Regulating morphological and electronic structures of polymeric carbon nitrides by successive copolymerization and stream reforming for photocatalytic CO_2 reduction

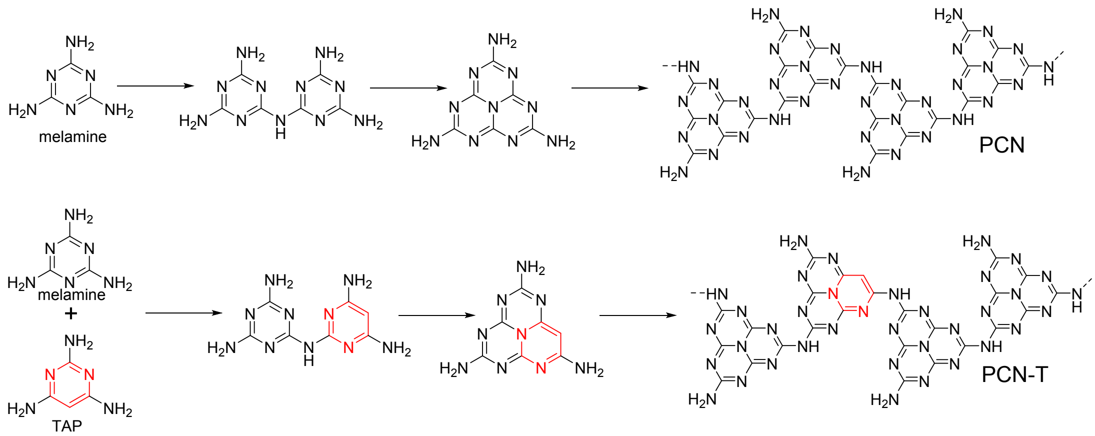
Ruirui Wang[1], Pengju Yang[1, 2], Sibo Wang[1] and Xinchen Wang[1]*

[1]*State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350002, China,* E-mail: *xcwang@fzu.edu.cn; http://wanglab.fzu.edu.cn*

[2]*School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan, 030006, China*

Characterization

Transmission electron microscopy (TEM) images were obtained from FEI TECNAIG2F20 instrument. Atomic Force Microscope (AFM) images were recorded by Bruker Dimension Icon. The nitrogen adsorption-desorption isotherms were collected at 77 K and CO_2 adsorption isotherms was acquired at 273 K using Micromeritics ASAP 2020. Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer. Fourier transformed infrared (FTIR) spectra were captured on Thermo Scientific Nicolet iS50. The Raman spectra were recorded on a Via-Reflex Raman spectroscopy system under light excitation at 325 nm. The X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo ESCALAB250 instrument. UV-vis diffuse reflectance spectra (DRS) tests performed on Agilent Technologies Cary 500. Steady-state Fluorescence (PL) spectra and time-resolved PL (TRPL) spectra were obtained by Edinburgh FL-FS 920 TCSPC. Electrochemical measurements were conducted on a BAS Epsilon electrochemical system in a conventional three electrode cell, using a Pt plate as the counter electrode and Ag/AgCl electrode (3 M KCl) as the reference electrode. A 0.2 M Na_2SO_4 aqueous solution was utilized as the electrolyte. The working electrode was prepared on indium-tin oxide (ITO) glass that was cleaned by sonication in ethanol for 30 min and was dried at 353 K. The photoresponse of the prepared electrode was obtained by measuring the photocurrent densities under chopped light irradiation at a bias potential of 0.4 V vs. Ag/AgCl.



Scheme S1. Illustration of the formation of PCN-T by incorporation of TAP into the network of PCN.

