

Supporting Information

Phosphorus-Doped Hollow Tubular g-C₃N₄ for Enhanced Photocatalytic CO₂ Reduction

Manying Sun¹, Chuanwei Zhu¹, Su Wei¹, Liuyun Chen¹, Hongbing Ji^{1,2}, Tongming Su^{1*}, Zuzeng Qin^{1*}

1. Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology,
School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China
2. Fine Chemical Industry Research Institute, Sun Yat-sen University, Guangzhou 510275, China

*Corresponding author:

E-mail: sutm@gxu.edu.cn (T. Su), qinzuzeng@gxu.edu.cn (Z. Qin)

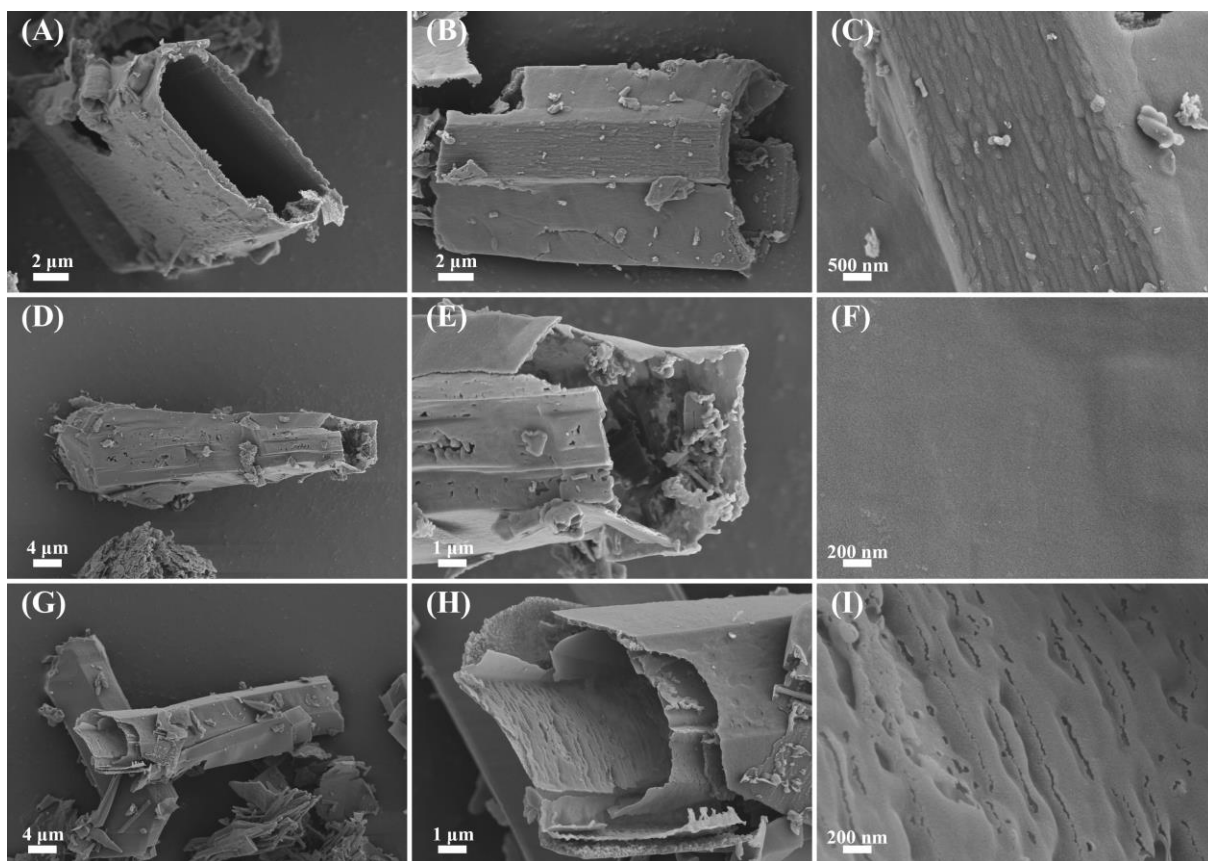


Figure S1. SEM images of 0.5-P-HCN (A, B, C), 1.5-P-HCN (D, E, F), and 2.0-P-HCN (G, H, I).

