

**Supplementary Material**

**An S-scheme heterojunction constructed from  $\alpha\text{-Fe}_2\text{O}_3$  and In-doped carbon nitride for high-efficiency  $\text{CO}_2$  photoreduction**

Jiaming Wu<sup>a</sup>, Keyan Li<sup>a,\*</sup>, Jiahui Li<sup>a</sup>, Jun Du<sup>a</sup>, Xiangyang Li<sup>a</sup>, Chunshan Song<sup>a,b</sup>,

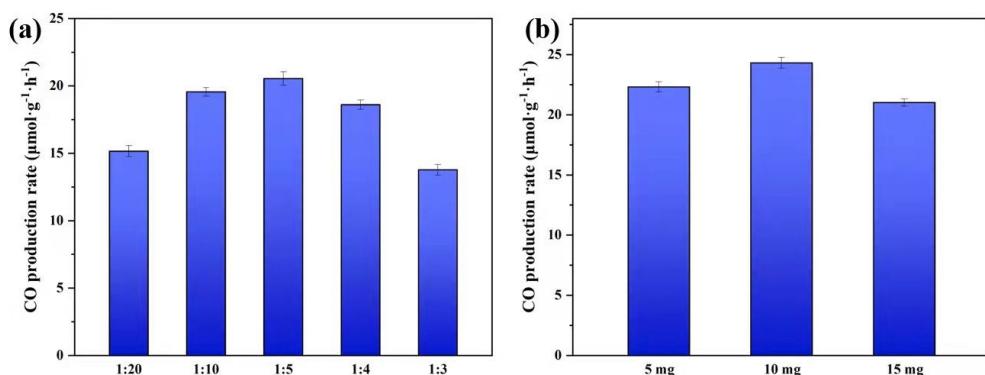
Xinwen Guo<sup>a,\*</sup>

<sup>a</sup>*State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy*

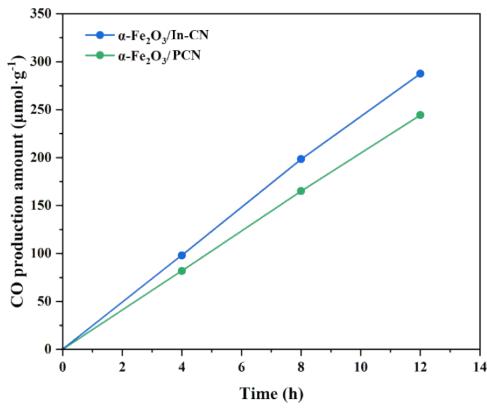
*Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China.*

<sup>b</sup>*Department of Chemistry, Faculty of Science, The Chinese University of Hong Kong, Shatin, Hong Kong 999077, China*

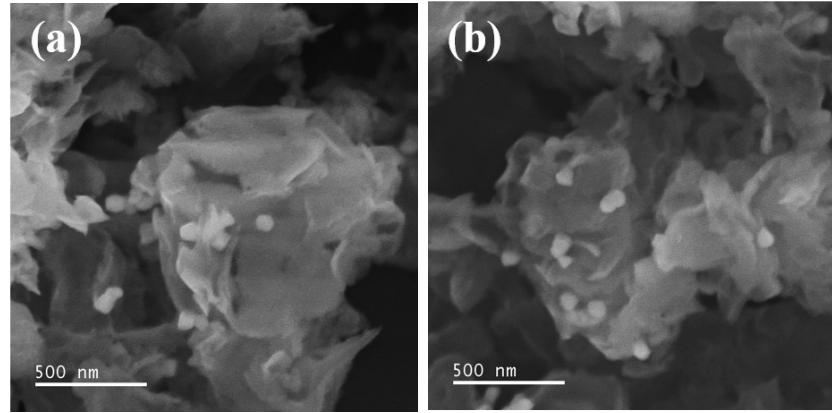
\*Corresponding Author. E-mail address: keyanli@dlut.edu.cn; guoxw@dlut.edu.cn.



