

Electronic Supplementary Information (ESI)

Direct Z-scheme CdS-NiPc heterojunctions as noble metal-free photocatalysts for enhanced photocatalytic hydrogen evolution

Jialiang Sheng, Chunqiang Wang, Fang Duan*, Shengrong Yan, Shuanglong Lu, Han Zhu, Mingliang Du, Xin Chen, Mingqing Chen

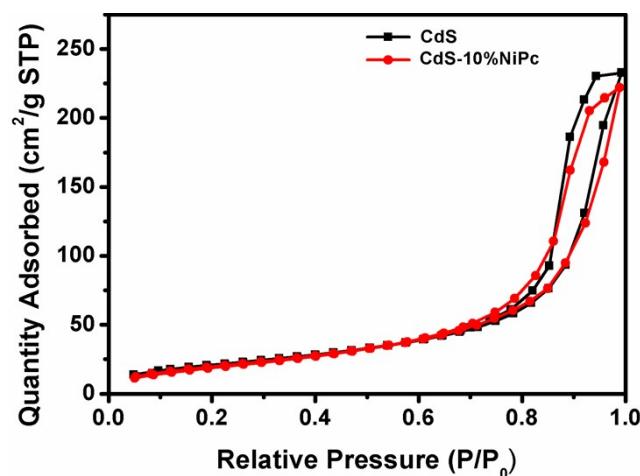


Fig. S1 N₂ adsorption-desorption isotherms of pure CdS and CdS-10%NiPc

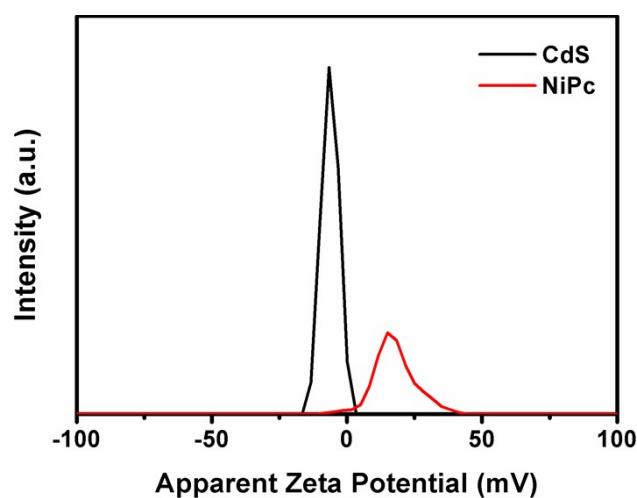


Fig. S2 Zeta potentials of CdS and NiPc in pure water