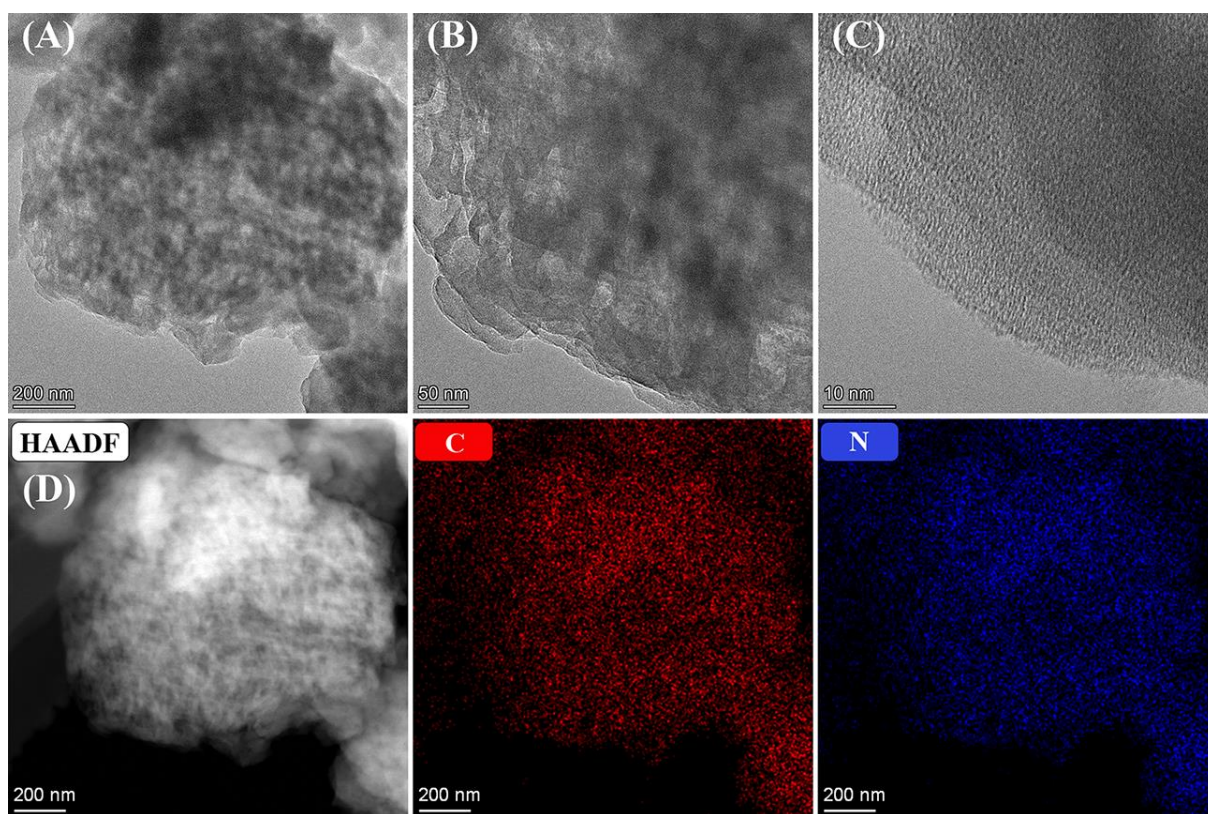


Figure S2. TEM images (A, B, C) and EDS elemental mapping (D) of g-C₃N₄.

