Supporting Information

Copolymerization Synthesis of Highly Hydrophilic Carbon Nitride for Efficient Solar Hydrogen Production

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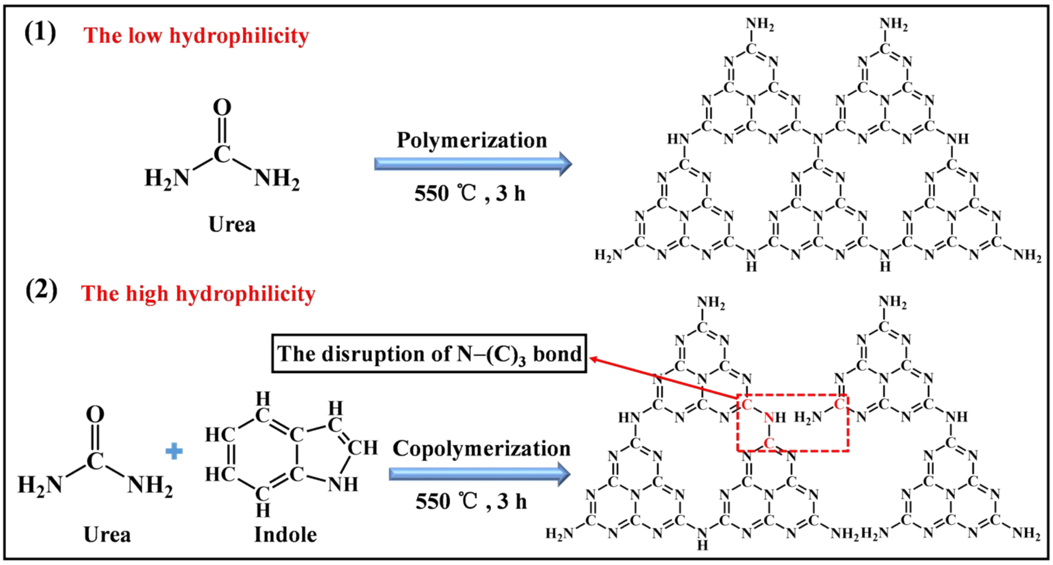

Fig. S1. Diagram for the synthesis of PCN and PCNInd$_x$.

