

Supporting Information

CdS QDs decorated on 3D flower-like Sn₃O₄: A hierarchical photocatalyst with boosted charge separation for hydrogen production

Pengfei Tan^a, Lu Yang^b, Hele Liu^b, Yi Zhang^{a, b}, Binhua Zhou^a, Jun Pan*^a*

^a State Key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, P. R. China

^b Hunan Key Laboratory of Applied Environmental Photocatalysis, Changsha University, Changsha 410022, P. R. China

** To whom correspondence should be addressed: z20180829@ccsu.edu.cn;*

jun.pan@csu.edu.cn

Material characterization

X-ray diffractometer (XRD) with scanning angles ranging from 10° to 80° was used to obtain the phase composition information of the samples. The surface chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM) of Helios NanoLab G3 UC and transmission electron microscopy (TEM, Titan G2 60-300) were used to detect the microstructure and morphology of the samples. Thermo Fisher Evolution 220 was used to obtain UV-vis diffuse reflectance spectra. The photoluminescence spectrum (PL) was obtained by PerkinElmer LS 55 fluorescence spectrophotometer (excitation wavelength 295 nm). Electron paramagnetic resonance (EPR) signals were measured on the Bruker EMXplus-6/1 spectrometer. And the time-resolved photoluminescence (TR-PL) spectra were obtained by Edinburgh FLS1000.

Photocatalytic performance test

The performance of the photocatalyst was assessed by the data of photocatalytic hydrogen production. First, 50 mg of photocatalyst, 20 mL of methanol, 80 mL of water were added to the quartz reactor. Then the solution in the reactor was ultrasonicated and stirred until it was completely dispersed. After that, the quartz reactor was connected to a closed circulating vacuum system. Circulating condensate was introduced and the temperature was set to 10 °C. In the whole experiment, 300 W Xenon lamp with a filter ($\lambda \geq 420$ nm) was used as the light source for light irradiation. The H₂ yield of the photocatalyst was analyzed by gas chromatograph (GC4000).

Photoelectrochemical measurement

Electrochemical tests were performed on CHI 660E electrochemical workstation to compare the photoelectrochemical properties of the prepared photocatalysts. The standard three-electrode system was used for testing. Platinum plate and saturated Ag/AgCl electrode played as the counter electrode and the reference electrode, respectively. Fluorine-doped tin dioxide (FTO) glass coated with the prepared sample acted as the working electrode. The electrolyte was 0.2 M Na₂SO₄ solution, and the

light source was 300 W Xenon lamp. The working electrode was prepared as follows: First, 5 mg of catalyst was dissolved in 2 mL of ethylene glycol and 200 L of Nafion under magnetic agitation for 24 hours. Then, 100 mL of the suspension was deposited on FTO (1 cm × 1 cm) glass, which was then heated to 80 °C and dried. Photocurrent response curves (I-t curves) were measured with a bias voltage of 0.1 V. The electrochemical impedance spectra (EIS) were obtained when the frequency range was set to 0.1-10⁵ Hz with an amplitude of 5 mV. At 1000 Hz, the Mott-Schottky (M-S) curves were examined with a measurement voltage ranging from -1.5 V to 1.0 V and an amplitude of 10 mV.

