

Supporting Information

Facile Construction of Hollow In₂S₃/Polymeric Carbon Nitride Heterojunction for Efficient Visible-Light-Driven CO₂ Reduction

Shuangchao Zhao^a, Keyan Li^{a,*}, Jun Du^a, Chunshan Song^{a,b}, Xinwen Guo^{a,*}

^a*State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China.*

^b*Department of Chemistry, Faculty of Science, The Chinese University of Hong Kong, Shatin, NT, Hong Kong, China*

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

Number of pages: 9

Number of figures: 8

Number of tables: 3

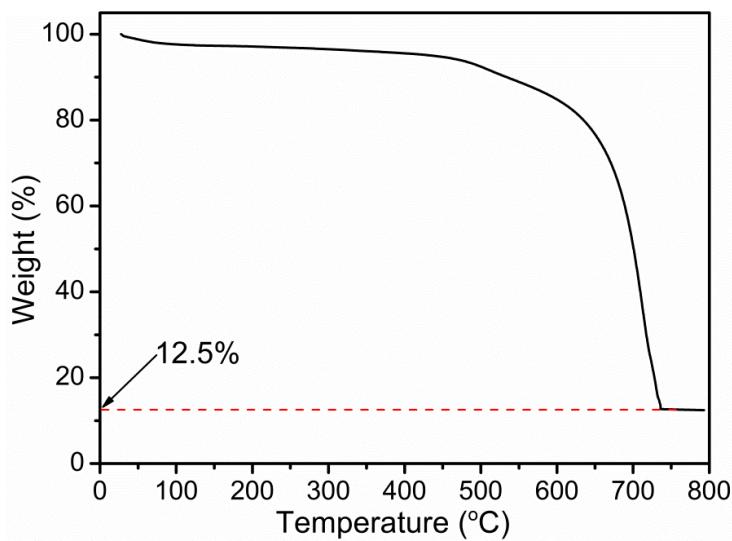


Figure S1. TG curve of IS/CN-5.

When IS/CN-5 is heated to 800 °C in air, CN is decomposed completely and In_2S_3 is transformed into In_2O_3 . The content of In_2O_3 is 12.5%, and the content of In_2S_3 is calculated to be 14.7% according to the conservation of indium.

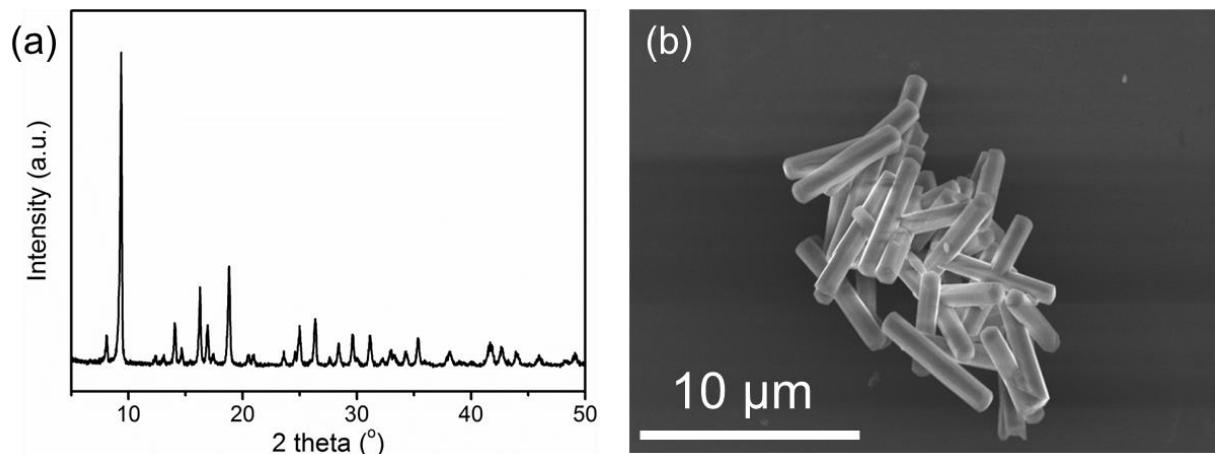


Figure S2. (a) XRD pattern and (b) SEM image of In-MIL-68.