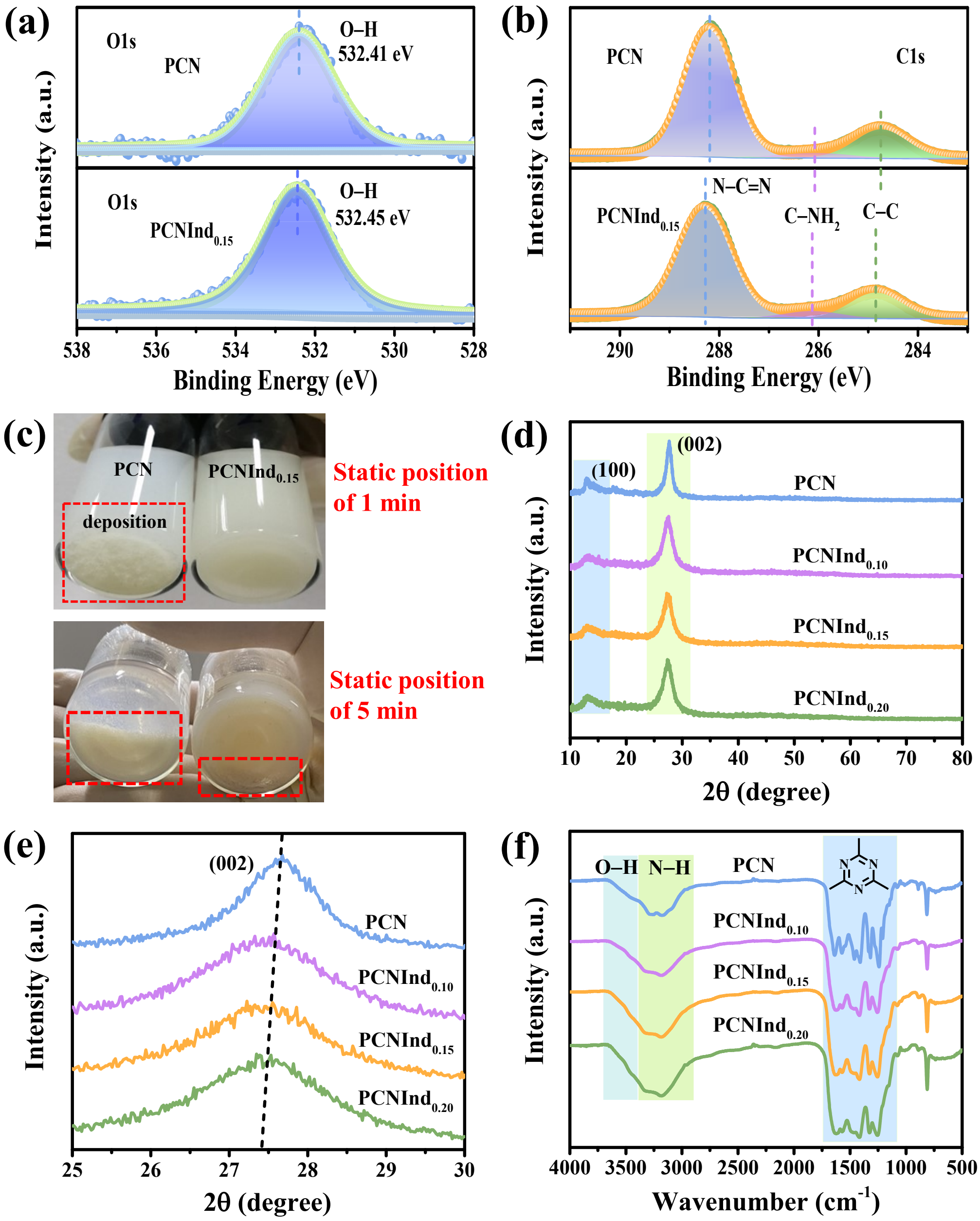

Fig. S2. (a) The O1s XPS analysis; (b) the C1s XPS analysis; (c) the photos of dispersion states on aqueous solutions for PCN after sonication of 30 min and $PCNInd_{0.15}$ after sonication of 5 min until standing for 1 min and 5 min later, respectively; (d) the XRD patterns; (e) the enlarged XRD spectra of the as-prepared samples; (f) FT-IR spectra.