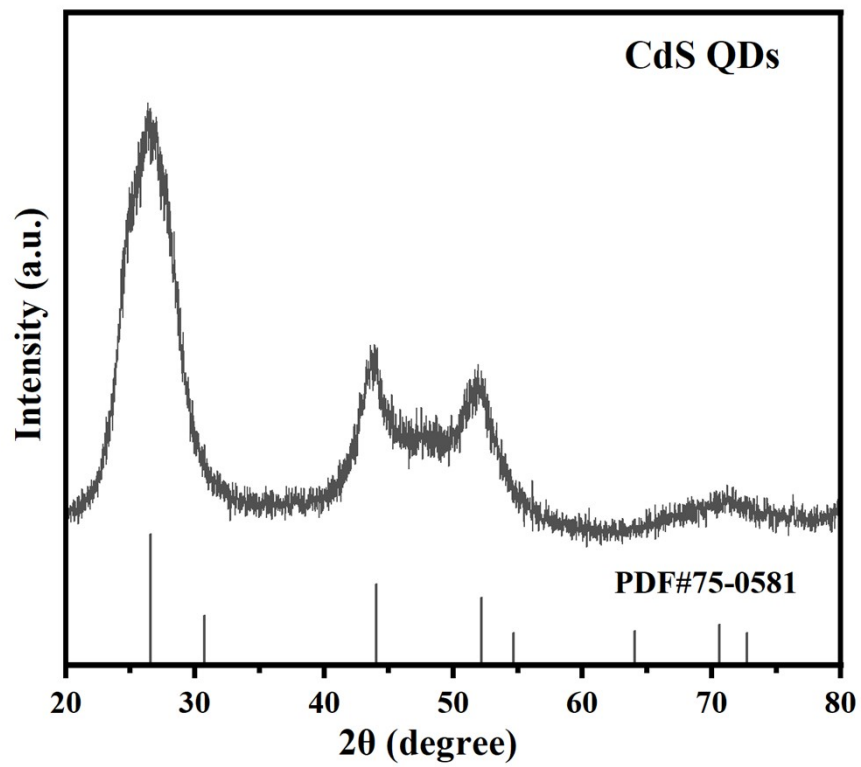


Fig. S1. XRD pattern of pure CdS QDs.