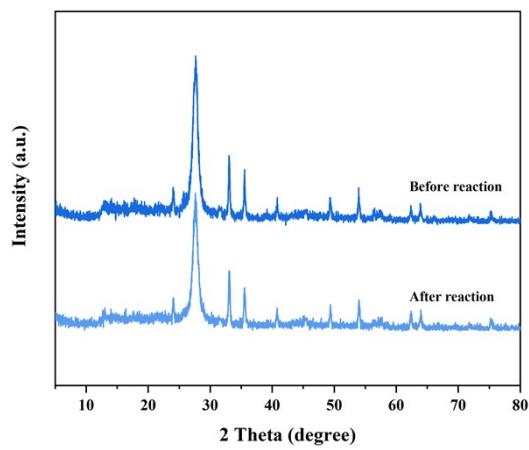
**Fig. S1** Photocatalytic  $\text{CO}_2$  reduction activity of (a)  $\alpha\text{-Fe}_2\text{O}_3/\text{PCN}$  with different mass ratios of  $\alpha\text{-Fe}_2\text{O}_3$  to PCN and (b)  $\alpha\text{-Fe}_2\text{O}_3/\text{In-CN}$  for which In-CN are prepared with different dosages of In-MOF. The corresponding In contents are 0.24 wt%, 0.41 wt% and 0.70 wt%, respectively.



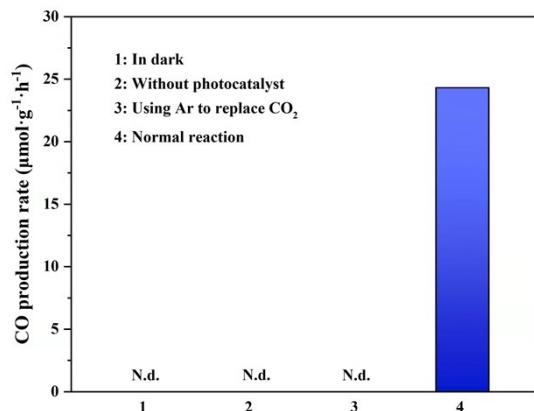
**Fig. S2** Time-dependent CO yield of  $\alpha\text{-Fe}_2\text{O}_3/\text{PCN}$  and  $\alpha\text{-Fe}_2\text{O}_3/\text{In-CN}$  heterojunctions.



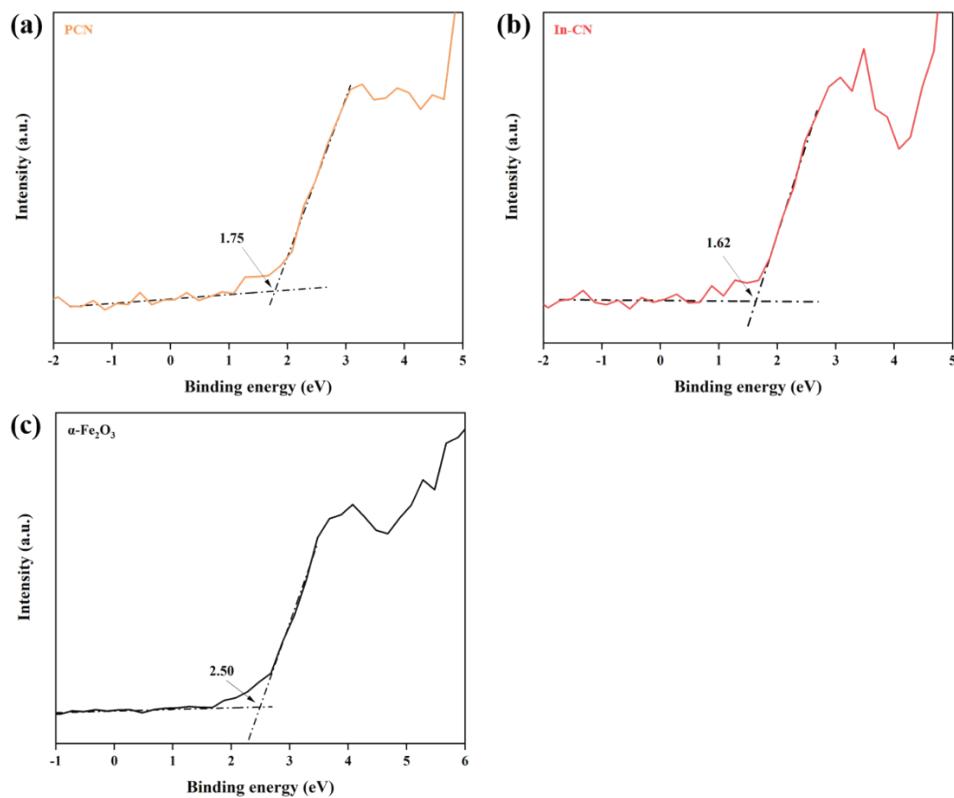
**Fig. S3** SEM images of  $\alpha\text{-Fe}_2\text{O}_3/\text{In-CN}$  (a) before reaction and (b) after continuous reaction for 12 h.



