

Supporting Information

Ultrathin CdS@BDC Nanosheets Derived from 2D Metal-Organic Frameworks for Enhanced Photoinduced-Stability and Photocatalytic Hydrogen Production

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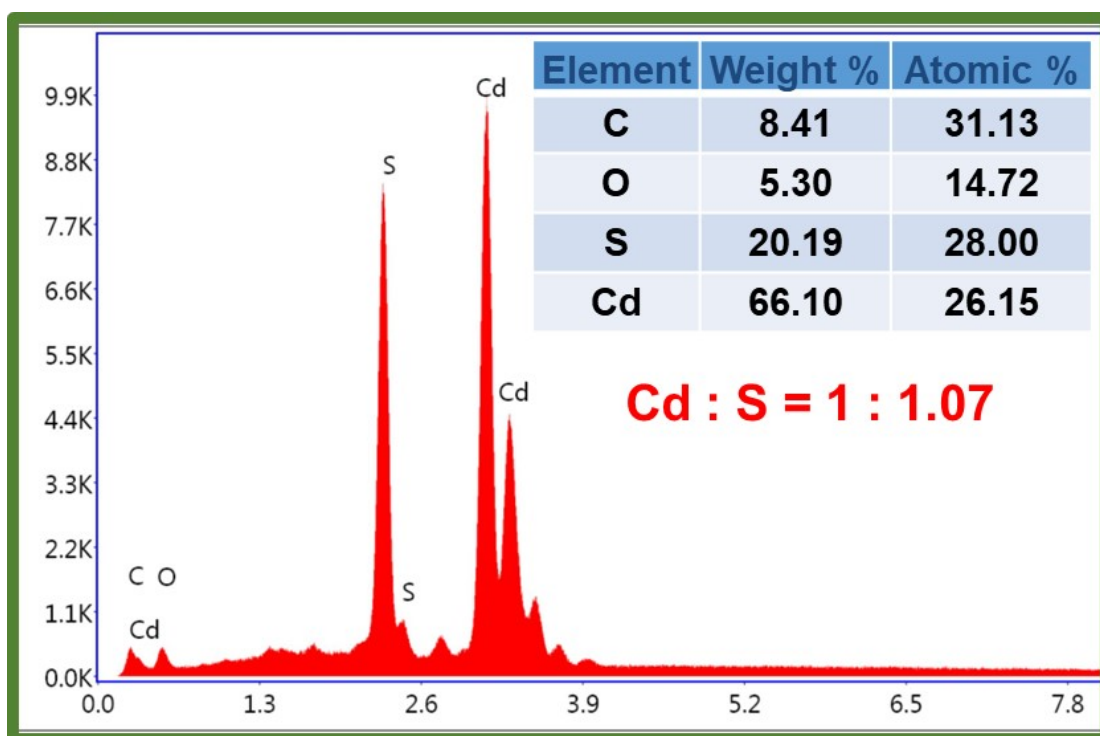


Figure S1. EDS spectra of CdS@BDC NSs.