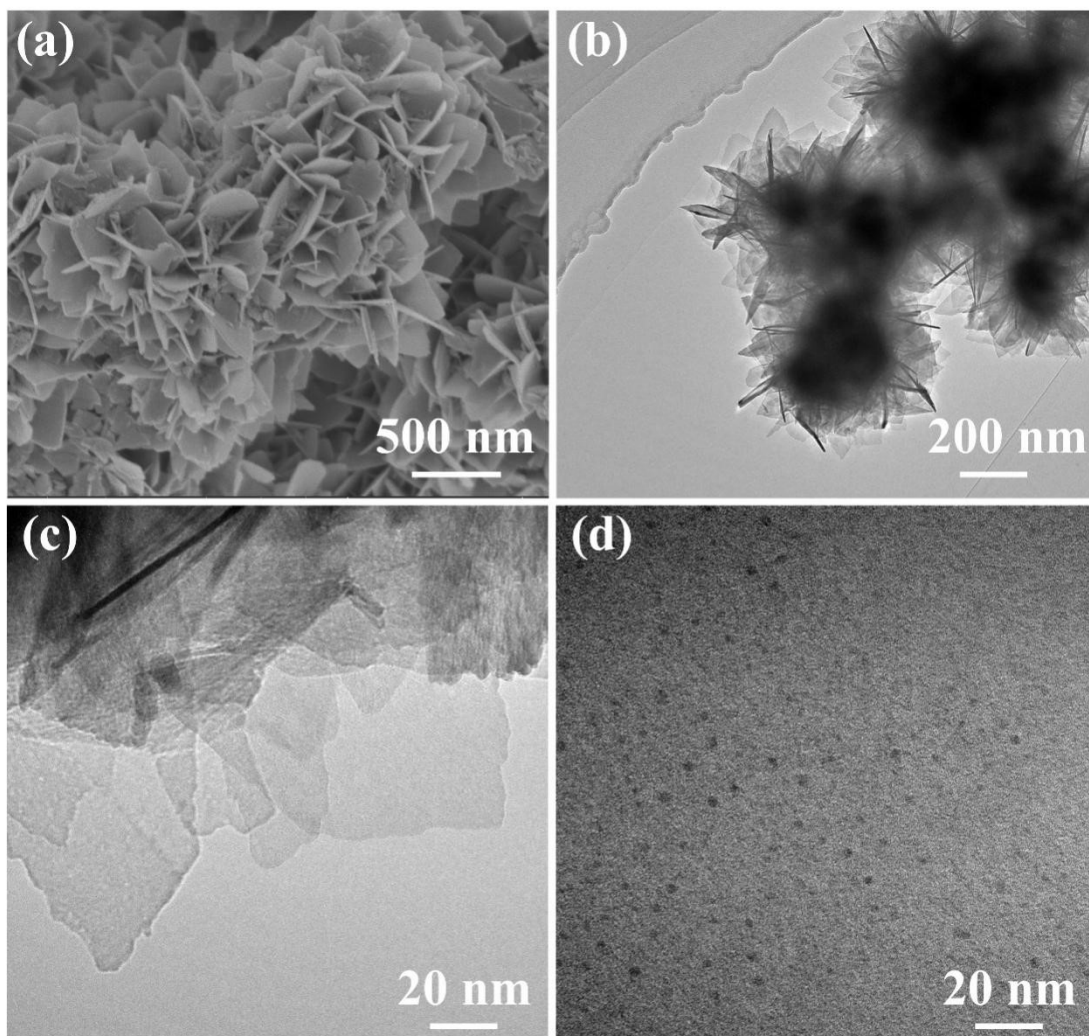


Fig. S2. SEM (a) and TEM (b, c) images of pure Sn_3O_4 . TEM (d) image of pure CdS QDs.

