f) HRTEM images of P-CdS@P-CoWO_x, (g) TEM and (h-i) HRTEM images of P-CdS@P-ZnWO_x. (j) TEM and (k-l) HRTEM images of P-CdS@P-FeWO_x. (m) TEM and (n-o) HRTEM images of P-CdS@P-CuWO_x.

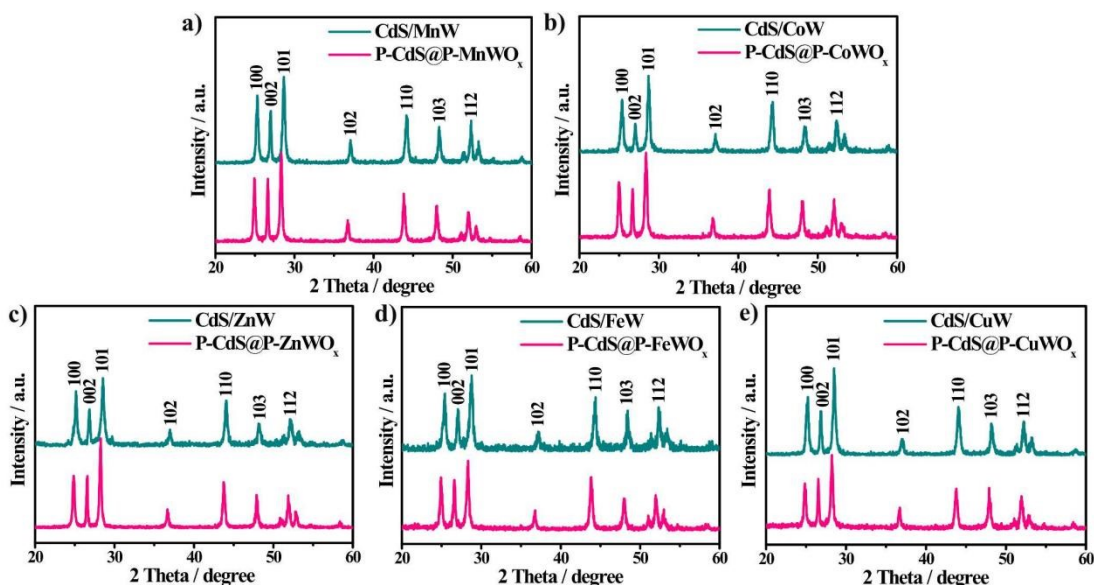


Fig. S8 The powder XRD spectra of P-CdS@P-MWO_x by using other different transition metal SiW₁₁M polyoxometalates: (b) P-CdS@P-MnWO_x, (c) P-CdS@P-CoWO_x, (d) P-CdS@P-ZnWO_x, (e) P-CdS@P-FeWO_x and (f) P-CdS@P-CuWO_x.

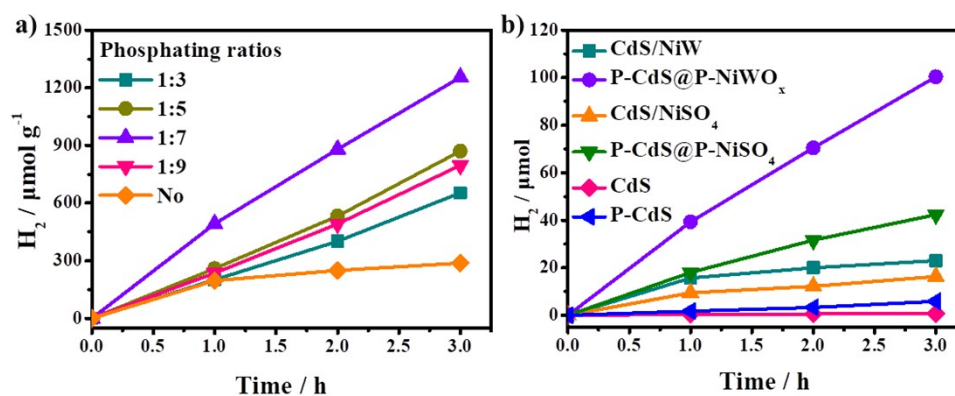


Fig. S9 (a) Photocatalytic H₂ evolution activity of P-CdS@P-NiWO_x prepared at different phosphating ratios with NaH₂PO₂·H₂O as phosphorus source. The phosphating ratios is the feeding mass ratios between CdS/NiW and NaH₂PO₂·H₂O. (b) A comparison of the time course of photocatalytic H₂ evolution over CdS, P-CdS, CdS/NiW, P-CdS@P-NiWO_x, CdS/NiSO₄ and P-CdS@P-NiSO₄.