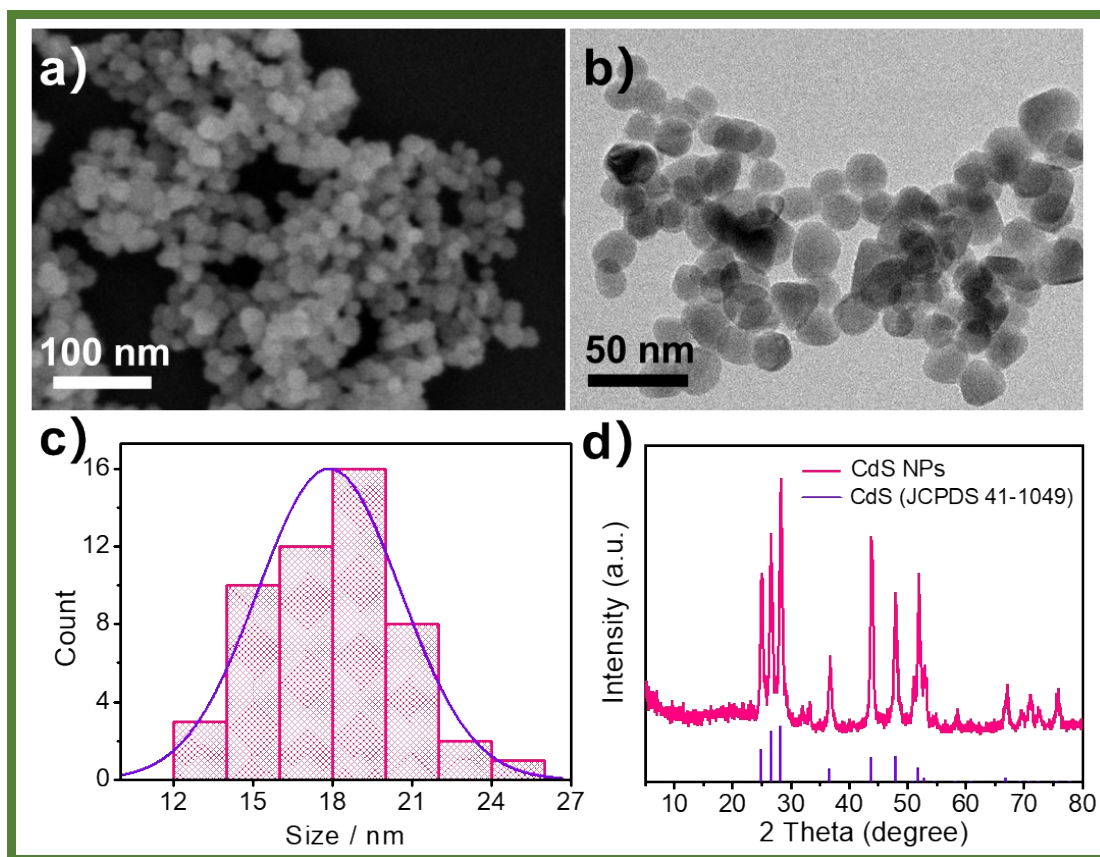


Figure S2. a) SEM image of CdS NPs, b) TEM image and corresponding particle size distribution (c) of CdS NPs, The sampling number is 50, and the center particle size is ≈ 18 nm, d) PXRD patterns for the CdS NPs. CdS NPs were synthesized for comparison. According to the SEM, TEM and corresponding particle size distribution (Fig. S2a-c), the resulting CdS NPs exhibited a good dispersion with a large particle size (12~27 nm). Moreover, as displayed in Fig. S2d, the diffraction peaks of the CdS NPs could be indexed to the hexagonal CdS phase (JCPDS no. 41-1049) with corresponding to the (100), (002), (101), (102), (110), (103), and (112) reflecting at 24.9° , 26.5° , 28.2° , 37.6° , 44.00° , 47.5° and 52.5° , respectively.