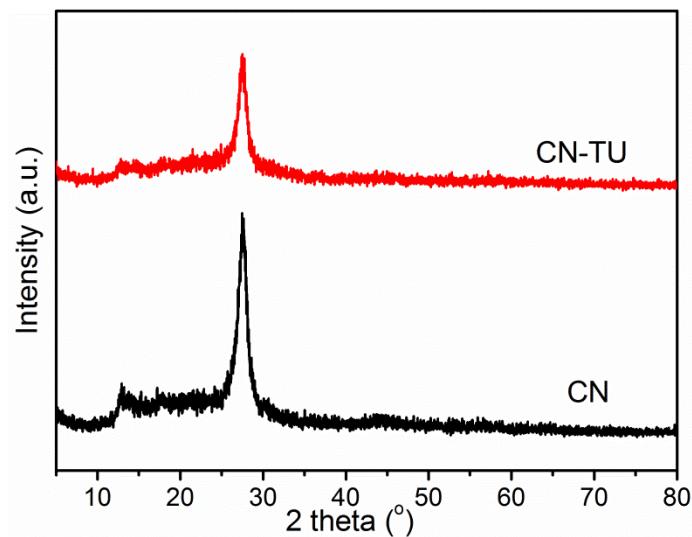


Figure S3. XRD patterns of CN and CN-TU.

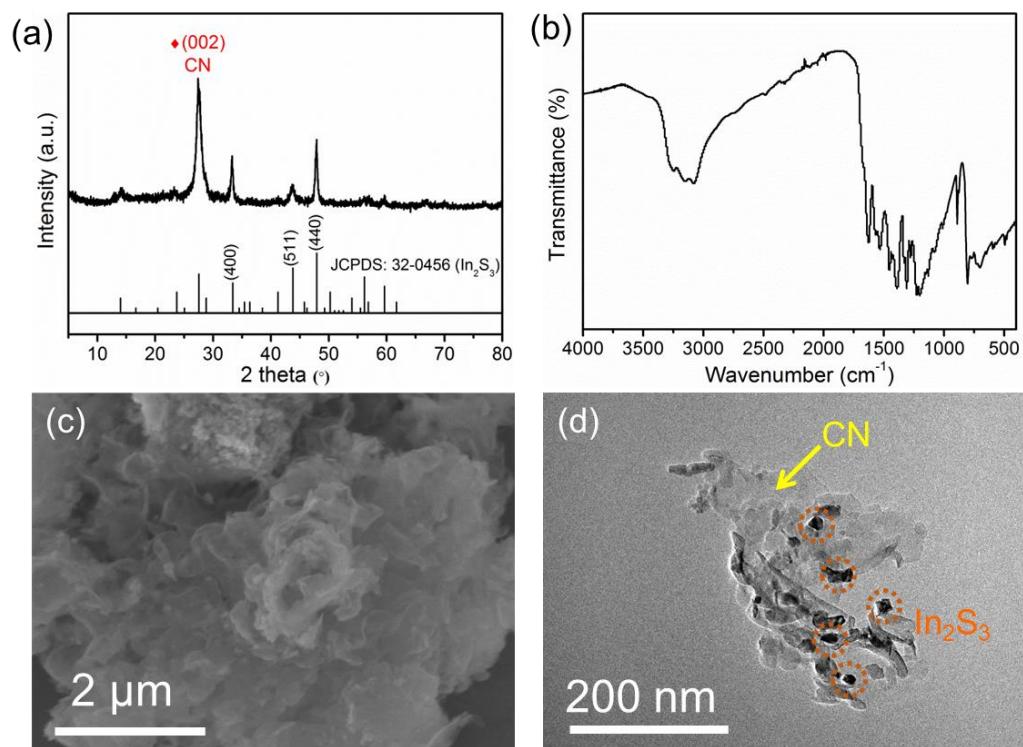


Figure S4. (a) XRD pattern, (b) FT-IR spectrum, (c) SEM image and (d) TEM image of IS-NP/CN.