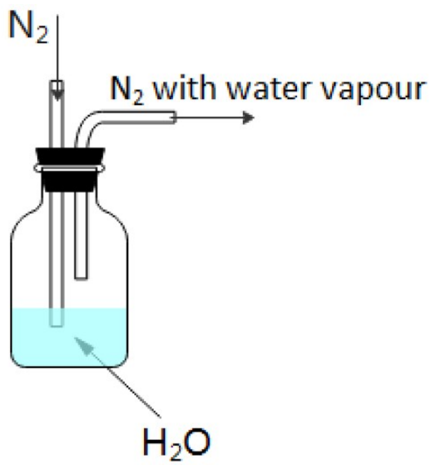


Fig. S1 Schematic diagram of steam generator

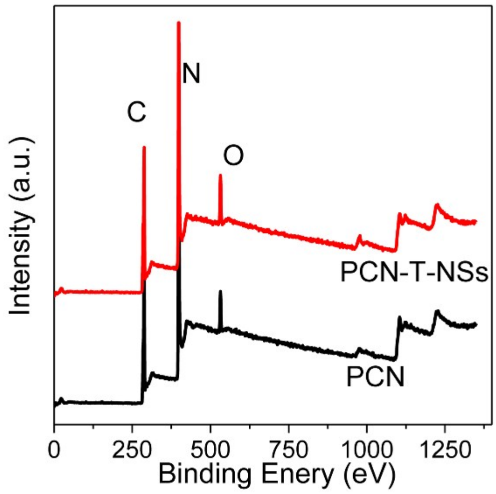


Fig. S2 XPS survey scan spectra of the PCN and PCN-T-NSs.

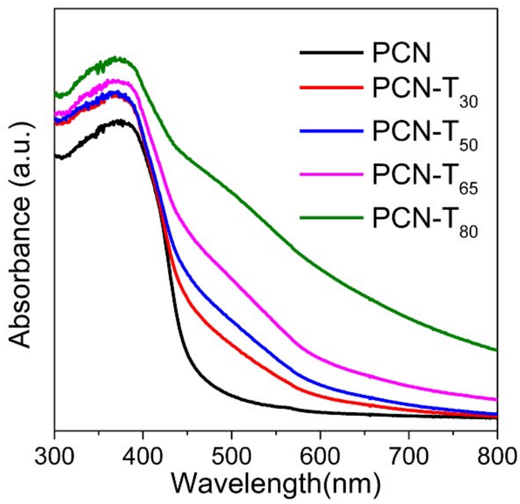


Fig. S3 UV-vis absorption spectra (DRS) of PCN and PCN-T_X.

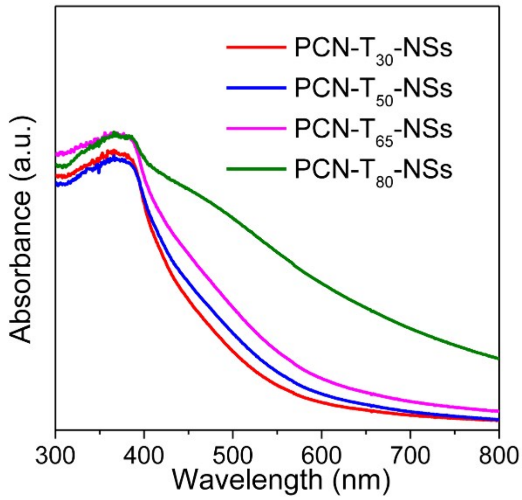


Fig. S4 UV-vis absorption spectra (DRS) of PCN-T_X -NSs.

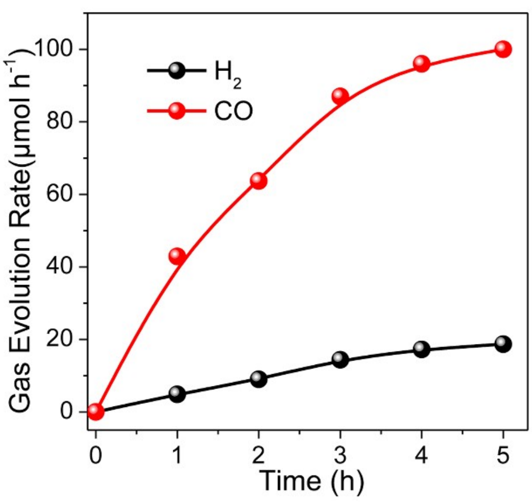


Fig. S5 Time-yield plots of CO/H_2 over PCN-T-NSs.