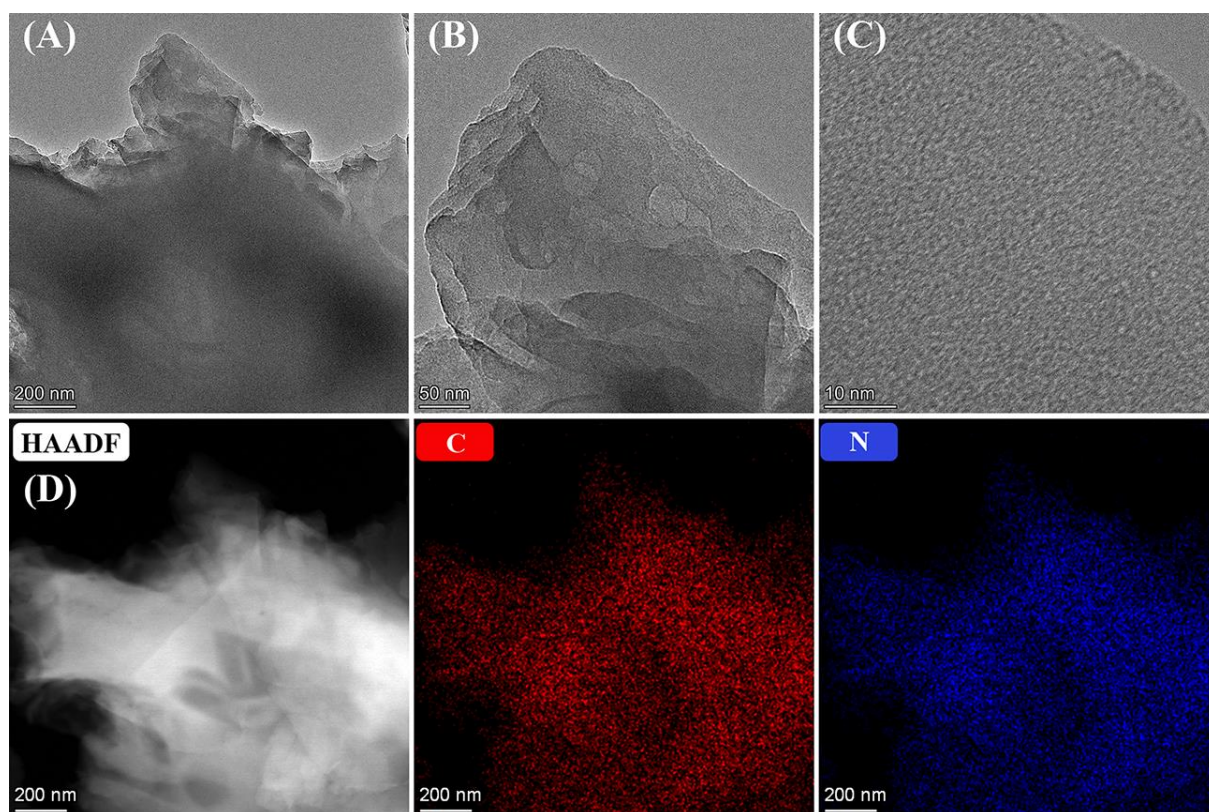


Figure S3. TEM images (A, B, C) and EDS elemental mapping (D) of HCN.

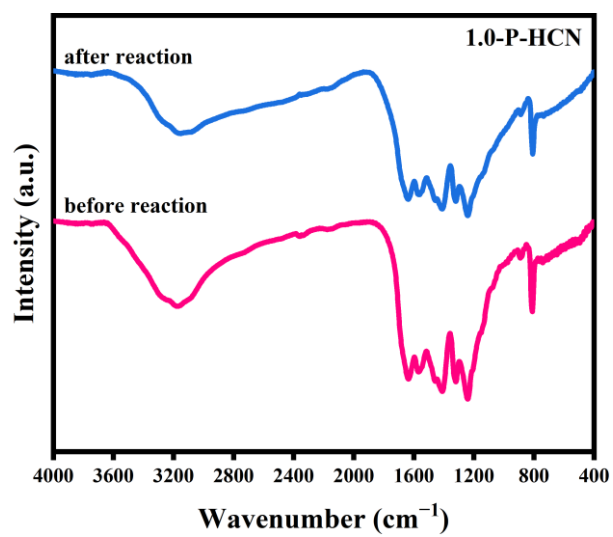


Figure S4. FT-IR spectra of 1.0-P-HCN before and after reaction for three cycles.

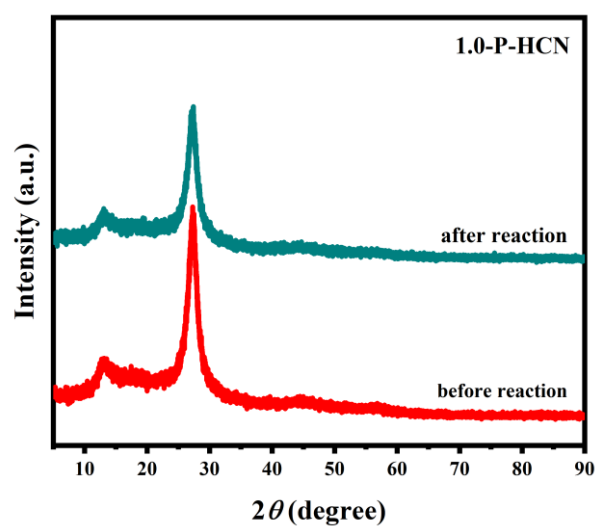


Figure S5. XRD patterns of 1.0-P-HCN before and after reaction for three cycles.