IS-NP/CN.

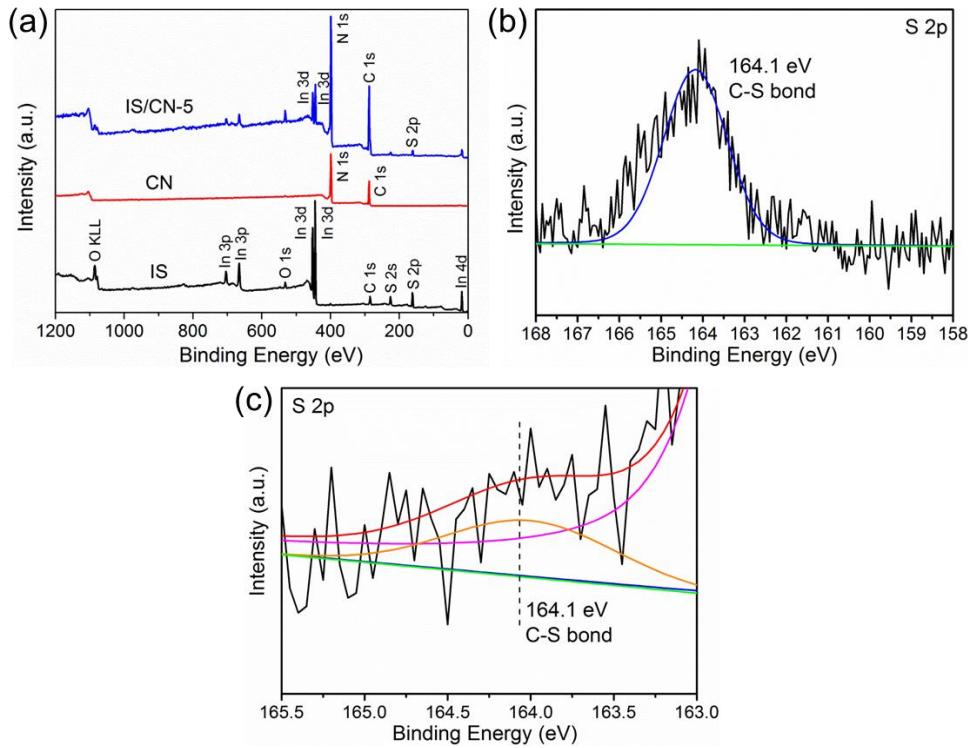


Figure S5. (a) XPS survey spectra of IS, CN and IS/CN-5, S 2p XPS spectra of (b) CN-TU and (c) IS/CN-5.

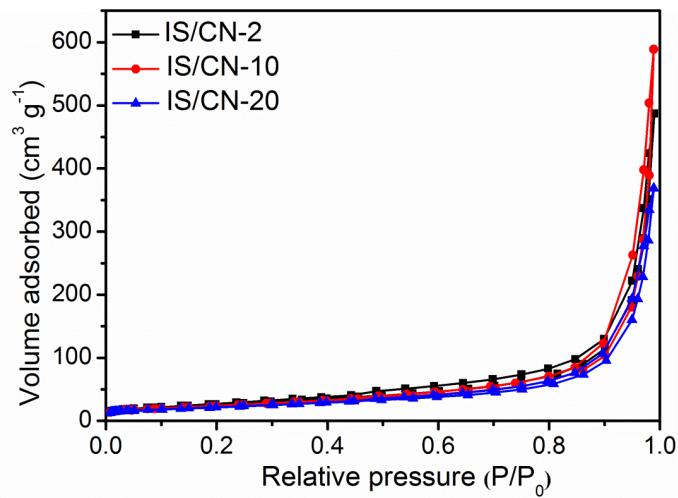


Figure S6. N_2 adsorption-desorption isotherms of IS/CN-2, IS/CN-10 and IS/CN-20.