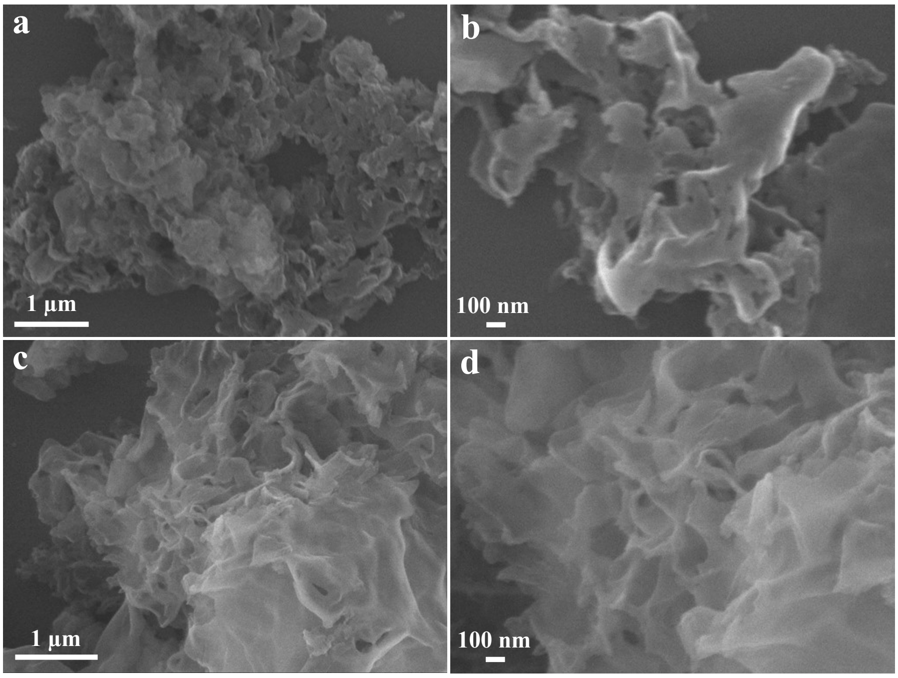

Fig. S3. SEM of PCN (a and b) and $PCNInd_{0.15}$ (c and d).

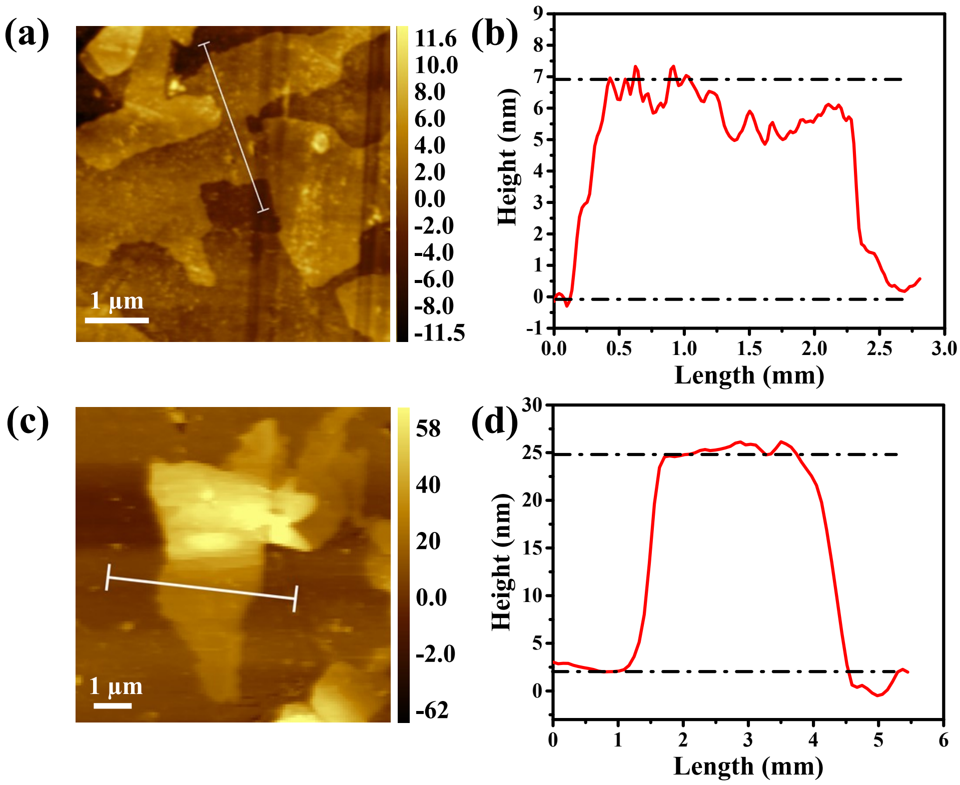

Fig. S4. (a and b) Typical AFM image and its height curve determined along the white line of PCN, respectively; (c and d) typical AFM image and its height curve determined along the white line of $PCNInd_{0.15}$, respectively.