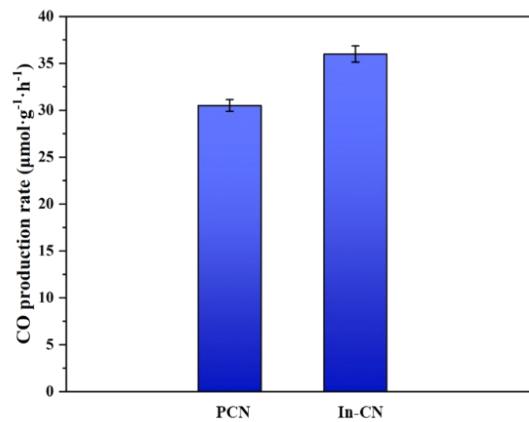
**Fig. S4** XRD patterns of  $\alpha\text{-Fe}_2\text{O}_3/\text{In-CN}$  before reaction and after continuous reaction for 12 h.



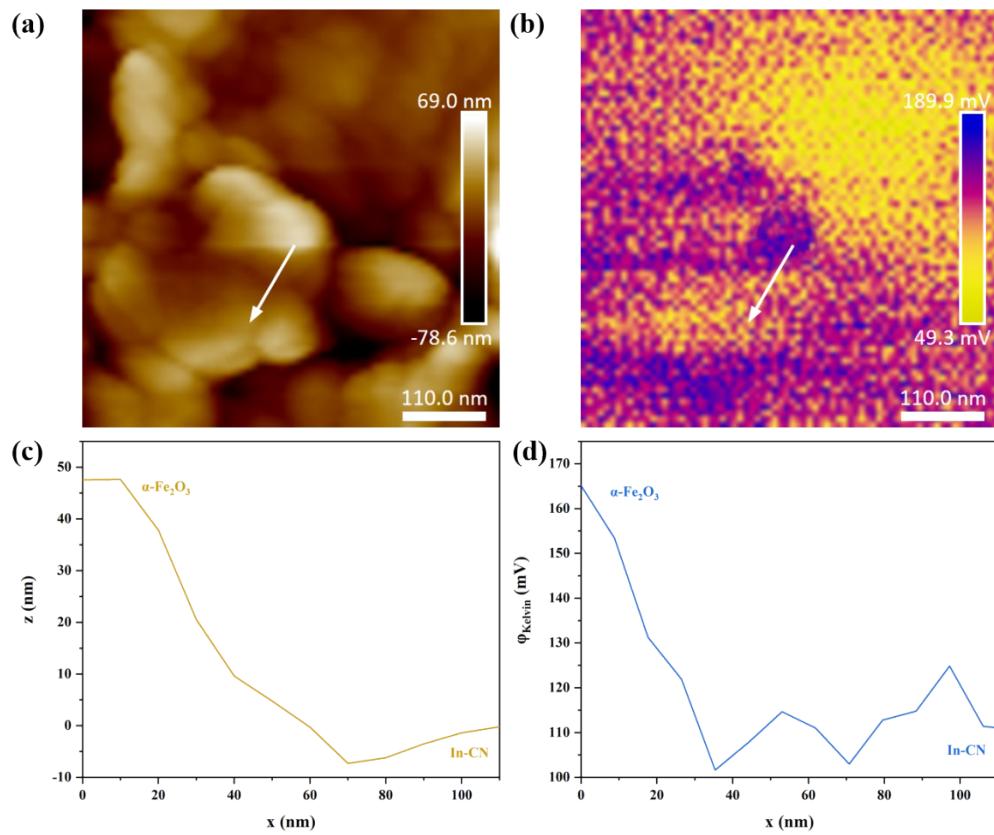
**Fig. S5** CO production rate over  $\alpha\text{-Fe}_2\text{O}_3/\text{In-CN}$  under various conditions (N.d.: not detected).