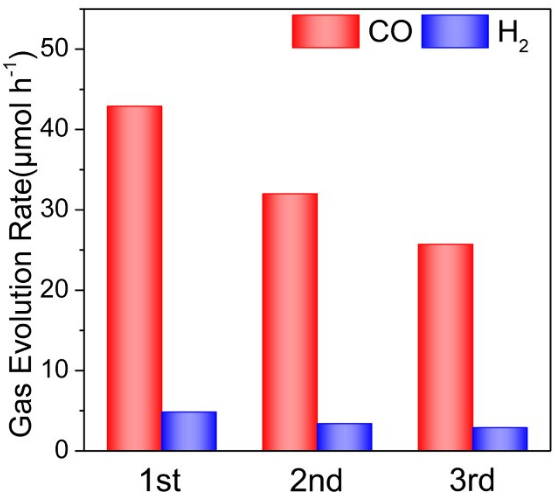


Fig. S6 Generation rates of CO and H_2 in the stability test for three cycles.

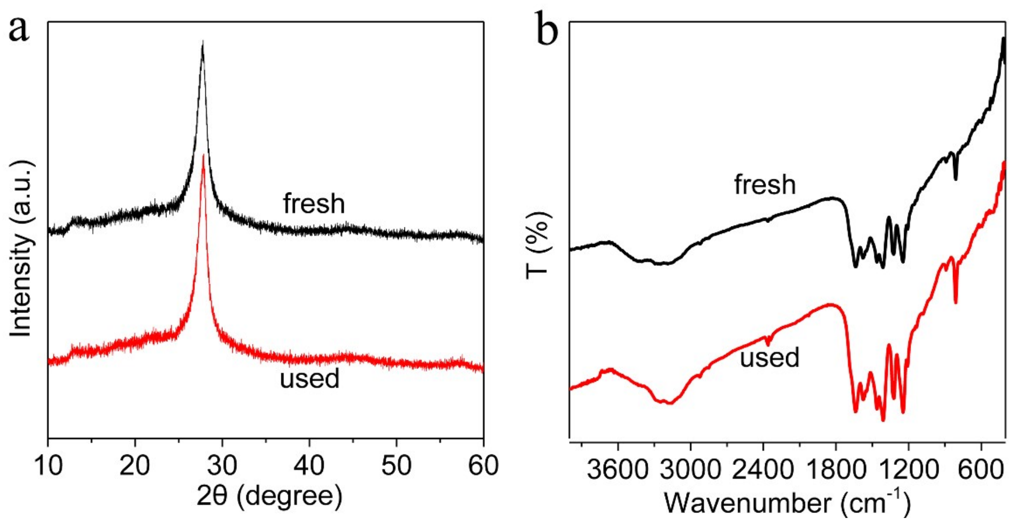


Fig. S7 (a) XRD and (b) FTIR patterns of the fresh and used PCN-T-NSs samples.

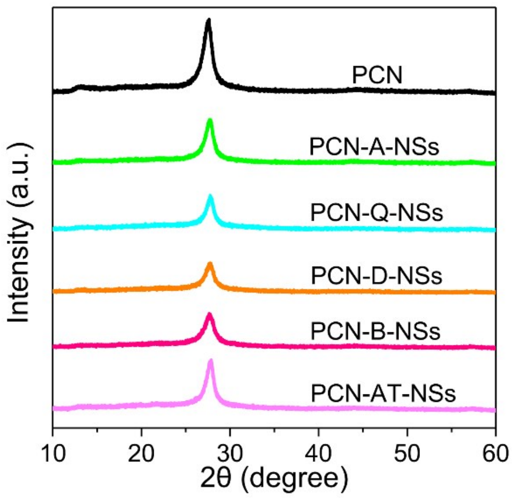


Fig. S8 XRD patterns of PCN, PCN-A-NSs, PCN-Q-NSs, PCN-D-NSs, PCN-B-NSs and PCN-AT-NSs.