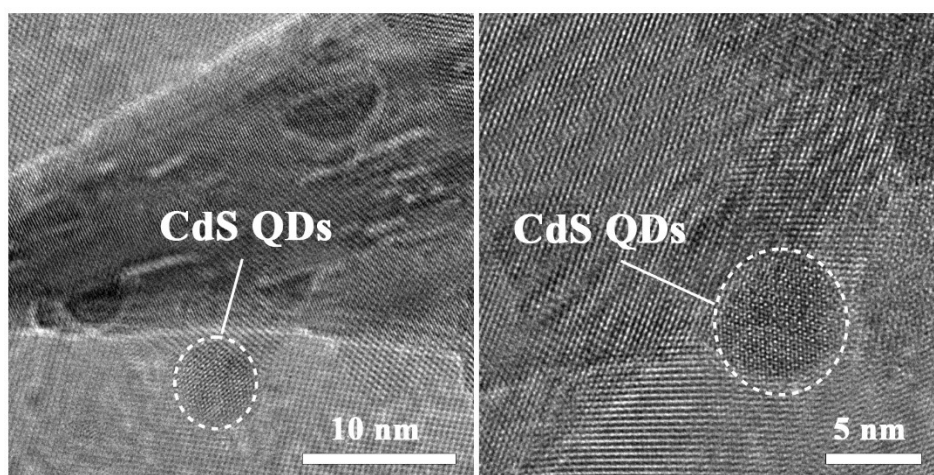


Fig. S3. TEM images of $\text{Sn}_3\text{O}_4/\text{CdS}$ QDs-2

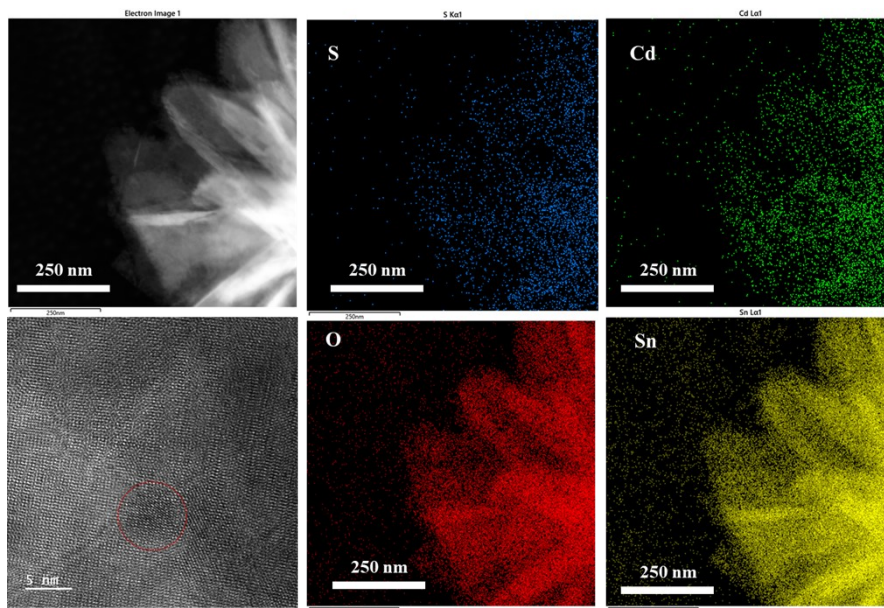


Fig. S4. HAADF and EDS mapping images of Sn, O, Cd, and S in $\text{Sn}_3\text{O}_4/\text{CdS}$ QDs-2.

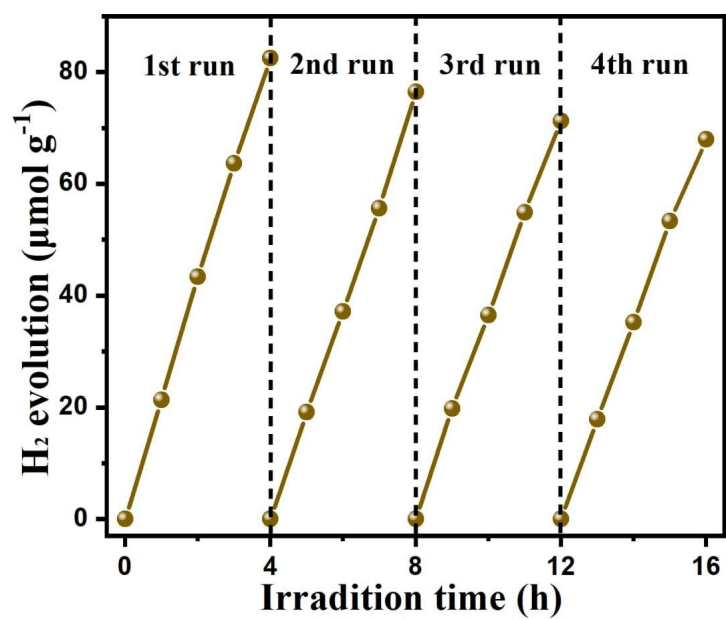


Fig. S5. Recyclability of H₂ evolution of the $\text{Sn}_3\text{O}_4/\text{CdS}$ QDs-2 composite.

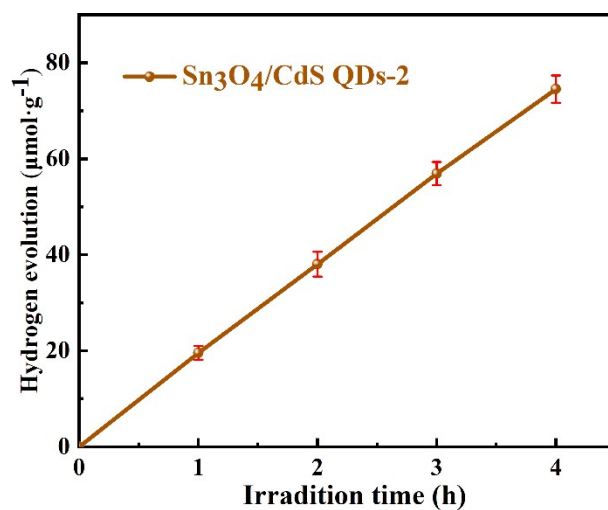


Fig. S6. The photocatalytic H_2 evolution curve of $\text{Sn}_3\text{O}_4/\text{CdS}$ QDs-2 with error bar.