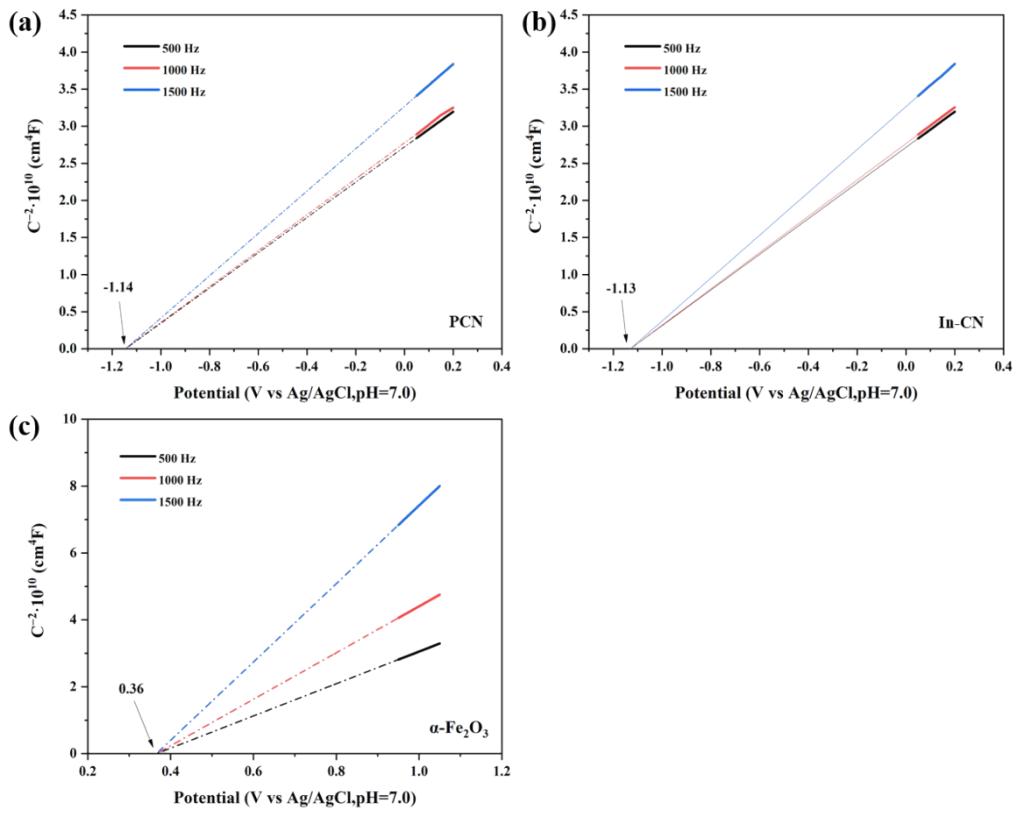
**Fig. S6** Valence band (VB)-XPS spectra of (a) PCN, (b) In-CN and (c)  $\alpha\text{-Fe}_2\text{O}_3$ .