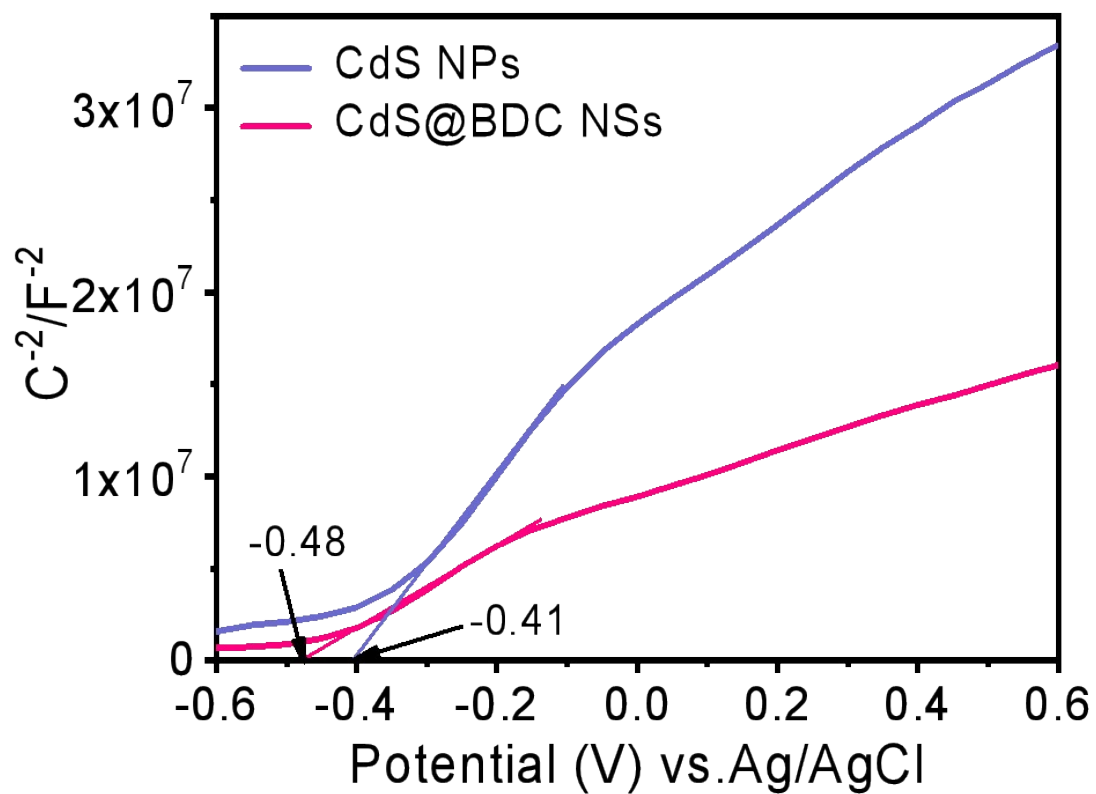


Figure S3. Mott-Schottky plots of the CdS NPs and CdS@BDC NSs.

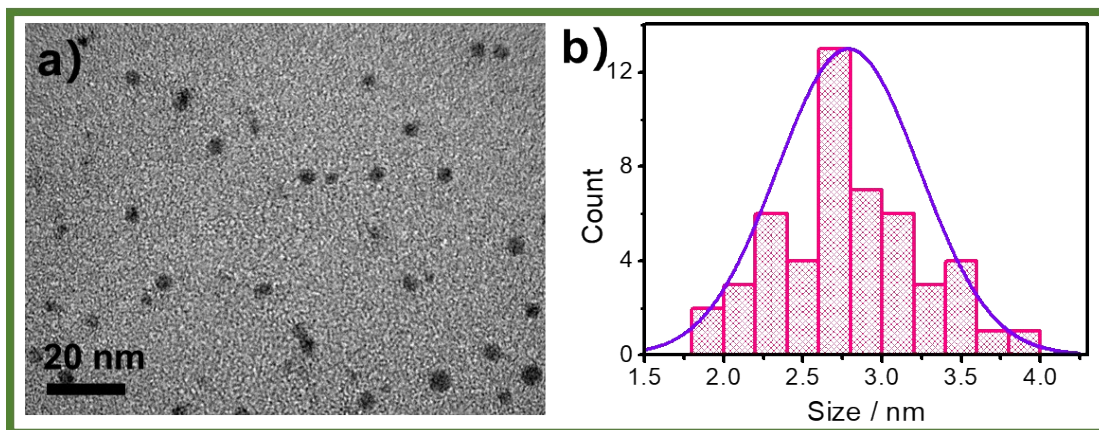


Figure S4. a) TEM image and corresponding particle size distribution (b) of CdS QDs.

The sampling number is 20, and the center particle size is ≈ 2.75 nm.

Synthesis of CdS Quantum Dots (QDs): CdS QDs were prepared by a reported aqueous phase approach.¹ In detail, 1 M NaOH solution was slowly dripped into 20.0 mL of 75 mM $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ solution until the pH value of the mixed solution is 10.5, and then 1.5 mM thioglycolic acid (TGA) was added to the above solution as a stabilizer. After adding 20 mL of 75 mM Na_2S solution, the mixture was stirred for 30 minutes at 65 °C and aged for 90 minutes. Subsequently, the sample was obtained by centrifugation and rinsed several times using distilled water, and redispersed in deionized water forming CdS QDs solution.