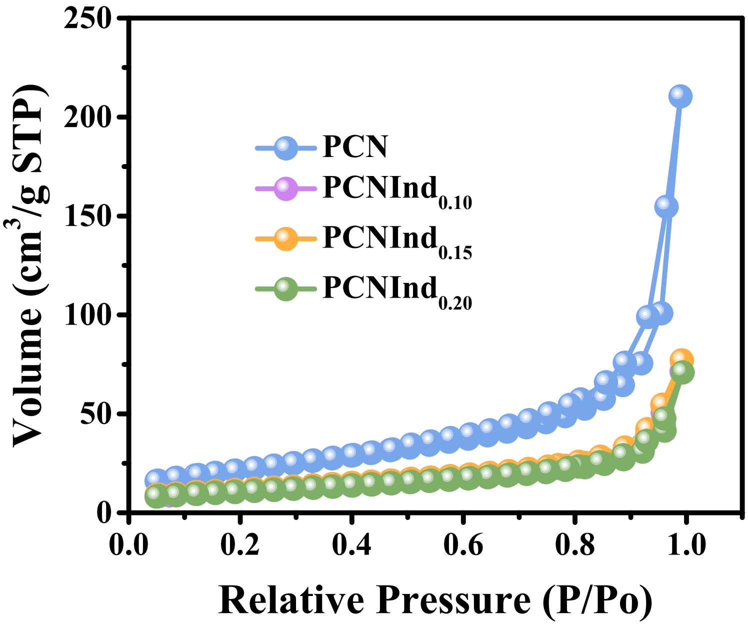

Fig. S5. N_2 adsorption/desorption isotherms of samples.

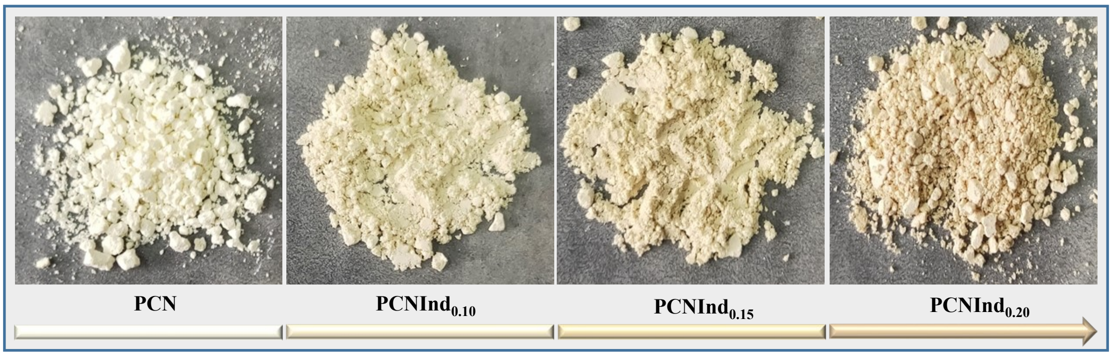

Fig. S6. The change in color of PCN with increasing amount of indole.

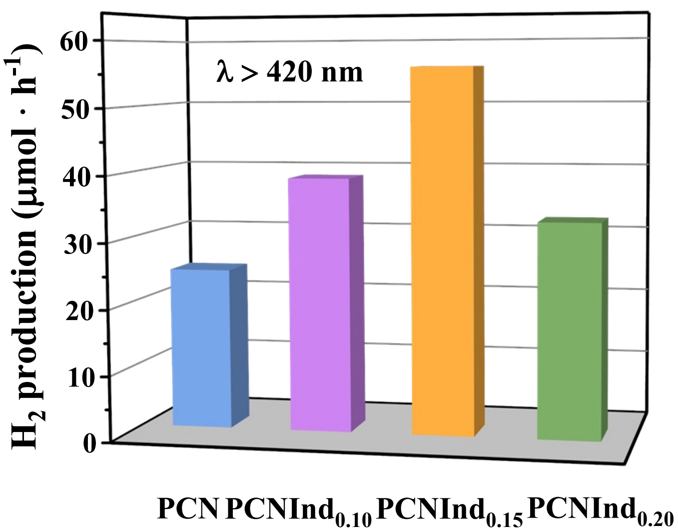

Fig. S7. H_2 production rate ($\lambda > 420$ nm).