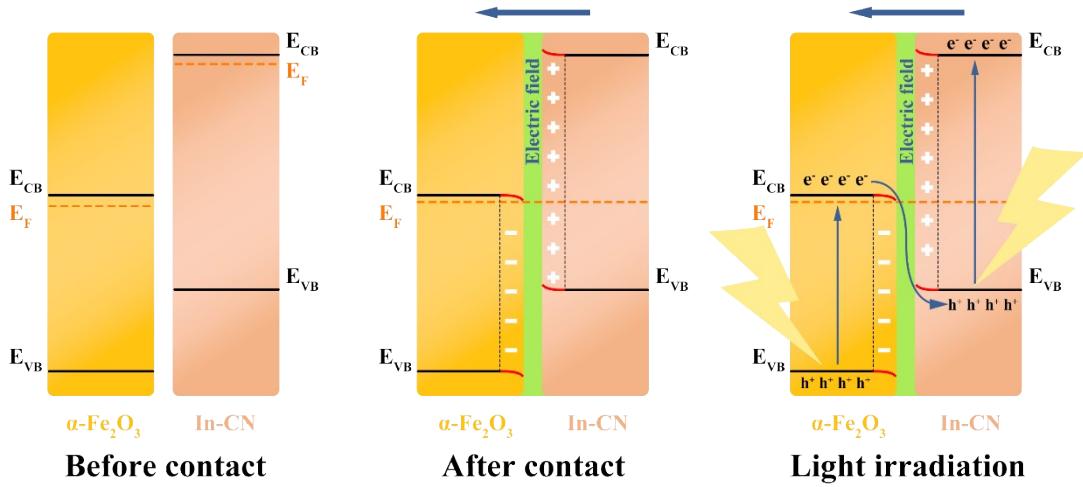
**Fig. S7** Comparison of the photocatalytic activity of PCN and In-CN in the presence of TEOA as hole sacrificial agent.



**Fig. S8** (a) Topography image and (b) surface potential of  $\alpha\text{-Fe}_2\text{O}_3/\text{In-CN}$ , (c,d) line-scanning profile and the corresponding Kelvin probe signal through one  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticle.



**Fig. S9** Mott-Schottky plots of (a) PCN, (b) In-CN and (c)  $\alpha\text{-Fe}_2\text{O}_3$ .



**Fig. S10** Energy band positions of  $\alpha\text{-Fe}_2\text{O}_3$  and In-CN (a) before contact, (b) after contact, and (c) S-scheme charge transfer mechanism under light irradiation.

**Table S1** Comparison of the CO<sub>2</sub> photoreduction performance of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/In-CN with those of other photocatalysts reported in the literature.