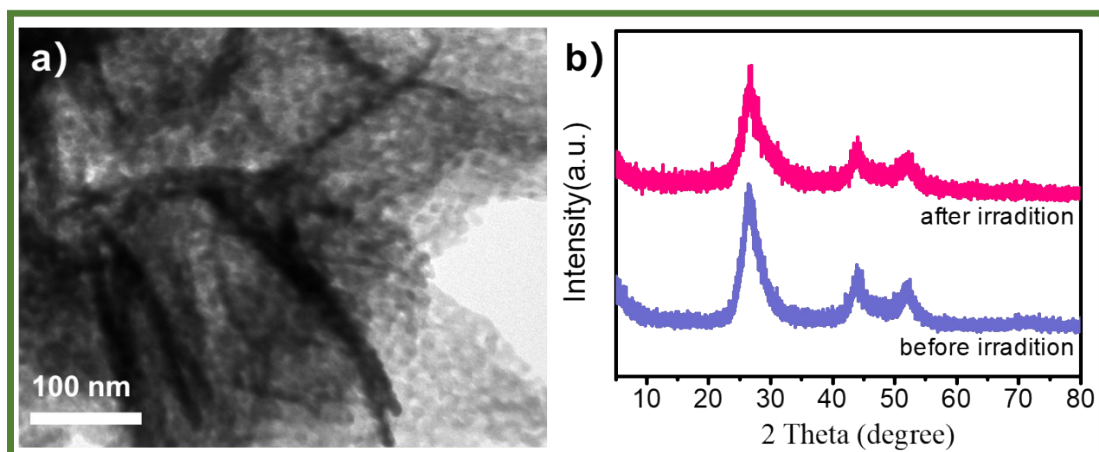


Figure S5. a) SEM image and (b) PXRD patterns of CdS@BDC NSs after four cycle photocatalytic H₂ production reactions.

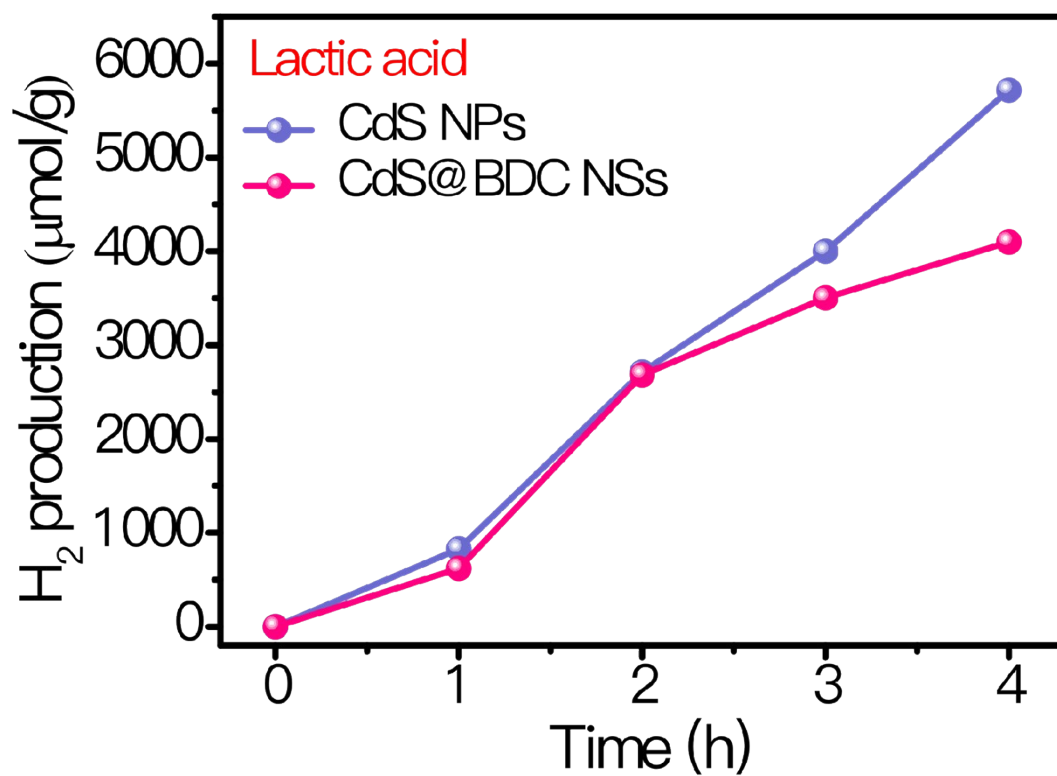


Figure S6. Photocatalytic H₂-evolution activity for CdS NCs and CdS@BDC NSs in 20.0 mL Na₂S/Na₂SO₃ solution under visible-light irradiation ($\lambda > 380$ nm).