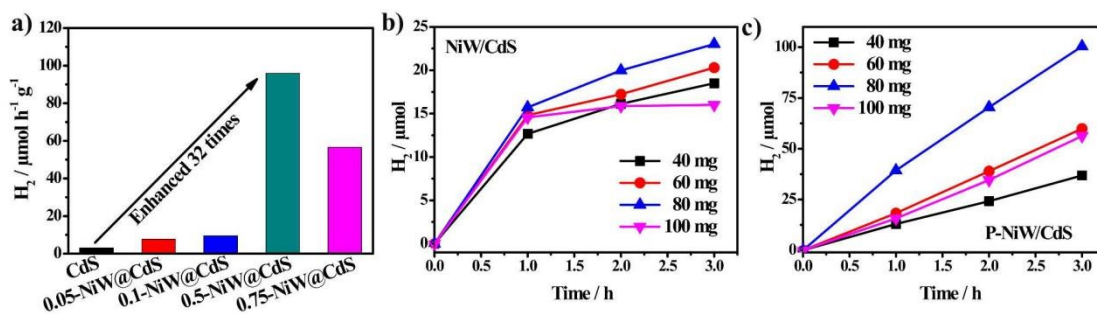


Fig. S10 Photocatalytic H₂ evolution of P-CdS@P-NiWO_x and the reference samples in pure water with 420 nm LED lamp. (a) H₂ evolution activity of x-CdS/NiW. The numerical prefix indicates the theoretical molarity of SiW₁₁Ni polyoxometalates added in the preparation CdS/NiW composite. (b) H₂ evolution activity using different mass CdS/NiW hybrid material. (c) H₂ evolution activity using different mass P-CdS@P-NiWO_x composite.

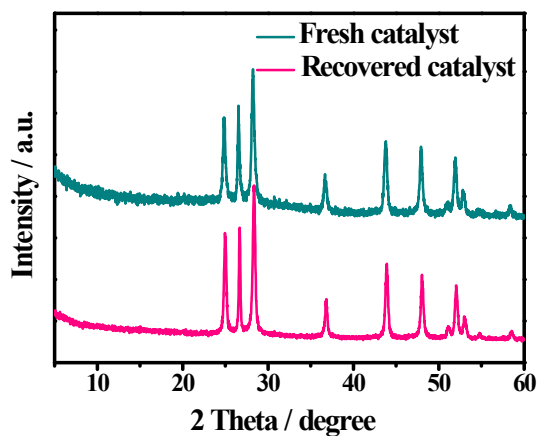


Fig. S11 XRD patterns of fresh and recovered P-CdS@P-NiWO_x.

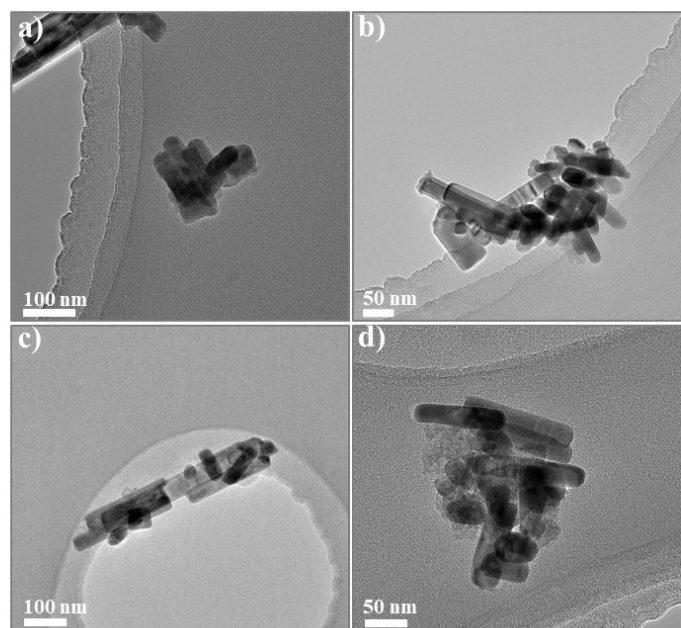


Fig. S12 TEM images of (a, b) fresh and (c, d) recovered P-CdS@P-NiWO_x.