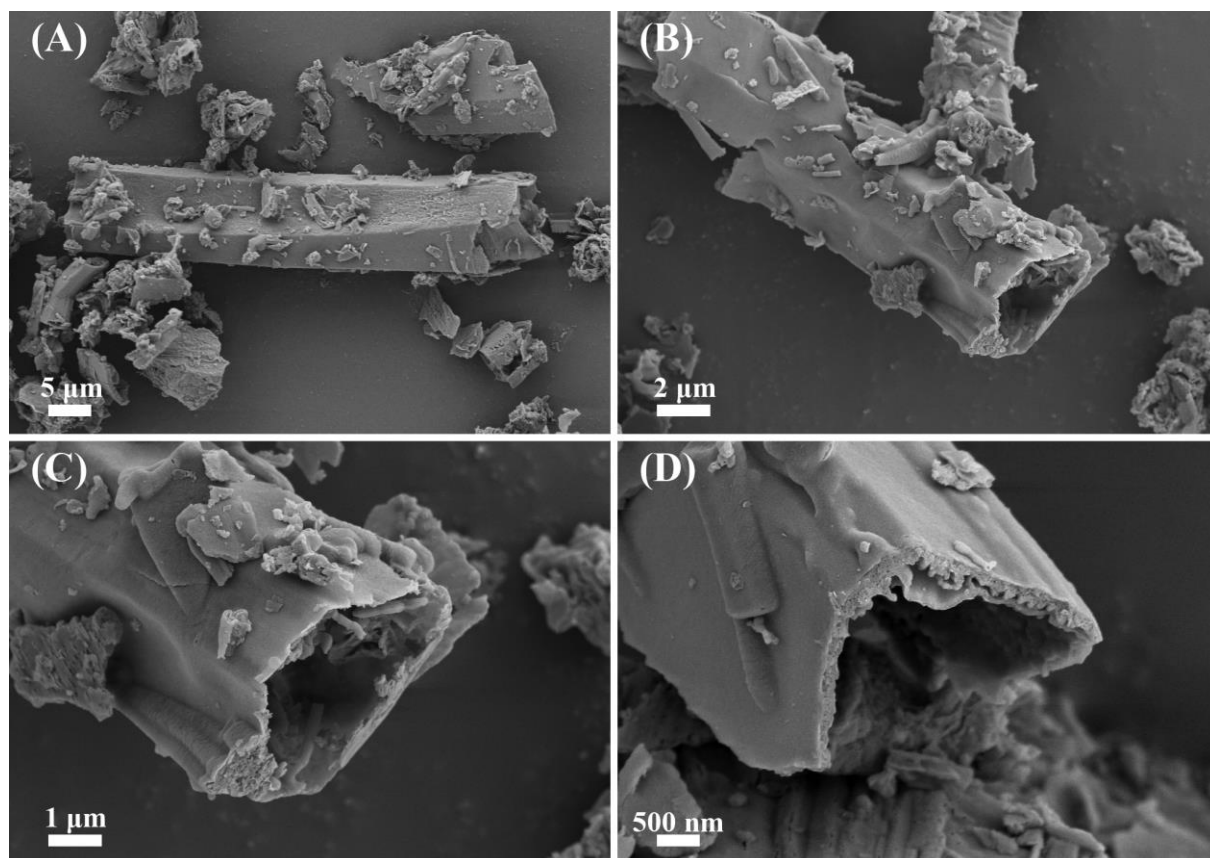


Figure S6. SEM images of 1.0-P-HCN after reaction for three cycles.