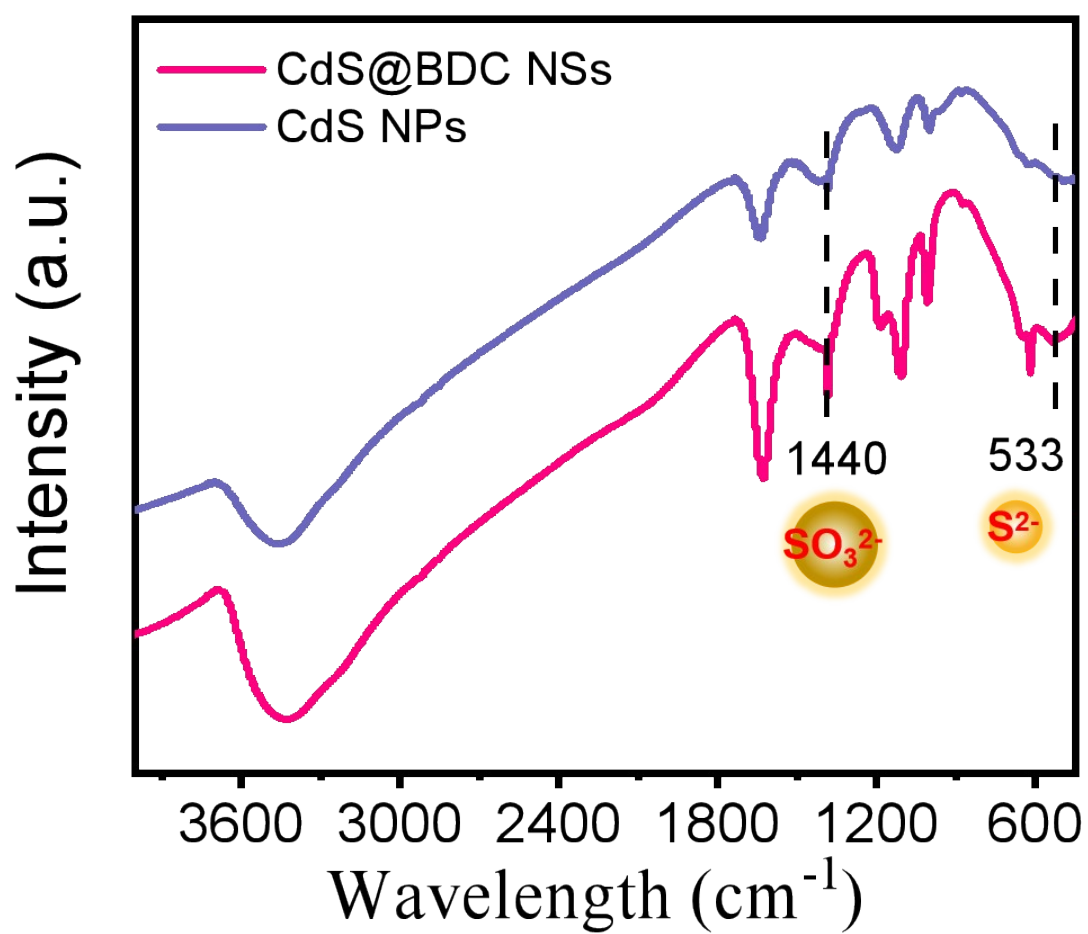


Figure S7. FTIR spectra of the CdS@BDC NSs and CdS NPs during the hydrogen production process.