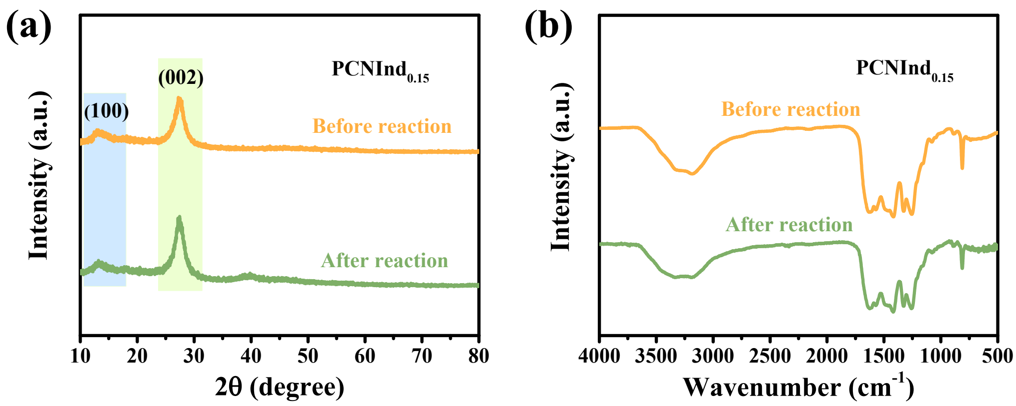

Fig. S8. (a) XRD pattern of $PCNInd_{0.15}$ before and after reaction; (b) FT-IR spectra of $PCNInd_{0.15}$ before and after reaction.

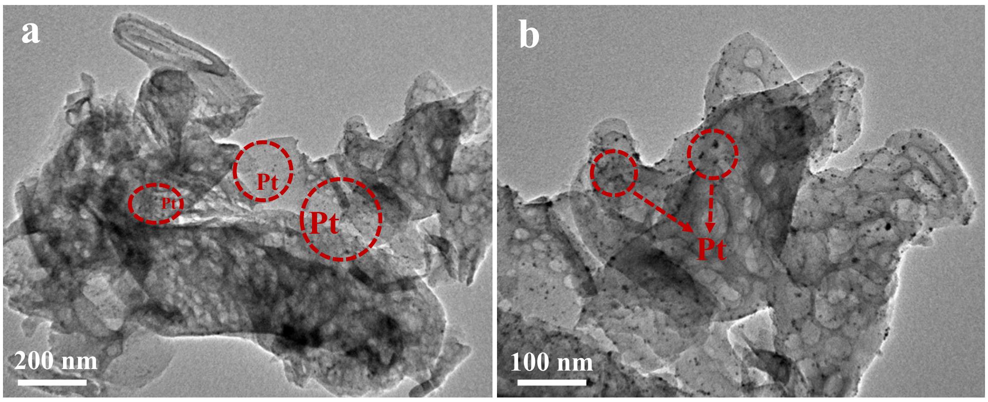

Fig. S9. TEM of $PCNInd_{0.15}$ after reaction.

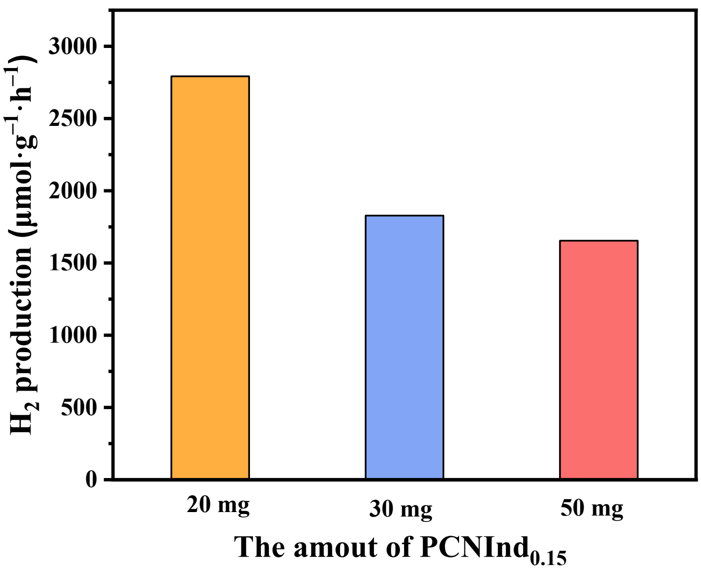

Fig. S10. The effect of photocatalysts amount on photocatalytic activity.