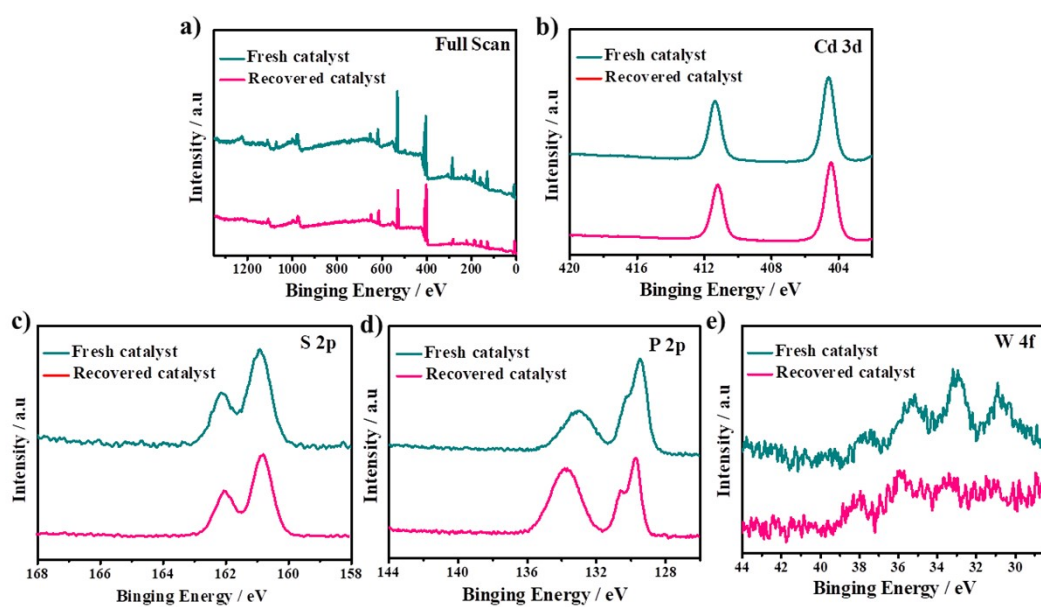


Fig. S13 XPS spectra of fresh and recovered P-CdS@P-NiWO_x in the energy regions of (a) full scan, (b) Cd 3d, (c) S 2p, (d) P 2p and (e) W 4f.

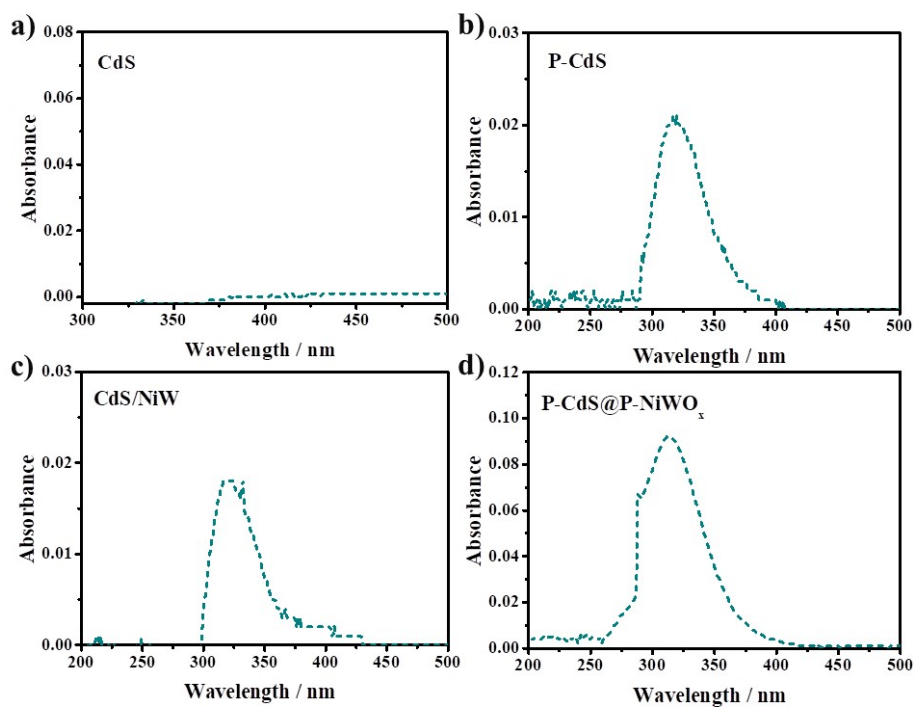


Fig. S14 UV-vis absorption spectrum for (a) CdS, (b) P-CdS, (c) CdS/NiW, and (d) P-CdS@P-NiWO_x after 3 h light irradiation under N₂ saturated atmosphere and centrifugation by adding potassium iodide solution and ammonium molybdate tetrahydrate solution.