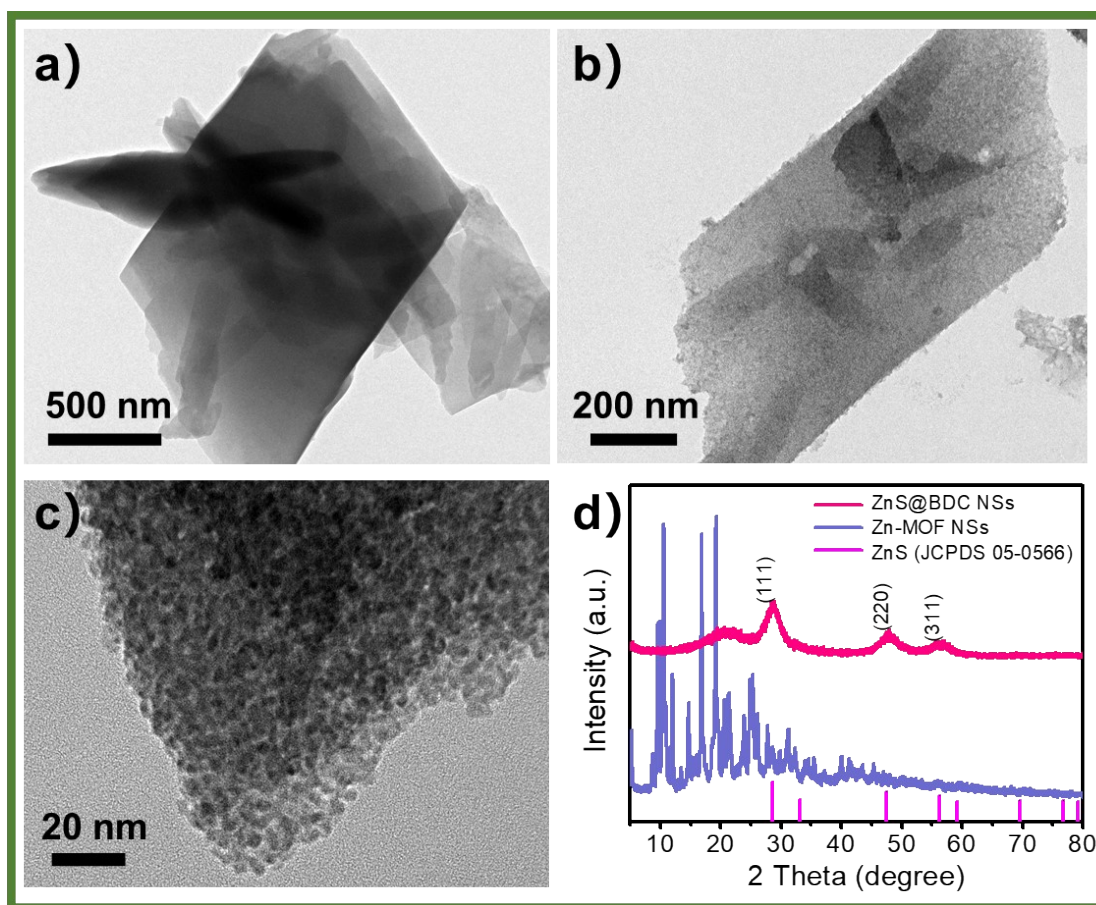


Figure S8. a) TEM image of Zn-MOF NSs, b-c) TEM images of Zn@BDC NSs, d) Powder XRD Profiles for Zn-MOF NSs and ZnS@BDC NSs.

The present synthesis method of Cd@BDC NSs was also applied to prepare ZnS@BDC NSs photocatalyst under an identical condition.