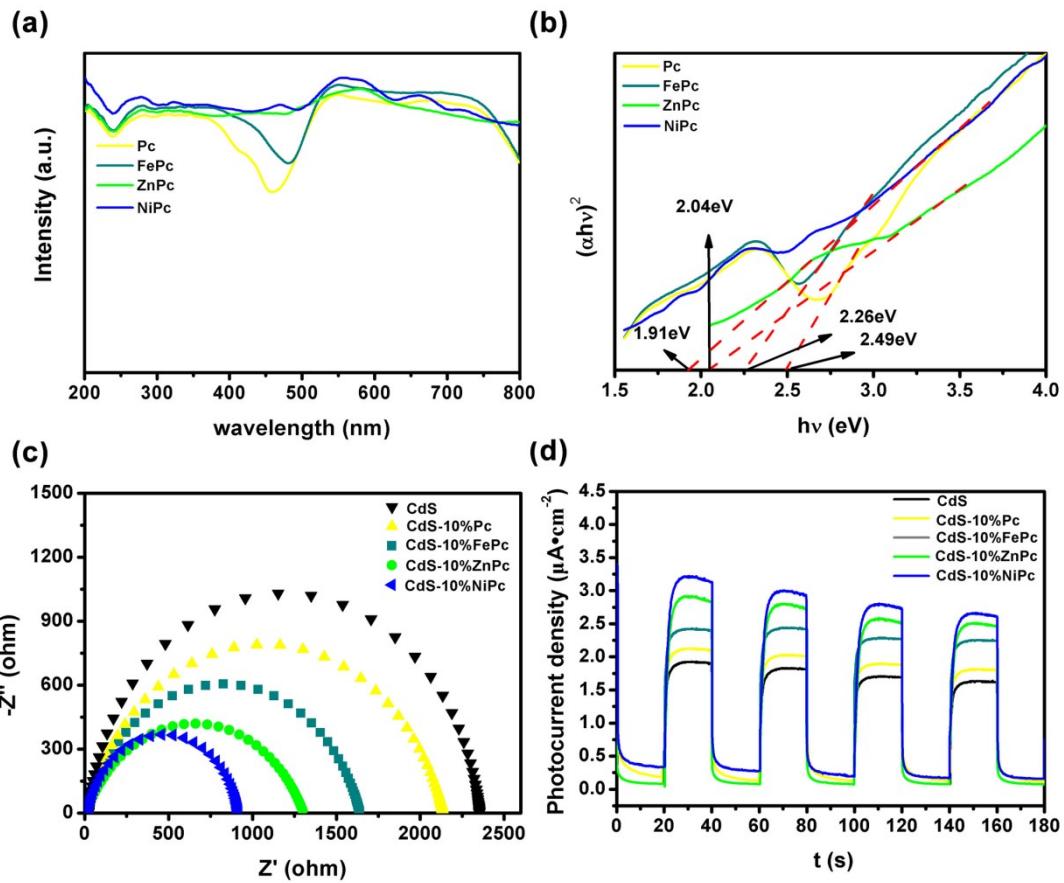


Fig. S3. (a) UV–vis absorption spectra and (b) tauc-plots of the UV–vis spectra of **Pc**, **FePc**, **ZnPc** and **NiPc**; (c) EIS spectra and (d) transient photocurrent response of **CdS**, **CdS-10%Pc**, **CdS-10%FePc**, **CdS-10%ZnPc** and **CdS-10%NiPc**

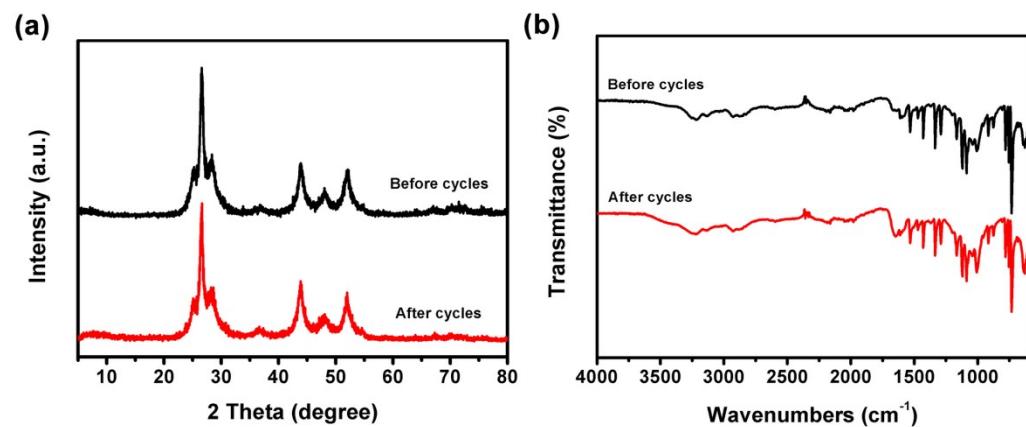


Fig. S4. (a) XRD patterns of **CdS-10%NiPc** before and after five cycles; (b) FT-IR spectra of **CdS-NiPc** composites before and after five cycles