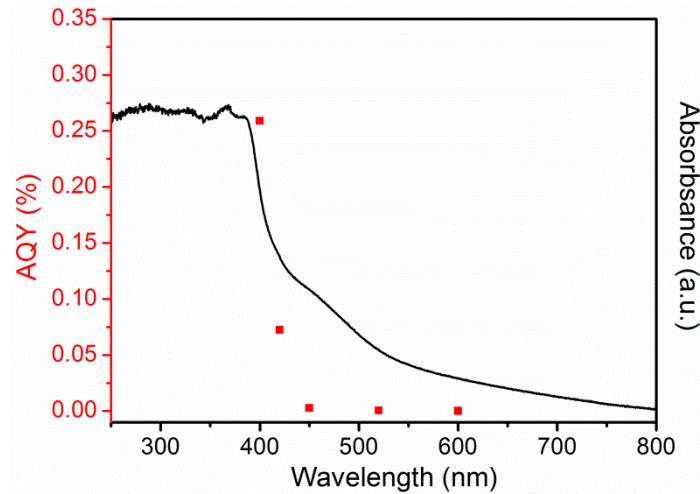


Figure S7. Wavelength dependent AQY of IS/CN-5.

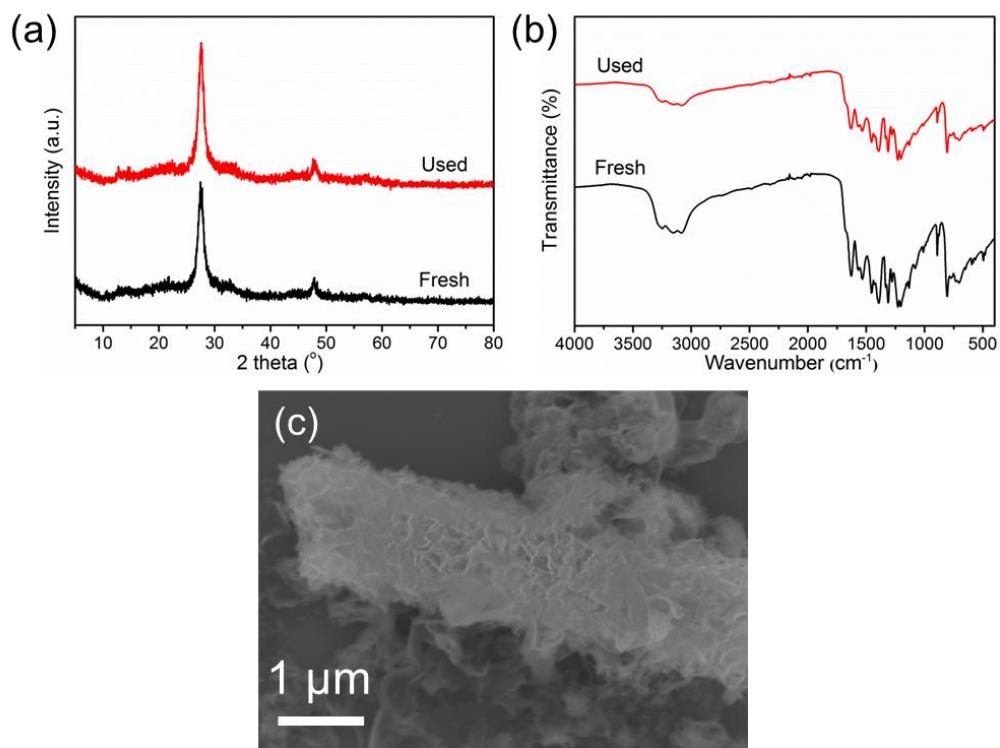


Figure S8. (a) XRD patterns and (b) FT-IR spectra of IS/CN-5 before and after reaction. (c) SEM image of IS/CN-5 after reaction.

Table S1. Zeta potentials of In-MIL-68 and CN.

Sample	Zeta potential (mV)
In-MIL-68	-8.53
CN	6.86

Table S2. BET surface area, CO and H₂ generation rates and the selectivity of CO of the as-prepared samples.