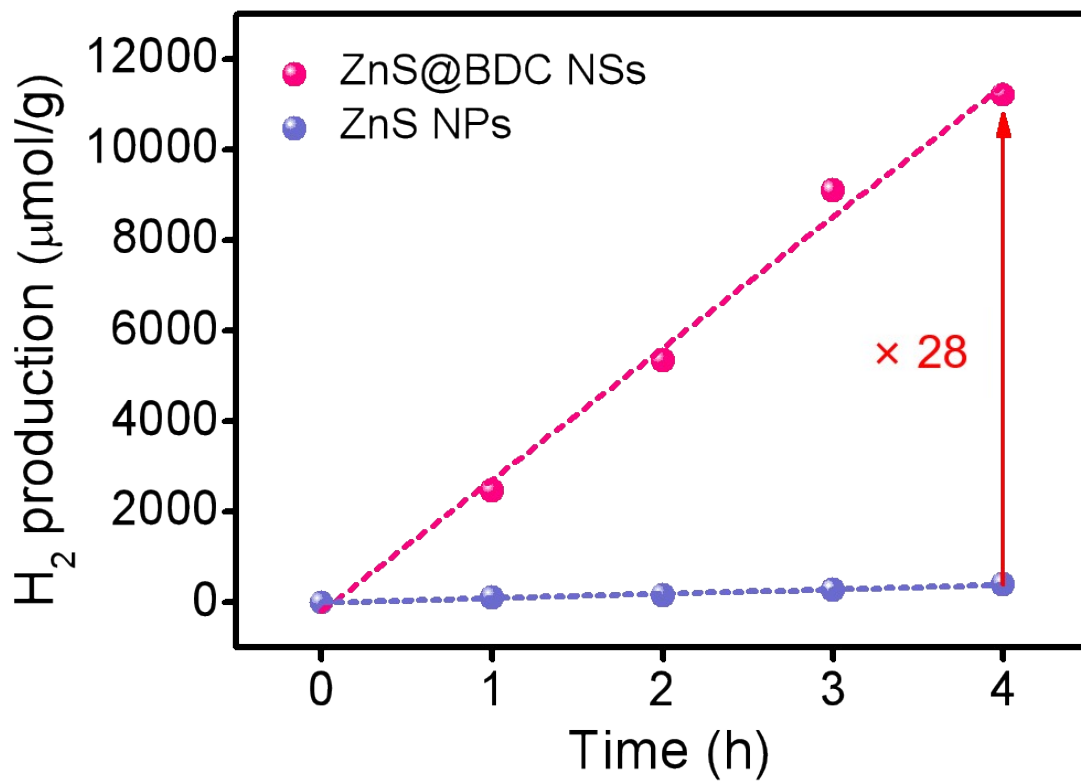


Figure S9. The photocatalytic activity for ZnS@BDC NSs and traditional ZnS NPs.

Table S1. Comparison of the H₂-production rates of CdS-based photocatalysts for water splitting

Photocatalyst	Light source	Sacrificial agent	Activity $\mu\text{mol h}^{-1} \text{g}^{-1}$	Recycled times	Ref
HP-CdS	Visible light (> 380 nm)	0.1 M Na ₂ S/Na ₂ SO ₃	634	16h	2
c-CdS NC	LEDs lights (= 420 nm)	0.35 M Na ₂ S and 0.25 M Na ₂ SO ₃	7200	7.5h	3
CdS nanosheet-assembled flowers	Visible light (> 420 nm)	10 vol% lactic acid (0.5 wt% Pt)	9374	15h	4
g-C ₃ N ₄ /CdS	Visible light (\geq 400 nm)	20 vol% lactic acid (1.0 wt% Pt)	13100	12h	5
NiS/Zn _x Cd _{1-x} S	Visible light (> 420 nm)	0.35 M Na ₂ S and 0.25 M Na ₂ SO ₃	16780	20h	6
CdS hexagonal plates	Visible light (\geq 420 nm)	0.35 M Na ₂ S and 0.25 M Na ₂ SO ₃ (0.5 wt% Pt)	1782	N.A.	7
Graphene oxide/CdS	Visible light (\geq 420 nm)	0.35 M Na ₂ S and 0.25 M Na ₂ SO ₃	3140	15h	8
Ni ₂ P@CdS	Visible light (> 420 nm)	None	837.94	12h	9

CdS-Au	Visible light (> 420 nm)	10 vol% lactic acid (0.5 wt% Pt)	6385	15h	10
C/CdS	Visible light (> 420 nm)	0.35 M Na ₂ S and 0.25 M Na ₂ SO ₃	5367	16h	11
CdS@BDC	Visible light (> 380 nm)	0.1 M Na ₂ S/Na ₂ SO ₃	13081	16h	This work

Table S2. The quantum efficiency QE of CdS-based photocatalysts and the previously reported CdS-based photocatalysts

Photocatalysts	Co-catalysts	Light sources	Sacrificial agents	QE (%)	References
CdS	-	400 nm	Na ₂ S-Na ₂ SO ₃	3.2	12
CdS	F/G	420 nm	methanol	7.24	13
CdS	Ni ₂ SP	420 nm	Na ₂ S-Na ₂ SO ₃	4.8	14
CdS	NiSe ₂	420nm	Na ₂ S-Na ₂ SO ₃	1.5	15
CdS/Cu ₇ S ₄ /g-C ₃ N ₄	-	420 nm	Na ₂ S-Na ₂ SO ₃	4.4	16
CdS/g-C ₃ N ₄	Pt	420 nm	lactic acid	2.79	17
CdS NPs	-	420 nm	Na ₂ S-Na ₂ SO ₃	0.23	This work
CdS QDs	-	420 nm	Na ₂ S-Na ₂ SO ₃	1.37	This work
CdS@BDC NSs	-	420 nm	Na ₂ S-Na ₂ SO ₃	4.61	This work

Table S3. The average fluorescence lifetimes of CdS@BDC NSs and CdS NPs in pure H₂O; [Catalysts] = 0.5 mg/mL.