Table S1. Elemental analysis of PCN and $PCNInd_{0.15}$.

Elemental analysis				
Sample	C (wt.%)	N (wt.%)	H (wt.%)	C/N (atomic ratio)
PCN	34.15	59.76	2.06	0.67
$PCNInd_{0.15}$	33.20	60.09	2.36	0.64

Table S2. EDS of PCN and $PCNInd_{0.15}$.

Elemental analysis				
Sample	C (wt.%)	N (wt.%)	O (wt.%)	C/N (atomic ratio)
PCN	31.85	51.40	16.76	0.72
$PCNInd_{0.15}$	30.87	53.36	15.77	0.67

Table S3. Summary of the previously reported hydrophilic PCN with regard to synthesis process.

Sample[a]	Precursors	E_g (eV)	Application	Water contact angle (º)	Synthetic methods	Synthetic steps	Ref.
$Fe(OH)_3$/PCN composite membrane	PCN NSs + $Fe(OH)_3$ + Anodic aluminum oxide support	---	Water purification	68.5	Preparation of PCN NSs (polymerization + calcination + ultrasonic treatment) + Preparation of $Fe(OH)_3$ nanoparticles + Fabrication of membranes (the deposition of g-C_3N_4 nanosheets layer + the deposition of $Fe(OH)_3$ nanoparticles)	Six	[1] *J. Membrane Sci.*, 2018, **564**, 372–381
Oxygen-containing and amino groups functional carbon nitride atomically-thin porous sheets	Bulk PCN	2.96	Photocatalytic H_2 evolution	28.45	Calcination + Continuous secondary calcination + Calcination under the flowing air + Calcination under NH_3	Four	[2] *Energy Environ. Sci.*, 2018, **11**, 566–571
Plasma-treated PCN	PCN	2.86	Photocatalytic degradation of Rhodamine B	51.8	Polymerization + Plasma treatment	Two	[3] *Carbon*, 2017, **123**, 651–659
Soluble PCN NSs/PCN	Soluble PCN NSs + PCN	2.70	Photocatalytic H_2 evolution	---	Preparation of bulk PCN (polymerization) + Preparation of soluble PCN NSs (treatment at 180 °C +	Four	[4] *Appl. Catal. B: Environ.*, 2019, **247**, 70–77