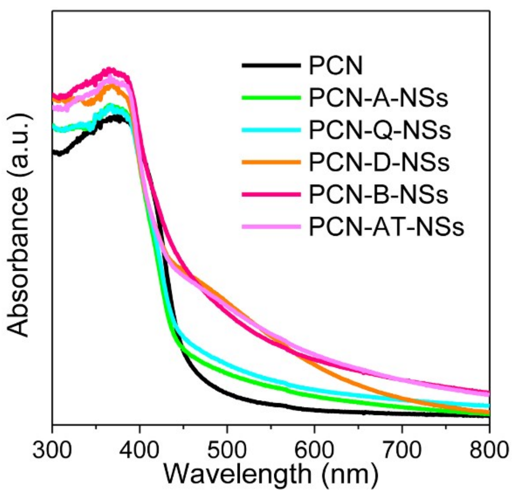


Fig. S9 UV-vis absorption spectra (DRS) of PCN, PCN-A-NSs, PCN-Q-NSs, PCN-D-NSs, PCN-B-NSs and PCN-

AT-NSs.

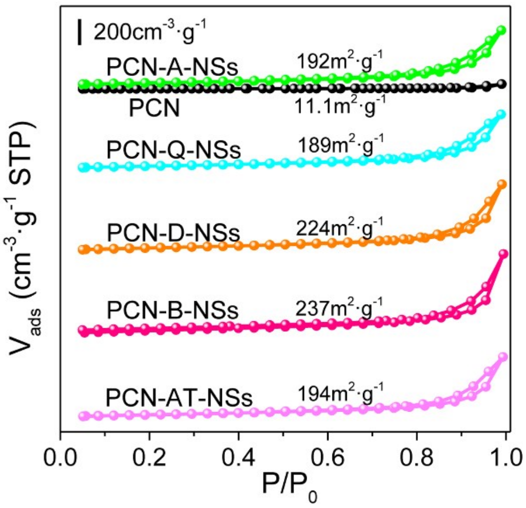


Fig. S10 Nitrogen adsorption-desorption isotherms of PCN, PCN-A-NSs, PCN-Q-NSs, PCN-D-NSs, PCN-B-NSs and PCN-AT-NSs.

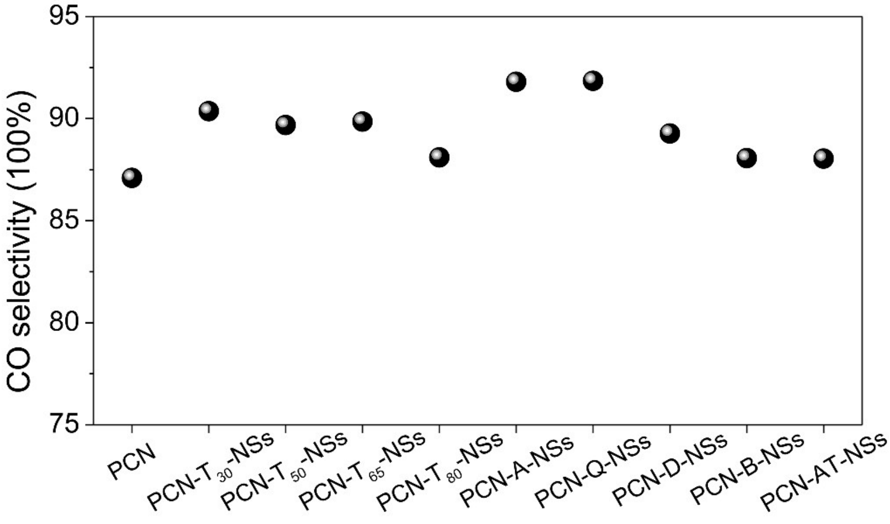


Fig. S11 CO selectivity of different samples.

Table S1. Comparison of CO_2 photoreduction performance of PCN-T-NSs with that of other catalysts in similar reaction systems under visible light irradiation.