Photocatalyst	Light source	Reaction medium	Product	Product generation rate ( $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ )	Ref.
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /In-CN	300W Xe lamp	Gas-solid, H <sub>2</sub> O	CO	24.3	This work
MoS <sub>2</sub> /TiO <sub>2</sub>	300W Xe lamp	Gas-solid, H <sub>2</sub> O	CO CH <sub>4</sub>	2.83 1.45	[1]
NH <sub>2</sub> -MIL-101(Fe)/g-C <sub>3</sub> N <sub>4</sub>	300W Xe lamp $\lambda>400$ nm 300W Xe lamp with AM1.5 G filter	Gas-solid, TEOA	CO	22.13	[2]
Bi <sub>3</sub> TiNbO <sub>9</sub>	300W Xe lamp with AM1.5 G filter	Gas-solid, H <sub>2</sub> O	CO	20.91	[3]
Mo/C <sub>3</sub> N <sub>4</sub>	300W Xe lamp $\lambda>420$ nm	Gas-solid, H <sub>2</sub> O	CO H <sub>2</sub>	18.0 37.0	[4]
Urchin-like $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	300W Xe lamp	Gas-solid, H <sub>2</sub> O	CO	27.2	[5]
InVO <sub>4</sub> / $\beta$ -AgVO <sub>3</sub>	300W Xe lamp $\lambda>420$ nm	Gas-solid, H <sub>2</sub> O	CO	12.61	[6]
ZnFe <sub>2</sub> O <sub>4</sub> /RGO/In <sub>2</sub> O <sub>3</sub>	300W Xe lamp	Gas-solid, H <sub>2</sub> O	CO CH <sub>4</sub>	8.85 1.95	[7]
Co <sub>1</sub> -C <sub>3</sub> N <sub>4</sub> @ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	300W Xe lamp	Gas-solid, H <sub>2</sub> O	CO	25.2	[8]
NiAl-LDH/Ti <sub>3</sub> C <sub>2</sub>	300W Xe lamp	Gas-solid, H <sub>2</sub> O	CO	11.82	[9]
LaPO <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	300W Xe lamp	Gas-solid, H <sub>2</sub> O	CO	14.4	[10]

**Table S2** The fitted parameters of time-resolved PL spectra.

Sample	$\tau_1$ (ns)	$f_1$ (%)	$\tau_2$ (ns)	$f_2$ (%)	$\tau$ (ns)
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /In-CN	3.87	72.35	16.50	27.65	11.69
In-CN	4.03	81.13	17.44	19.77	10.76
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /PCN	2.05	82.35	8.50	17.65	5.09
PCN	1.90	80.24	7.53	19.76	4.68

## References

- [1] Y. Li, J. Tang, Y. Wei, W. He, Z. Tang, X. Zhang, J. Xiong and Z. Zhao. *J. CO<sub>2</sub> Util.*, 2021, **51**, 101648.
- [2] X.-Y. Dao, X.-F. Xie, J.-H. Guo, X.-Y. Zhang, Y.-S. Kang and W.-Y. Sun. *ACS Appl. Energy Mater.*, 2020, **3**, 3946-3954.
- [3] H. Yu, F. Chen, X. Li, H. Huang, Q. Zhang, S. Su, K. Wang, E. Mao, B. Mei, G. Mul, T. Ma and Y. Zhang. *Nat. Commun.*, 2021, **12**, 4594.
- [4] R. Zhang, P. Li, F. Wang, L. Ye, A. Gaur, Z. Huang, Z. Zhao, Y. Bai and Y. Zhou. *Appl. Catal. B: Environ.*, 2019, **250**, 273-279.
- [5] Z. Jiang, W. Wan, H. Li, S. Yuan, H. Zhao and P. K. Wong. *Adv. Mater.*, 2018, **30**, 1706108.
- [6] J. Yang, J. Hao, S. Xu, Q. Wang, J. Dai, A. Zhang and X. Pang. *ACS Appl. Mater. Inter.*, 2019, **11**, 32025-32037.
- [7] J. Li, F. Wei, C. Dong, W. Mu and X. Han. *J. Mater. Chem. A*, 2020, **8**, 6524-6531.
- [8] B.-C. He, C. Zhang, P.-P. Luo, Y. Li and T.-B. Lu. *Green Chem.*, 2020, **22**, 7552-7559.
- [9] Q. Shi, X. Zhang, Y. Yang, J. Huang, X. Fu, T. Wang, X. Liu, A. Sun, J. Ge, J. Shen, Y. Zhou and Z. Liu. *J. Energy Chem.*, 2021, **59**, 9-18.
- [10] M. Li, L. Zhang, X. Fan, M. Wu, M. Wang, R. Cheng, L. Zhang, H. Yao and J. Shi. *Appl. Catal. B: Environ.*, 2017, **201**, 629-635.