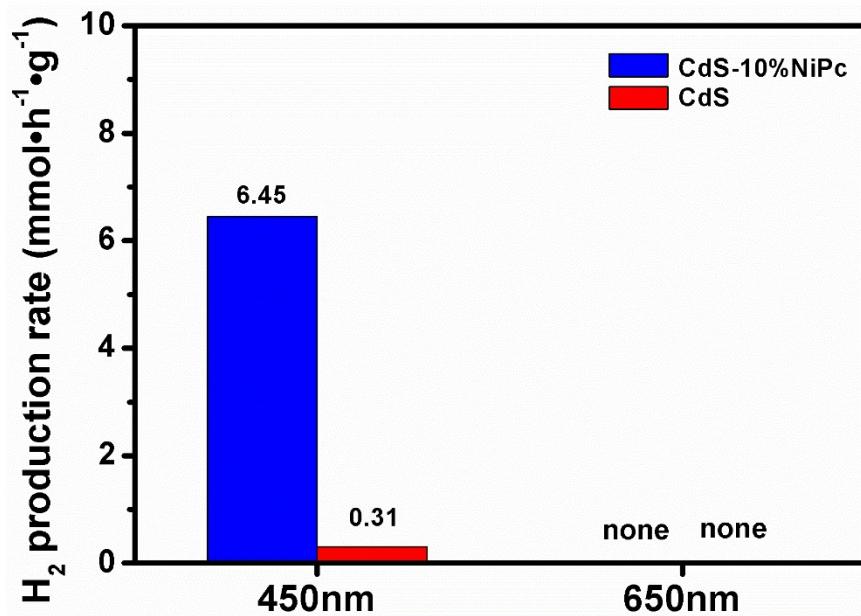


Fig. S5. Photocatalytic H_2 generation rates for CdS-10%NiPc and CdS under 450 nm and 650 nm wavelength illumination.

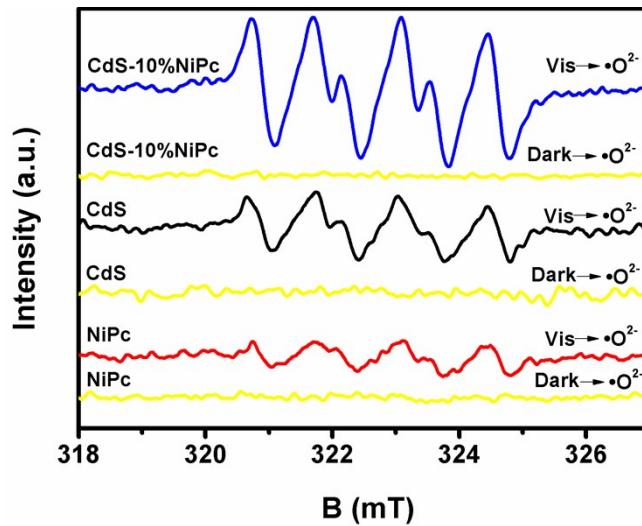


Fig. S6 DMPO spin-trapping ESR spectra of CdS, NiPc, and CdS-10%NiPc composite

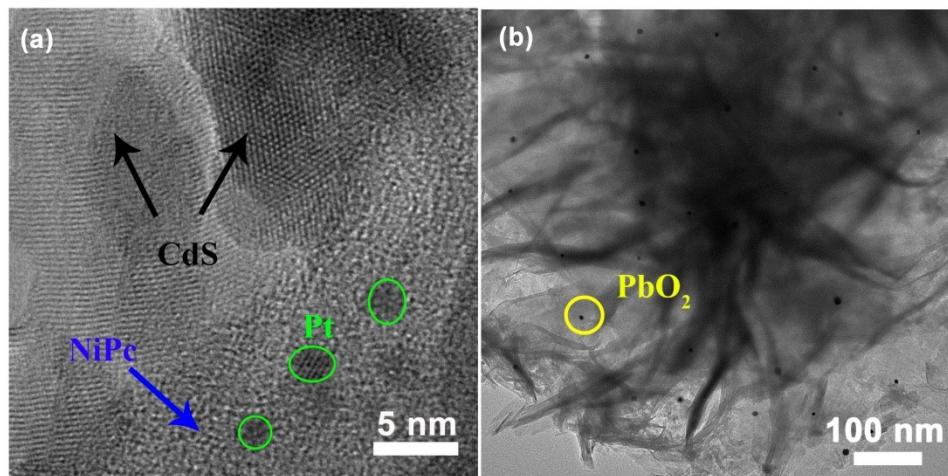


Fig. S7 TEM images of photodeposition of (a) Pt and (b) PbO_2 nanoparticles on the CdS-10%NiPc composite

Table S1 Comparisons of the H_2 evolution rate and AQE over the CdS-NiPc composite with different contents of NiPc