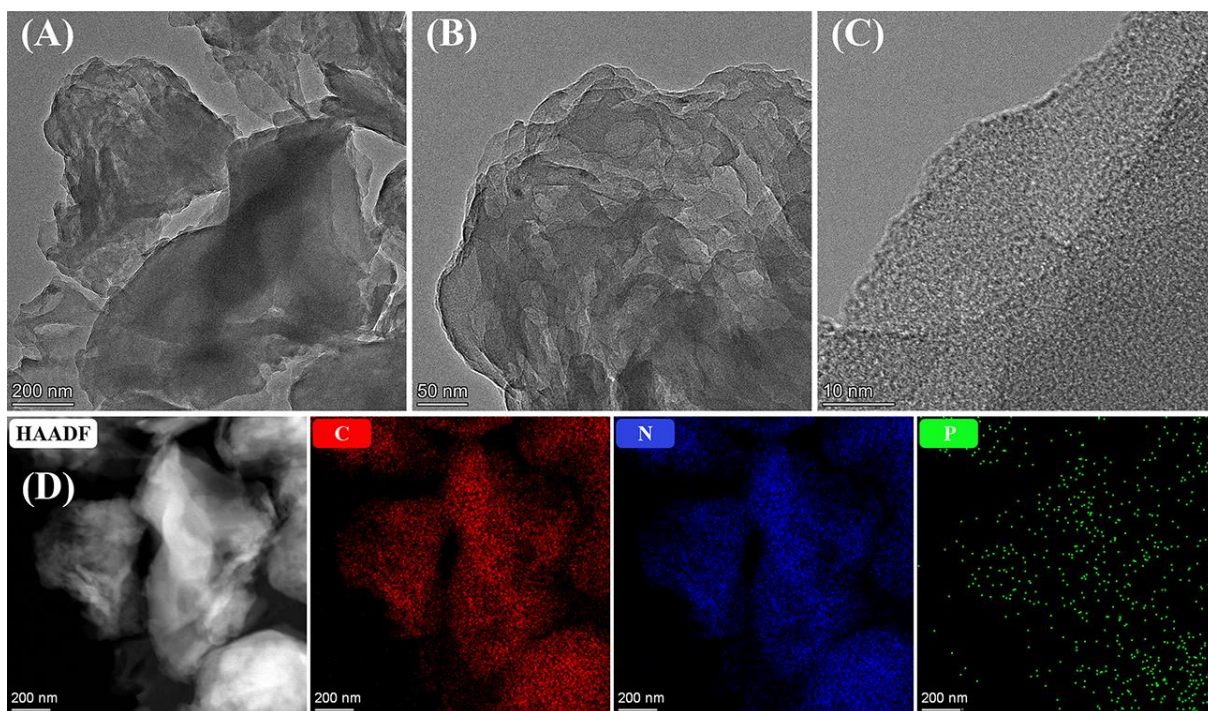


Figure S7. TEM images (A, B, C) and EDS elemental mapping (D) of 1.0-P-HCN after reaction for three cycles.

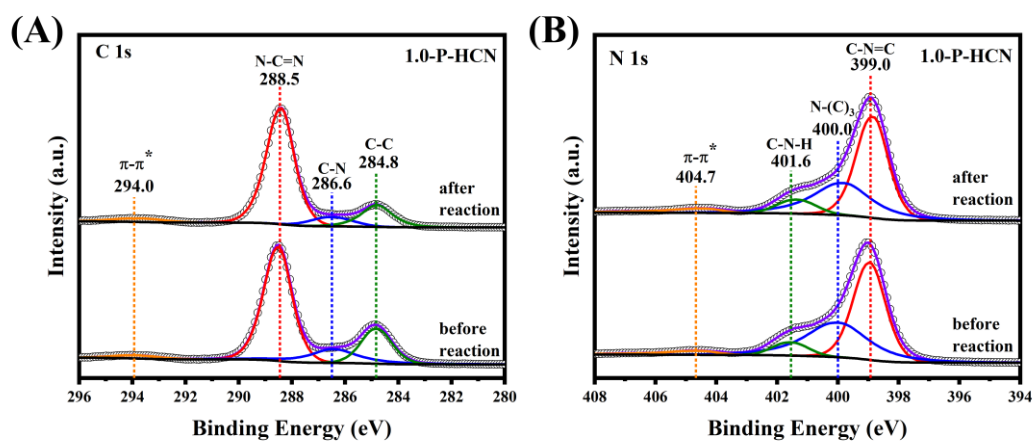


Figure S8. XPS spectra of C 1s (A), N 1s (B) of 1.0-P-HCN before and after reaction for three cycles.