Sample	BET surface area (m ² g ⁻¹)	CO generation rate (μmol g ⁻¹ h ⁻¹)	H ₂ generation rate (μmol g ⁻¹ h ⁻¹)	CO selectivity (%)
IS	95	4.9	16.0	23.4
IS/CN-2	96	351.2	79.3	81.6
IS/CN-5	86	483.4	112.7	81.1
IS/CN-10	87	439.5	98.6	81.7
IS/CN-20	79	397.0	78.6	83.5
CN	112	80.6	19.2	80.8

Table S3. Comparison of the photocatalytic CO₂ conversion performance of IS/CN-5 with those of other photocatalysts reported in the literature.

Photocatalyst	Cocatalyst	Sacrificial agent	Main product generation rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	Ref.
CdS/BCN	Co(bpy) ₃ ²⁺	TEOA	CO: 250	1
Co ₄ @g-C ₃ N ₄	Co(bpy) ₃ ²⁺	TEOA	CO: 114.4	2
UiO-66/CNNS	/	TEOA	CO: 9.9	3
HR-CN	Co(bpy) ₃ ²⁺	TEOA	CO: 296.7	4
Co ₃ O ₄ /2D g-C ₃ N ₄	Co(bpy) ₃ ²⁺	TEOA	CO: 419	5
BCN-30	Co(bpy) ₃ ²⁺	TEOA	CO: 93	6
TiO _{2-x} /MCN	Co(bpy) ₃ ²⁺	TEOA	CO: 77.8	7
Co doped TiO ₂ /g-C ₃ N ₄	Co(bpy) ₃ ²⁺	TEOA	CO: 287.4	8
In ₂ S ₃ -CuInS ₂	Co(bpy) ₃ ²⁺	TEOA	CO: 19	9
BiFeWO _x @In ₂ S ₃	/	TEOA	CO: 28.9 CH ₄ : 49.9	10
TCN(NH ₃)	Co(bpy) ₃ ²⁺	TEOA	CO: 103.6	11
BIF-20@g-C ₃ N ₄	/	TEOA	CO: 53.9 CH ₄ : 15.5	12
ZnIn ₂ S ₄ @CNO	Co(bpy) ₃ ²⁺	TEOA	CO: 253.8	13
g-C ₃ N ₄ /CdS	Co(bpy) ₃ ²⁺	TEOA	CO: 234.6	14
DA-CTF	Co(bpy) ₃ ²⁺	TEOA	CO: 155	15
IS/CN-5	Co(bpy) ₃ ²⁺	TEOA	CO: 483.4	This work

References

1. Zhou, M.; Wang, S.; Yang, P.; Huang, C.; Wang, X. Boron Carbon Nitride Semiconductors Decorated with CdS Nanoparticles for Photocatalytic Reduction of CO₂. *ACS Catal.* **2018**, *8*, 4928-4936.
2. Zhou, J.; Chen, W.; Sun, C.; Han, L.; Qin, C.; Chen, M.; Wang, X.; Wang, E.; Su, Z. Oxidative Polyoxometalates Modified Graphitic Carbon Nitride for Visible-Light CO₂ Reduction. *ACS Appl. Mater. Interfaces* **2017**, *9*, 11689-11695.
3. Shi, L.; Wang, T.; Zhang, H.; Chang, K.; Ye, J. Electrostatic Self-Assembly of Nanosized Carbon Nitride Nanosheet onto a Zirconium Metal-Organic Framework for Enhanced Photocatalytic CO₂ Reduction. *Adv. Funct. Mater.* **2015**, *25*, 5360-5367.
4. Zheng, Y.; Lin, L.; Ye, X.; Guo, F.; Wang, X. Helical Graphitic Carbon Nitrides with Photocatalytic and Optical Activities. *Angew. Chem., Int. Ed.* **2014**, *53*, 11926-11930.
5. Zhu, X.; Ji, H.; Yi, J.; Yang, J.; She, X.; Ding, P.; Li, L.; Deng, J.; Qian, J.; Xu, H.; Li, H. A Specifically Exposed Cobalt Oxide/Carbon Nitride 2D Heterostructure for Carbon Dioxide Photoreduction. *Ind. Eng. Chem. Res.* **2018**, *57*, 17394-17400.
6. Huang, C.; Chen, C.; Zhang, M.; Lin, L.; Ye, X.; Lin, S.; Antonietti, M.; Wang, X. Carbon-Doped BN Nanosheets for Metal-Free Photoredox Catalysis. *Nat. Commun.* **2015**, *6*, 7698-7705.
7. Shi, H.; Long, S.; Hu, S.; Hou, J.; Ni, W.; Song, C.; Li, K.; Gurzadyan, G. G.; Guo, X. Interfacial Charge Transfer in 0D/2D Defect-Rich Heterostructures for Efficient Solar-Driven CO₂ Reduction. *Appl. Catal., B* **2019**, *245*, 760-769.
8. Shi, H.; Du, J.; Hou, J.; Ni, W.; Song, C.; Li, K.; Gurzadyan, G. G.; Guo, X. Solar-Driven CO₂ Conversion over Co²⁺ Doped 0D/2D TiO₂/g-C₃N₄ Heterostructure: Insights into the Role of Co²⁺