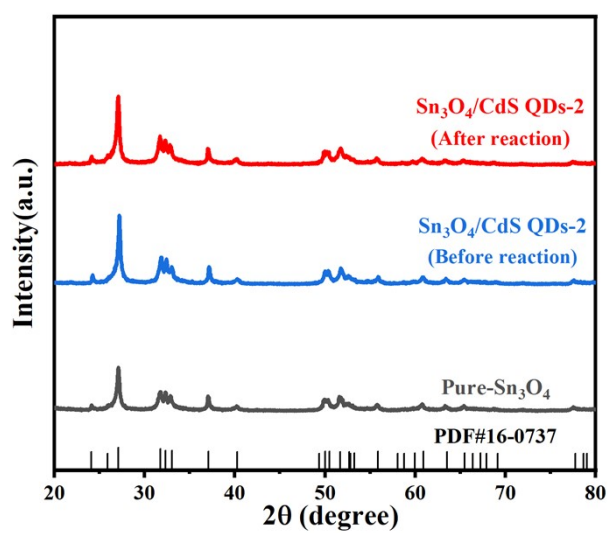


Fig. S7. XRD patterns of pure Sn_3O_4 and $\text{Sn}_3\text{O}_4/\text{CdS}$ QDs-2 after photocatalytic reaction.

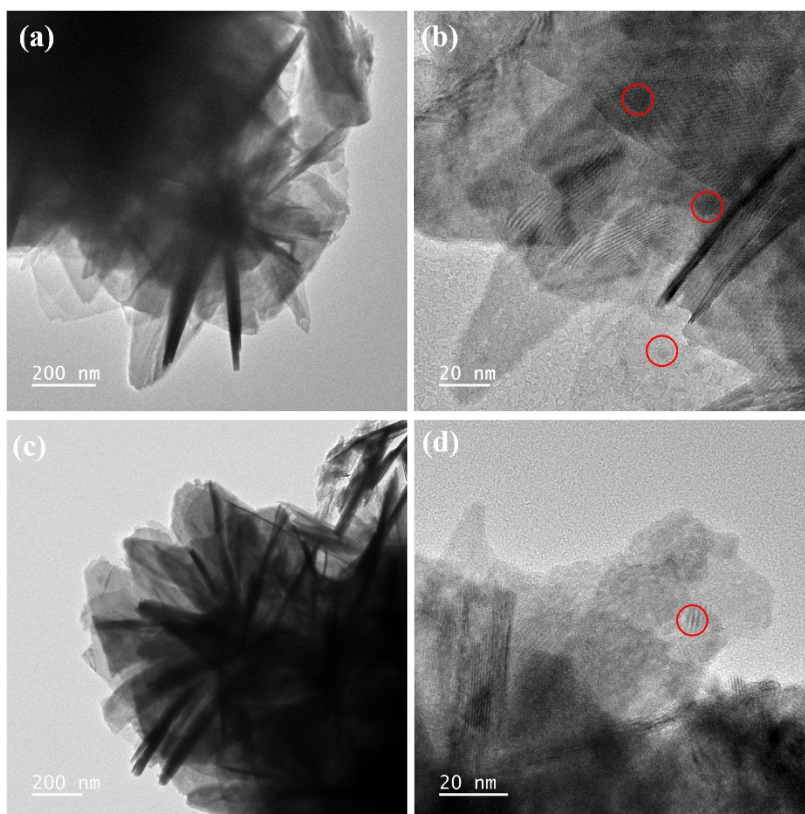


Fig. S8. TEM images of $\text{Sn}_3\text{O}_4/\text{CdS}$ QDs-2 (a, b) before photocatalytic reaction, (c, d) after photocatalytic reaction

Table S1 The average crystallite sizes of pure Sn₃O₄ and Sn₃O₄/CdS QDs samples.

Crystallite size	nm
Sn ₃ O ₄	25.96
Sn ₃ O ₄ /CdS QDs-1	26.46
Sn ₃ O ₄ /CdS QDs-2	32.49
Sn ₃ O ₄ /CdS QDs-3	32.81
Sn ₃ O ₄ /CdS QDs-4	31.20

The average crystallite sizes are obtained by the Scherer's formula.