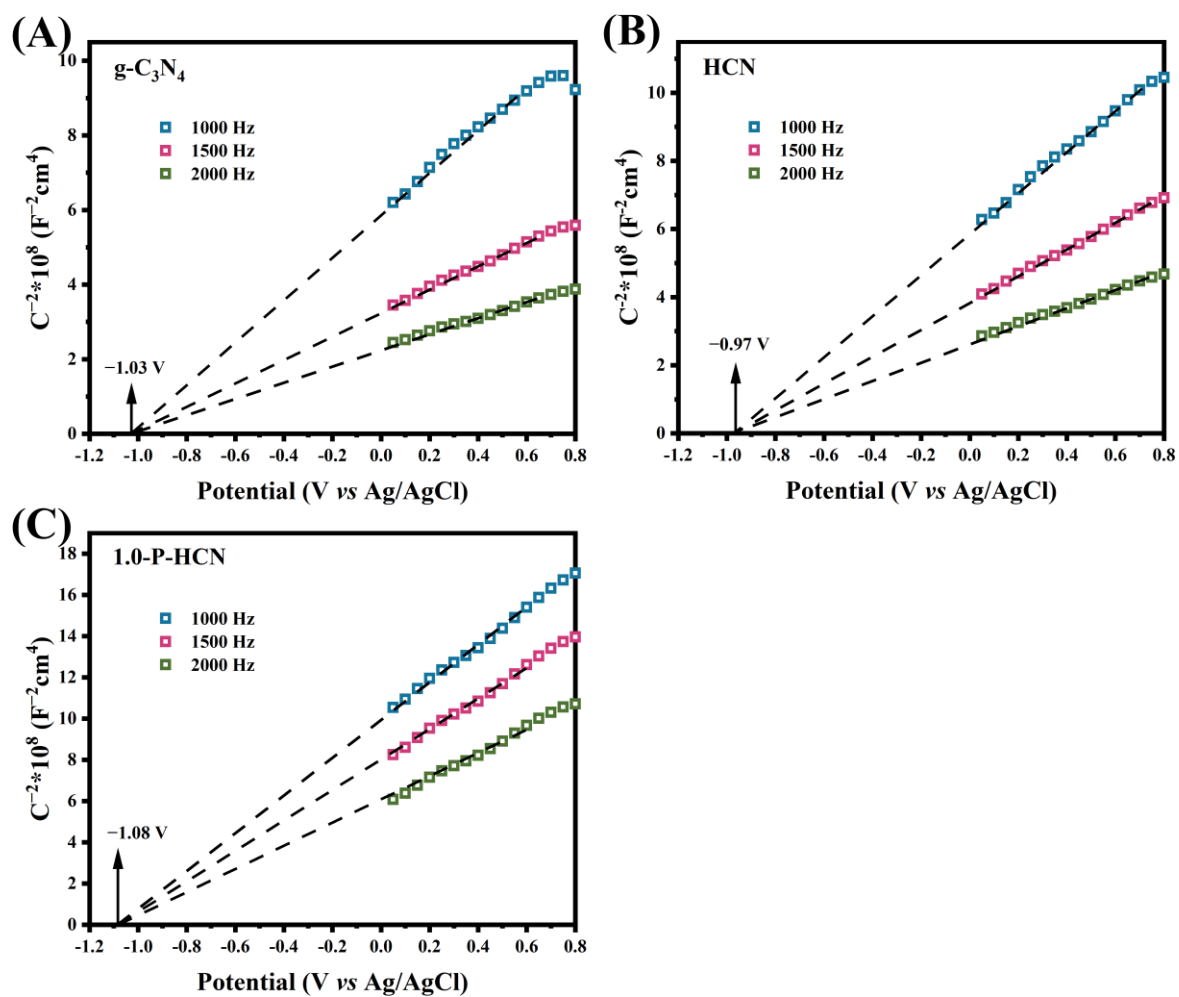


Figure S9. Mott-Schottky plots of $\text{g-C}_3\text{N}_4$ (A), HCN (B), and 1.0-P-HCN (C) at the frequency of 1000 Hz, 1500 Hz, and 2000 Hz.