Samples	Lifetime τ (ns)	Pre-exponential factors B	Average Lifetime, $\langle \tau \rangle$ (ns)	χ^2
CdS@BDC NSs	$\tau_1 = 1.577$ $\tau_2 = 9.489$ $\tau_3 = 0.032$	$B_1 = 2.86$ $B_2 = 4.50$ $B_3 = 92.64$	0.035	1.1664
CdS NPs	$\tau_1 = 2.330$ $\tau_2 = 0.019$ $\tau_3 = 11.204$	$B_1 = 4.80$ $B_2 = 90.03$ $B_3 = 5.17$	0.021	1.2371

Reference:

- 1 L. Ge, F. Zuo, J. K. Liu, Q. Ma, C. Wang, D. Z. Sun, L. Bartels, P. Y. Feng, *J. Phys. Chem. C*, 2012, **116**, 13708-13714.
- 2 J. D. Xiao, H. L. Jiang, *Small*, 2017, **13**, 1700632.
- 3 H. G. Yu, W. Zhong, X. Huang, P. Wang, J. G. Yu, *ACS Sustain. Chem. Eng.*, 2018, **6**, 5513-5523.
- 4 Q. J. Xiang, B. Cheng, J. G. Yu, *Appl. Catal. B*, 2013, **138**, 299-303.
- 5 J. He, L. Chen, Z. Q. Yi, D. Ding, C. T. Au, S. F. Yin, *Catal. Commun.*, 2017, **99**, 79-82.
- 6 X. X. Zhao, J. R. Feng, J. Liu, W. Shi, G. M. Yang, G. C. Wang, P. Cheng, *Angew. Chem. Int. Ed.*, 2018, **57**, 9790-9794.
- 7 D. Lang, F. Liu, G. H. Qiu, X. H. Feng, Q. J. Xiang, *ChemPlusChem*, 2014, **79**, 1726-1732.

- 8 T. Y. Peng, K. Li, P. Zeng, Q. G. Zhang, X. G. Zhang, *J. Phys. Chem. C*, 2012, **116**, 22720-22726.
- 9 W. L. Zhen, X. F. Ning, B. J. Yang, Y. Q. Wu, Z. Li, G. X. Lu, *Appl. Catal. B*, 2018, **221**, 243-257.
- 10 J. Xu, W. M. Yang, S. J. Huang, H. Yin, H. Zhang, P. Radjenovic, Z. L. Yang, Z. Q. Tian, J. F. Li, *Nano Energy*, 2018, **49**, 363-371.
- 11 Z. Q. Xiang, J. X. Nan, J. W. Deng, Y. Shi, Y. F. Zhao, B. Zhang, X. Xiang, *J. Alloys Compd.*, 2019, **770**, 886-895.
12. P. Zhang, D. Luan, X. W. Lou, *Adv. Mater.* 2020, 32, 2004561.
13. W. C. Wang, Y. Tao, J. C. Fan, Z. P. Yan, H. Shang, D. L. Phillips, M. Chen, G. S. Li, *Adv. Funct. Mater.* 2022, 32, 2201357
14. D. Ren, Z. Liang, Y. H. Ng, P. Zhang, Q. Xiang, X. Li, *Chem. Eng. J.* 2020, 390, 124496.
15. Z. Chen, H. Gong, Q. Liu, M. Song, C. Huang, *ACS Sustainable Chem. Eng.* 2019, 7, 16720-16728.
16. J. Chu, X. Han, Z. Yu, Y. Du, B. Song, P. Xu, *ACS Appl. Mater. Interfaces* 2018, 10, 20404.
- 17 J. Wu, W. Xia, M. H. Lan, X. J. Xing, J. C. Hu, L. Huang, J. Liu, Y. Y. Ren, H. F. Liu, F. Wang, *J. Mater. Chem. A*, 2020, 8, 21690