					vacuum freeze-drying treatment) + Preparation of soluble PCN NSs/PCN (ultrasonic treatment)		
G-C_3N_4-COOH	g-C_3N_4 NSs + Chloroacetic acid	---	Reverse osmosis desalination	58.5 ± 1.2	Polymerization + Functionalization reaction	Two	[5] *Sep. Purif. Technol.*, 2020, **235**, 116134
Porous PCN NSs	PCN	2.76	Photocatalytic H_2 evolution	48	Polymerization + Calcination	Two	[6] *Mater. Today Chem.*, 2022, **26**, 101084
Functional carbon nitride with amphiphilic carbon and C–O–C chain linked melem units	Melem + Formaldehyde	2.52	Photocatalytic H_2 evolution and photocatalytic selective oxidation of sulfide	39.8	Calcination + Purification of melem + Formaldehyde treatment + Calcination	Four	[7] *J. Mater. Chem. A*, 2021, **9**, 21732–21740
Microporous carbon nitride ($C_3N_{5.4}$) with tetrazine based molecular structure	Aminoguanidine + Ultra-stable Y zeolite	2.27	Adsorption of CO_2 and water	---	Pretreatment of aminoguanidine + Polymerization + Treating with 5 wt.% hydrofluoric acid	Three	[8] *Angew. Chem. Int. Ed.*, 2021, **60**, 21242–21249
S-doped carbon nitride/graphene oxide 3D hierarchical framework	S-doped g-C_3N_4 + Large flake size graphene oxide	---	Mercury removal from desulfurization slurry	42	Preparation of S doped carbon nitride (S-doped g-C_3N_4) (pretreatment of melamine + calcination) + Fabrication of large flake size graphene oxide (LGO) (centrifugal classification method) + Preparation of S-doped g-C_3N_4/LGO aerogel (SGA) (hydrothermal treatment)	Four	[9] *Sep. Purif. Technol.*, 2020, **239**, 116515
Interfacial coupling perovskite $CeFeO_3$ on layered graphitic carbon nitride	Melamine + a mixed Fe and Ce solution and NH_4OH	PCN (2.85) and $CeFeO_3$ (1.96)	Nitrogen fixation and organic pollutants demineralization	65.5	Co-precipitation + Calcination	Two	[10] *Chem. Eng. J.*, 2022, **427**, 131406
GCN (graphite phase carbon nitride)-SA (sulfuric acid) membrane	GCN-SA	---	Selective permeation	24	Preparation of pristine GCN NSs (polymerization + ultrasonic treatment) + Preparation of GCN-SA composite (heating treatment with SA) + Preparation of membranes (vacuum filtration method)	Four	[11] *Nat. Commun.*, 2019, **10**, 2500
PCN with surface N-hydroxymethylation	PCN	2.79	Photocatalytic H_2O_2 production	52.5	Polymerization + Ultrasonic washing at 80 °C + Being treated by formaldehyde solution	Three	[12] *Adv. Funct. Mater.*, 2022, **32**, 2111125
Superficial hydroxyl and amino groups synergistically	PCN	---	CO_2 electroreduction	22.5	Polymerization + Calcination under the flowing air + Calcination under the	Three	[13] *ACS Catal.*, 2019, **9**, 10983–10989

active PCN					NH_3		
Loofah-like carbon nitride sponge	Supramolecular precursor	2.92	Photocatalytic transfer hydrogenation of nitrophenols with water as the hydrogen source	47	Preparation of supramolecular precursor (microwave irradiation under 180 ◦C + stirring, filtering, washing and drying + treatment with cyanuric acid) + Preparation of loofah-like carbon nitride sponge (calcination + calcination)	Five	[14] *Chem. Eng. J.*, 2022, **444**, 136430
Multiple Doped Carbon Nitrides	Dicyandiamide + NaI	2.63	Photocatalytic H_2 evolution	44.12	Calcination	One	[15] *ACS Appl. Mater. Interfaces*, 2019, **11**, 22255–22263 Our previous work
$PCNInd_{0.15}$	Urea + Indole	2.62	Photocatalytic H_2 evolution	39.9	Copolymerization	One	**This work**

[a] PCN denotes polymer carbon nitride; NSs denotes nanosheets and "---" denotes no applicable.

Table S4. A set of control parameters were carried out as follows. Entry 14 displayed the optimized conditions.

Entry	The content of Pt	$PCNInd_{0.15}$ (mg)	pH of the solution	Sacrificial agent	Wavelength (nm)	Activity ($\mu mol \cdot h^{-1}$)
pH dependence (Sodium hydroxide solution regulation)						
1	2 wt%	20	1	Lactic acid	$\lambda > 420$	55.85
2	2 wt%	20	3	Lactic acid	$\lambda > 420$	49.20
3	2 wt%	20	5	Lactic acid	$\lambda > 420$	37.37
4	2 wt%	20	7	Lactic acid	$\lambda > 420$	25.80
5	2 wt%	20	9	Lactic acid	$\lambda > 420$	22.92
Wavelength dependence						
6	2 wt%	20	1	Lactic acid	$\lambda > 420$	55.85
7	2 wt%	20	1	Lactic acid	$\lambda = 420$	17.12
8	2 wt%	20	1	Lactic acid	$\lambda = 450$	2.03
9	2 wt%	20	1	Lactic acid	$\lambda = 500$	0.17
Pt cocatalyst dependence						
10	0.5 wt%	20	1	Lactic acid	$\lambda > 420$	26.34