Catalyst (used amount)	Cocatalyst	Sacrificial agent	Visible light	CO yield rate ($\mu mol\ h^{-1}$)	AQE (420nm)	Refs.
PCN-T-NSs (30 mg)	$Co(bpy)_3^{2+}$	TEOA	λ > 420 nm	43.0	4.2%	This work
CoOx/MCN (50mg)	$Co(bpy)_3^{2+}$	TEOA	λ > 420 nm	10.2	0.25%	1
Co4@g-C_3N_4 (50 mg)	$Co(bpy)_3^{2+}$	TEOA	λ > 420 nm	5.4	n.d.[a]	2
CNU-$BA_{0.03}$ (50 mg)	$Co(bpy)_3^{2+}$	TEOA	λ > 420 nm	31.1	n.d.	3
TiO_2/g-C_3N_4 (5 mg)	$Co(bpy)_3^{2+}$	TEOA	λ > 400 nm	1.2	n.d.	4
HR-CN (30 mg)	$Co(bpy)_3^{2+}$	TEOA	λ > 420 nm	8.9	n.d.	5
MP-500-4 (30 mg)	$Co(bpy)_3^{2+}$	TEOA	λ > 420 nm	21.5	4.8%	6
$BINA_2$-CN (50 mg)	$Co(bpy)_3^{2+}$	TEOA	λ > 420 nm	8.1	n.d.	7
CPs-BT (15 mg)	$Co(bpy)_3^{2+}$	TEOA	λ > 420 nm	18.2	1.7%	8
Co_3O_4@$CdIn_2S_4$ (10mg)	$Co(bpy)_3^{2+}$	TEOA	λ > 420 nm	15.0	1.9%	9
$ZnIn_2S_4$-In_2O_3 (4 mg)	$Co(bpy)_3^{2+}$	TEOA	λ > 420 nm	5.2	n.d.	10
In_2S_3 -$CdIn_2S_4$ (4 mg)	$Co(bpy)_3^{2+}$	TEOA	λ > 420 nm	1.6	n.d.	11
CdS/BCN (50 mg)	$Co(bpy)_3^{2+}$	TEOA	λ > 420 nm	12.5	n.d.	12

[a] n.d.: not detected.

Supplementary References

1. J. Lin, Z. Pan, and X. Wang, ACS. *Sustain. Chem. Eng.*, 2014, **2**, 353−358.
2. J. Zhou, W. Chen, C. Sun, L. Han, C. Qin, M. Chen, X. Wang, E. Wang and Z. Su, *ACS Appl. Mater. Interfaces,* 2017, **9**, 11689−11695.
3. J. Qin, S. Wang, H. Ren, Y. Hou and X. Wang, *Appl. Catal. B Environ*., 2015, **179**, 1-8.
4. H. Shi, J. Du, J. Hou, W. Nia, C. Song, K. Lia, G. Gurzadyan, X. Guo, *J. CO_2. Util.,* 2020, **38**, 16-23.
5. Y. Zheng, L. Lin, X. Ye, F. Guo and X. Wang, *Angew. Chem. Int. Ed*., 2014, **53**, 11926-11930.
6. P. Yang, Z. Zhu, R. Wang, W. Lin and X. Wang, *Angew. Chem. Int. Ed.,* 2019, **58**,1134 –1137
7. Z. Pan, P. Niu, M. Liu, G. Zhang, Z. Zhu and X. Wang, *ChemSusChem,* 2020, **13**, 888-892.
8. C. Yang, W. Huang, L. Silva, K. Zhang, and X. Wang, *Chem. Eur. J.,* 2018, **24**, 17454 – 17458.
9. L. Huang, B. Li, B. Su, Z. Xiong, C. Zhang, Y. Hou, Z. Ding and S. Wang, *J. Mater. Chem. A*, 2020, **8**, 7177–7183.
10. S. Wang, B. Y. Guan and X. W. Lou, *J. Am. Chem. Soc.*, 2018, **140**, 5037-5040
11. S. Wang, B. Y. Guan, Y. Lu and X. W. Lou, *J. Am. Chem. Soc.,* 2017, **139**, 17305-17308.
12. M. Zhou, S. Wang, P. Yang, C. Huang and X. Wang, *ACS Catal.,* 2018, **8**, 4928-4936.