Table S2 Summary of hydrogen evolution rates of Sn₃O₄-based materials in recent studies

Catalyst	Reaction Solution	H ₂ evolution rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	Light source	Ref.
Sn ₃ O ₄ /CdS QDs-2	CH ₃ OH aqueous solution	20.74	Visible light ($\lambda > 420 \text{ nm}$)	This work
Sn ₃ O ₄ /rGO	CH ₃ OH aqueous solution	20.00	Visible light ($\lambda > 420 \text{ nm}$)	1
BiVO ₄ -QD@Sn ₃ O ₄	CH ₃ OH aqueous solution	12.10	Simulated sunlight	2
Ni-Sn ₃ O ₄	CH ₃ OH aqueous solution	25.6	Visible light ($\lambda > 420 \text{ nm}$)	3
Sn ₃ O ₄ /NiS	CH ₃ OH aqueous solution	17.43	Visible light ($\lambda > 420 \text{ nm}$)	4
Sn ₃ O ₄ /TiO ₂	CH ₃ OH aqueous solution	19.00	Visible light ($\lambda > 420 \text{ nm}$)	5
Sn ₃ O ₄ /Pt	CH ₃ OH aqueous solution	16.66	Visible light ($\lambda > 420 \text{ nm}$)	6
Sn ₃ O ₄	CH ₃ OH aqueous solution	9.00	Visible light ($\lambda > 400 \text{ nm}$)	7
Phosphoric acid modified Sn ₃ O ₄	Overall water splitting	9.60	Simulated sunlight	8
Ultrathin nanosheet Sn ₃ O ₄	CH ₃ OH aqueous solution	15.50	Visible light ($\lambda > 400 \text{ nm}$)	9

Table S3 The fitting results of the TR-PL decay curve.

Samples	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_{av} (ns)
Sn ₃ O ₄	0.87	1.03	6.18	0.03	1.78
Sn ₃ O ₄ /CdS QDs-2	0.76	1.02	6.62	0.04	2.25
CdS QDs	0.84	1.01	4.12	0.04	1.37

The average lifetime (τ_{av}) is obtained by the equation: $\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

Reference

1. X. Yu, Z. Zhao, D. Sun, N. Ren, J. Yu, R. Yang, H. Liu, *Appl. Catal., B.*, 2018, **227**, 470-476.
2. L. Chen, C. Hou, Z. Liu, Y. Qu, M. Xie, W. Han, *Chem. Commun.*, 2020, **56**, 13884-13887.
3. R. Yang, Y. Ji, L. Wang, G. Song, A. Wang, L. Ding, N. Ren, Y. Lv, J. Zhang, X. Yu, *ACS Appl. Nano Mater.*, 2020, **3**, 9268-9275.
4. H. Liu, P. Tan, H. Zhai, M. Zhang, J. Chen, R. Ren, Z. Wang, J. Pan, *New J. Chem.*, 2022, **46**, 14043-14051.
5. X. Yu, L. Wang, J. Zhang, W. Guo, Z. Zhao, Y. Qin, X. Mou, A. Li, H. Liu, *J. Mater. Chem. A.*, 2015, **3**, 19129-19136.
6. M. Manikandan, T. Tanabe, P. Li, S. Ueda, G. V. Ramesh, R. Kodiyath, J. Wang, T. Hara, A. Dakshanamoorthy, S. Ishihara, K. Ariga, J. Ye, N. Umezawa and H. Abe, *ACS Appl. Mater. Interfaces*, 2014, **6**, 3790-3793.
7. T. Tanabe, T. Tanikawa, K. Nakamori, S. Ueda, B. Nanzai, Y. Matsubara and F. Matsumoto, *Int. J. Hydrogen Energy*, 2020, **45**, 28607-28615.
8. L. Chen, S. Yue, J. Wang, W. Chen, Y. Zhang, M. Xie and W. Han, *Appl. Catal., B*, 2021, **299**, 120689.
9. T. Tanabe, K. Nakamori, T. Tanikawa, Y. Matsubara and F. Matsumoto, *J. Photochem. Photobiol., A*, 2021, **420**, 113486.