Photocatalyst	Light source	Activity ($\text{mmol g}^{-1} \text{h}^{-1}$)	AQE (%) (450 nm)	Ref.
CdS-10%NiPc	300 W Xe-lamp, $\lambda \geq 420 \text{ nm}$	17.74	4.86	This work
CdS	300 W Xe-lamp, $\lambda \geq 420 \text{ nm}$	0.93	0.26	This work
CdS-1%NiPc	300 W Xe-lamp, $\lambda \geq 420 \text{ nm}$	4.65	1.27	This work
CdS-5%NiPc	300 W Xe-lamp, $\lambda \geq 420 \text{ nm}$	8.78	2.4	This work
CdS-8%NiPc	300 W Xe-lamp, $\lambda \geq 420 \text{ nm}$	11.29	3.09	This work
CdS-12%NiPc	300 W Xe-lamp, $\lambda \geq 420 \text{ nm}$	14.57	3.99	This work
CdS-15%NiPc	300 W Xe-lamp, $\lambda \geq 420 \text{ nm}$	13.24	3.63	This work

Table S2 Comparisons of the H₂ evolution rate and AQE over the CdS-10%NiPc and other materials

Photocatalyst	Light source	Activity (mmol g ⁻¹ h ⁻¹)	AQE (%)	Ref.
CdS-10%NiPc	300 W Xe-lamp, $\lambda \geq 420$ nm	17.74	4.86 ($\lambda=450$ nm)	This work
RGO/SiPc/Pt	150 W Xe-lamp	~4.5	0.56 ($\lambda=420$ nm)	[1]
MnPcG/Pt	150 W Xe-lamp $\lambda > 400$ nm	8.46	1.9 ($\lambda=420$ nm)	[2]
CdS/CTF-1	300 W Xe-lamp, $\lambda \geq 420$ nm	11.43	11.1 ($\lambda=420$ nm)	[3]
CdS/g-C ₃ N ₄	300 W Xe-lamp, $\lambda \geq 420$ nm	4.15	4.3 ($\lambda=420$ nm)	[4]
CdS/ZnO	500W Xe lamp ($\lambda \geq 400$ nm)	0.85	3 ($\lambda=420$ nm)	[5]
MoS ₂ /TpPa-1-COF	300 W Xe-lamp, $\lambda \geq 420$ nm	5.59	0.76 ($\lambda=420$ nm)	[6]
g-C ₃ N ₄ /MoS ₂	300 W Xe-lamp, $\lambda \geq 420$ nm	1.03	2.1 ($\lambda=420$ nm)	[7]

Table S3 The fluorescence lifetimes and electron transfer rate constants (k_{ET}) of CdS-NiPc composites with different contents of NiPc

Sample	Average fluorescence lifetimes (ns)	Transfer rate constants k_{ET} (s ⁻¹)
CdS	3.18	/
CdS-1%NiPc	3.07	1.1×10^7
CdS-5%NiPc	2.98	2.1×10^7
CdS-8%NiPc	2.91	2.9×10^7
CdS-10%NiPc	2.75	4.9×10^7
CdS-12%NiPc	2.81	4.1×10^7
CdS-15%NiPc	2.84	3.7×10^7

References:

- [1] J. Huang, Y. J. Wu, D. D. Wang, Y. F. Ma, Z. K. Yue, Y. T. Lu, M. X. Zhang, Z. J. Zhang and P. Yang, *Accts Appl. Mater. Inter.*, **2015**, 7, 3732-3741.
- [2] D. Wang, J. Huang, X. Li, *J. Mater. Chem. A*, **2015**, 3(8): 4195-4202.
- [3] D. K. Wang, H. Zeng, X. Xiong, M. F. Wu, M. R. Xia, M. L. Xie, J. P. Zou and S. L. Luo,

Sci. Bull., **2020**, 65, 113-122.

- [4] L. Liu, Y. H. Qi, J. S. Hu, Y. H. Liang and W. Q. Cui, *Appl Surf Sci*, 2015, 351, 1146-1154.
- [5] X. X. Zou, P. P. Wang, C. G. Li, J. Zhao, D. J. Wang, T. Asefa and G. D. Li, *J. Mater. Chem. A*, **2014**, 2, 4682-4689.
- [6] M. Y. Gao, C. C. Li, H. L. Tang, X. J. Sun, H. Dong and F. M. Zhang, *J. Mater. Chem. A*, **2019**, 7, 20193-20200.
- [7] Y. Hou, A. B. Laursen, J. Zhang, G. Zhang, Y. Zhu, X. Wang, S. Dahl, I. Chorkendorff, *Angew. Chem. Int. Ed*, **2013**, 52, 3621-3625.