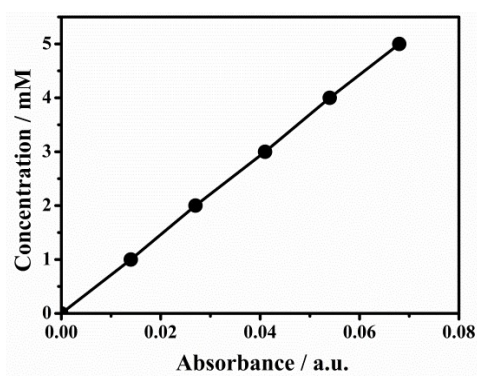


Fig. S15 Standard curve of H₂O₂.

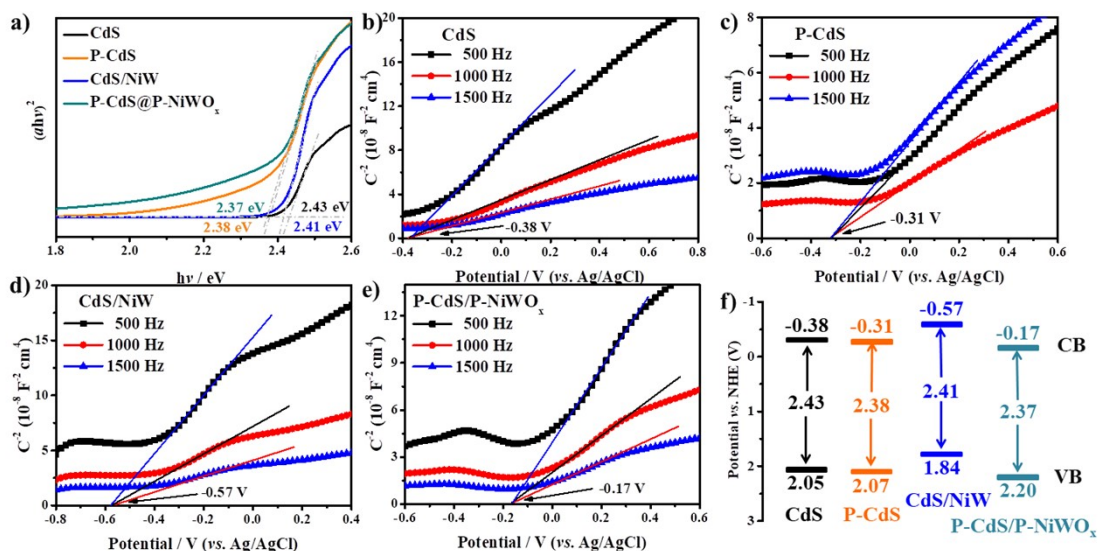


Fig. S16 (a) Corresponding Tauc plots using Kubelka–Munk parameter as a function versus the photon energy. Mott-Schottky plots of (b) CdS; (c) P-CdS; (d) CdS/NiW and (e) P-CdS@P-NiWO_x. (f) Schematic illustration of band structures for CdS, P-CdS, CdS/NiW and P-CdS@P-NiWO_x.

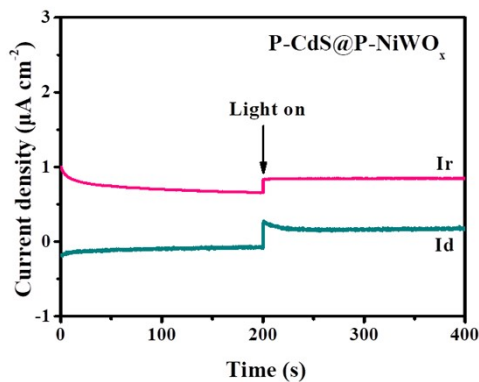


Fig. S17 DMPO spin trapping EPR technique to measure $\cdot\text{O}_2^-$ generated photoreaction over P-CdS@P-NiWO_x under dark or light.

References

- 1 T. J. R. Weakley and S. A. J. Malik, *Inorg, Nucl. Chem.*, 1967, **29**, 2935.
- 2 F.Xue, Y. T. Si, M. Wang, M. C. Liu and L. J. Guo, *Nano Energy*, 2019, **62**, 823.

3 Y. J. Fu, C. A. Liu, M. L. Zhang, C. Zhu, H. Li, H. B. Wang, Y. X. Song, H. Huang, Y. Liu and Z. H. Kang, *Adv. Energy Mater.*, 2018, 1802525.

4 Y. Xia, X.H. Zhao, C. Xia, Z. Y. Wu, P. Zhu, J. Y. Kim, X. W. Bai, G. H. Gao, Y. F. Hu, J. Zhong, Y. Y. Liu and H. T. Wang, *Nat. Commun.*, 2021, **12**, 4225.