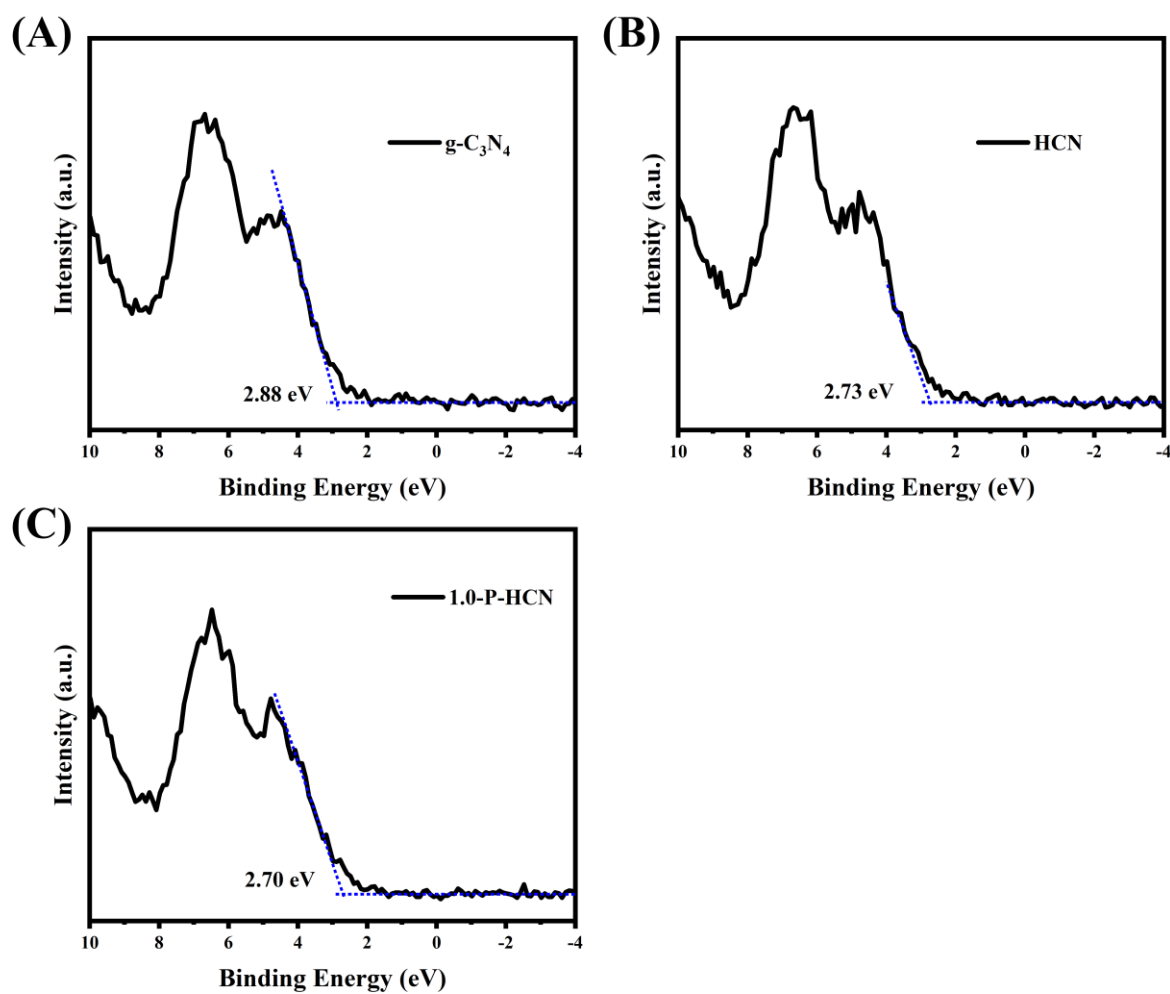


Figure S10. XPS valence band spectra of $g\text{-C}_3\text{N}_4$ (A), HCN (B) and 1.0-P-HCN (C).

Table S1. Specific surface area and average pore diameter of g-C₃N₄, HCN, and x-P-HCN

Samples	Specific surface Area (m ² ·g ⁻¹)	Average pore diameter (nm)
g-C ₃ N ₄	6.81	16.4
HCN	7.91	15.7
0.5-P-HCN	9.61	15.3
1.0-P-HCN	13.85	17.7
1.5-P-HCN	17.55	17.1
2.0-P-HCN	20.01	16.3

Table S2. Summary of the photocatalytic CO₂ reduction performance over g-C₃N₄ and phosphorus doped g-C₃N₄ photocatalysts.