and Cocatalyst. *J. CO₂ Util.* **2020**, *38*, 16-23.

9. Yang, J.; Zhu, X.; Mo, Z.; Yi, J.; Yan, J.; Deng, J.; Xu, Y.; She, Y.; Qian, J.; Xu, H.; Li, H. A Multidimensional In₂S₃-CuInS₂ Heterostructure for Photocatalytic Carbon Dioxide Reduction.

Inorg. Chem. Front. **2018**, *5*, 3163-3169.

10. Wang, Y.; Zeng, Y.; Wan, S.; Zhang, S.; Zhong, Q. Construction of Octahedral BiFeWO_x Encapsulated in Hierarchical In₂S₃ Core@Shell Heterostructure for Visible-Light-Driven CO₂ Reduction. *J. CO₂ Util.* **2019**, *29*, 156-162.

11. Mo, Z.; Zhu, X.; Jiang, Z.; Song, Y.; Liu, D.; Li, H.; Yang, X.; She, Y.; Lei, Y.; Yuan, S.; Li, H.; Song, L.; Yan, Q.; Xu, H. Porous Nitrogen-Rich g-C₃N₄ Nanotubes for Efficient Photocatalytic CO₂ Reduction. *Appl. Catal., B* **2019**, *256*, 117854.

12. Xu, G.; Zhang, H.; Wei, J.; Zhang, H. X.; Wu, X.; Li, Y.; Li, C.; Zhang, J.; Ye, J. Integrating the g-C₃N₄ Nanosheet with B-H Bonding Decorated Metal-Organic Framework for CO₂ Activation and Photoreduction. *ACS Nano* **2018**, *12*, 5333-5340.

13. Zhu, K.; Ou-Yang, J.; Zeng, Q.; Meng, S.; Teng, W.; Song, Y.; Tang, S.; Cui, Y. Fabrication of Hierarchical ZnIn₂S₄@CNO Nanosheets for Photocatalytic Hydrogen Production and CO₂ Photoreduction. *Chin. J. Catal.* **2020**, *41*, 454-463.

14. Vu, N.-N.; Kaliaguine, S.; Do, T.-O. Synthesis of the g-C₃N₄/CdS Nanocomposite with a Chemically Bonded Interface for Enhanced Sunlight-Driven CO₂ Photoreduction. *ACS Appl. Energy Mater.* **2020**, *3*, 6422-6433.

15. Zhong, H.; Hong, Z.; Yang, C.; Li, L.; Xu, Y.; Wang, X.; Wang, R. A Covalent Triazine-Based Framework Consisting of Donor-Acceptor Dyads for Visible-Light-Driven Photocatalytic CO₂ Reduction. *ChemSusChem* **2019**, *12*, 4493-4499.