11	1 wt%	20	1	Lactic acid	λ > 420	33.12
12	2 wt%	20	1	Lactic acid	λ > 420	55.85
13	3 wt%	20	1	Lactic acid	λ > 420	49.86
14	5 wt%	20	1	Lactic acid	λ > 420	38.58

References

1 Y. J. Wang, L. F. Liu, J. D. Hong, J. Cao and C. L. Deng, *J. Membrane Sci.*, 2018, **564**, 372–381.

2 N. N. Meng, J. Ren, Y. Liu, Y. Huang, T. Petit and B. Zhang, *Energy Environ. Sci.*, 2018, **11**, 566–571.

3 Z. Y. Mao, J. J. Chen, Y. F. Yang, L. J. Bie, B. D. Fahlman and D. J. Wang, *Carbon*, 2017, **123**, 651–659.

4 X. H. Wu, X. F. Wang, F. Z. Wang and H. G. Yu, *Appl. Catal. B: Environ.*, 2019, **247**, 70–77.

5 S. S. Shahabi, N. Azizi, V. Vatanpour and N. Yousefimehr, *Sep. Purif. Technol.*, 2020, **235**, 116134.

6 L. Bao, Y. Liu, Z. Yu, Y. Xue, S. Yan and H. Gao, *Mater. Today Chem.*, 2022, **26**, 101084.

7 S. L. Yang, Q. Wang, Q. C. Wang, G. Li, T. X. Zhao, P. Chen, F. Liu and S.-F. Yin, *J. Mater. Chem. A*, 2021, **9**, 21732–21740.

8 C. I. Sathish, S. Premkumar, X. Z. Chu, X. J. Yu, M. B. H. Breese, M. Al-Abri, A. H. Al-Muhtaseb, A. Karakoti, J. B. Yi and A. Vinu, *Angew. Chem. Int. Ed.*, 2021, **60**, 21242–21249.

9 M. Li, B. Wang, M. Q. Yang, Q. H. Li, D. G. Calatayud, S. H. Zhang, H. Y. Wang, L. D. Wang and B. Y. Mao, *Sep. Purif. Technol.*, 2020, **239**, 116515.

10 C. E. Choong, C. M. Park, Y.-Y. Chang, J.-K. Yang, J. R. Kim, S.-E. Oh, B.-H. Jeon, E. H. Choi, Y. Yoon and M. Jang, *Chem. Eng. J.*, 2022, **427**, 131406.

11 Y. Wang, N. N. Wu, Y. Wang, H. Ma, J. X. Zhang, L. L. Xu, M. K. Albolkany and B. Liu, *Nat. Commun.*, 2019, **10**, 2500.

12 B. Y. Liu, J. Y. Du, G. L. Ke, B. Jia, Y. J. Huang, H. C. He, Y. Zhou and Z. G. Zou, *Adv. Funct. Mater.*, 2022, **32**, 2111125.

13 N. N. Meng, W. Zhou, Y. F. Yu, Y. Liu and B. Zhang, *ACS Catal.*, 2019, **9**, 10983–10989.

14 F. L. Yao, L. M. Dai, J. B. Bi, W. K. Xue, J. Y. Deng, C. C. Fang, L. T. Zhang, H. A. Zhao, W. Y. Zhang, P. Xiong, Y. S. Fu, J. W. Sun and J. W. Zhu, *Chem. Eng. J.*, 2022, **444**, 136430.

15 Z. Y. Fang, D. Li, R. J. Chen, Y. Y. Huang, B. F. Luo and W. D. Shi, *ACS Appl. Mater. Interfaces*, 2019, **11**, 22255–22263.