Photocatalyst	Yields of products	Light source	Reaction conditions	Ref.
g-C ₃ N ₄	CO, 0.75 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	300 W Xe lamp 350 nm-780 nm	CO ₂	[1]
TCN	CO, 3.12 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$			
TCN-1	CO, 7.06 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$			
g-C ₃ N ₄	CO, 0.53 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	300 W Xe lamp >420 nm	CO ₂ H ₂ O MeCN TEOA	[2]
CNF-1.2	CO, 2.9 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$			
g-C ₃ N ₄	CO, 0.76 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ CH ₄ , 0.13 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	300 W Xe lamp	CO ₂ 5 M H ₂ SO ₄	[3]
P-g-C ₃ N ₄	CO, 2.37 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ CH ₄ , 1.81 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$			
g-C ₃ N ₄	CO, 1.05 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ CH ₄ , 0.37 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	300 W Xe lamp	CO ₂ H ₂ O vapor	[4]
g-C ₃ N ₄ /Ti ₃ C ₂	CO, 2.67 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ CH ₄ , 0.66 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$			
g-C ₃ N ₄	CO, 0.24 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	300 W Xe lamp >420 nm	CO ₂ 1 wt% HAuCl ₄ 1 M NaHCO ₃	[5]
P-doped g-C ₃ N ₄	CO, 0.38 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$			
g-C ₃ N ₄	CO, 67.01 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ H ₂ , 3.55 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	500 W Xe lamp	CO ₂ 2,2'-bipyridine CoCl ₂ DMF H ₂ O TEOA	[6]
P-g-C ₃ N ₄	CO, 447.5 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ H ₂ , 16.1 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$			
g-C ₃ N ₄	CO, 0.88 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	300 W Xe lamp >400 nm	CO ₂ H ₂ O vapor	This work
HCN	CO, 2.78 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$			
1.0-P-HCN	CO, 9.00 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$			

Reference

- [1] Liu, Y. Z.; Zhao, L.; Zeng, X. H.; Xiao, F.; Fang, W.; Du, X.; He, X.; Wang, D. H.; Li, W. X.; Chen, H. Efficient Photocatalytic Reduction of CO₂ by Improving Adsorption Activation and Carrier Utilization Rate through N-Vacancy g-C₃N₄ Hollow Microtubule. *Mater. Today Energy* **2023**, *31*, 101211.
- [2] Wan, S. P.; Ou, M.; Zhong, Q.; Cai, W. Haloid Acid Induced Carbon Nitride Semiconductors for Enhanced Photocatalytic H₂ Evolution and Reduction of CO₂ under Visible Light. *Carbon* **2018**, *138*, 465-474.
- [3] Liu, B.; Ye, L. Q.; Wang, R.; Yang, J. F.; Zhang, Y. X.; Guan, R.; Tian, L. H.; Chen, X. B. Phosphorus-Doped Graphitic Carbon Nitride Nanotubes with Amino-Rich Surface for Efficient CO₂ Capture, Enhanced Photocatalytic Activity, and Product Selectivity. *ACS Appl. Mater. Interfaces* **2018**, *10*, 4001-4009.
- [4] Liu, W. Z.; Sun, M. X.; Ding, Z. P.; Gao, B. W.; Ding, W. Ti₃C₂ MXene Embellished g-C₃N₄ Nanosheets for Improving Photocatalytic Redox Capacity. *J. Alloy. Compd.* **2021**, *877*, 160223.
- [5] Liu, X. L.; Wang, P.; Zhai, H. S.; Zhang, Q. Q.; Huang, B. B.; Wang, Z. Y.; Liu, Y. Y.; Dai, Y.; Qin, X. Y.; Zhang, X. Y. Synthesis of Synergetic Phosphorus and Cyano Groups (Cn) Modified g-C₃N₄ for Enhanced Photocatalytic H₂ Production and CO₂ Reduction under Visible Light Irradiation. *Appl. Catal. B: Environ.* **2018**, *232*, 521-530.
- [6] Wang, W. F.; Qiu, L. Q.; Chen, K. H.; Li, H. R.; Feng, L. F.; He, L. N. Morphology and Element Doping Effects: Phosphorus-Doped Hollow Polygonal g-C₃N₄ Rods for Visible Light-Driven CO₂ Reduction. *New J. Chem.* **2022**, *46*, 3017-3025.