Graphitic carbon nitride metal-free visible light photocatalyst with controllable carbon self-doping towards efficient hydrogen evolution

Lin Lei,†[a] Weijia Wang,†*[a] Zhengfeng Xie,[a] Xiaobo Wu,[a] Arun Kumar Yadav,[a] Peter Müller-Buschbaum,[bc] Huiqing Fan*[a]

[a]State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China

[b]Lehrstuhl für Funktionelle Materialien, Physik Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany.

[c]Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Lichtenbergstr. 1, 85748 Garching, Germany.

†equally contributed

*Corresponding author: Email: weijia.wang@nwpu.edu.cn

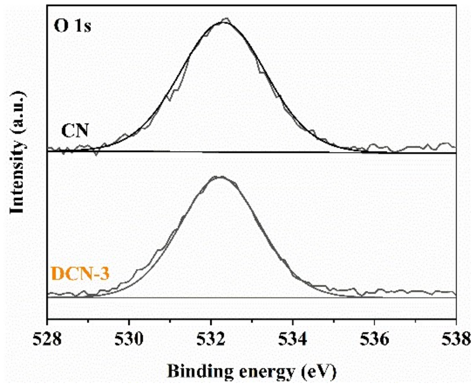

Fig. S1. XPS O1s spectra of CN (top) and DCN-3 (bottom) samples.

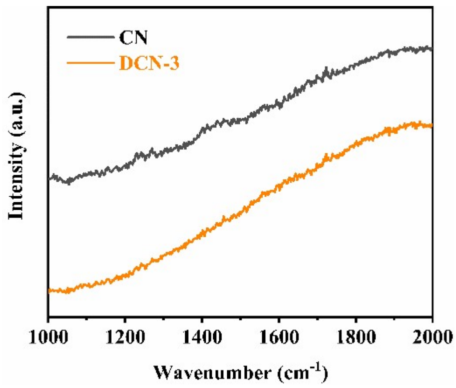

Fig. S2. Raman spectra of CN and DCN-3 samples.

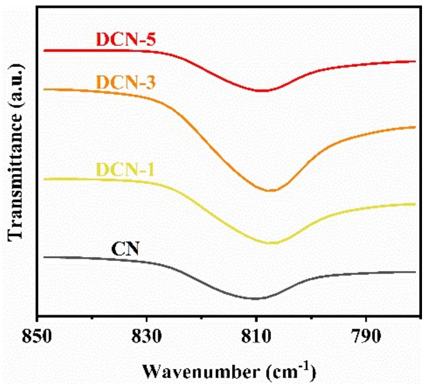

Fig. S3. Magnifying FTIR spectra of CN (black), DCN-1 (yellow), DCN-3 (orange) and DCN-5 (red) samples.

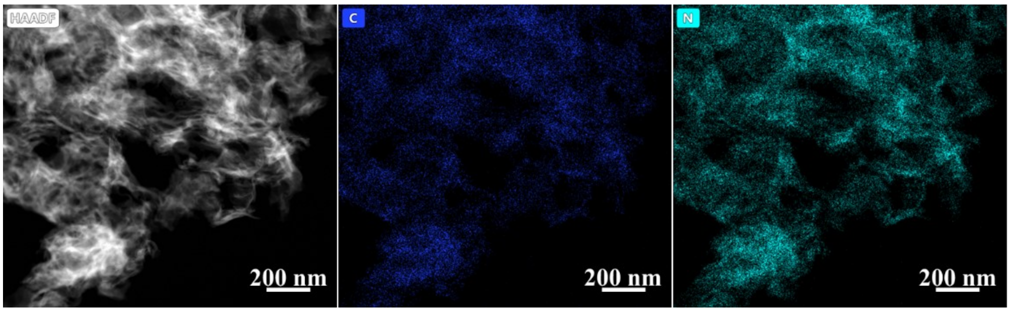

Fig. S4. Corresponding elemental mapping of C and N elements of DCN-3.

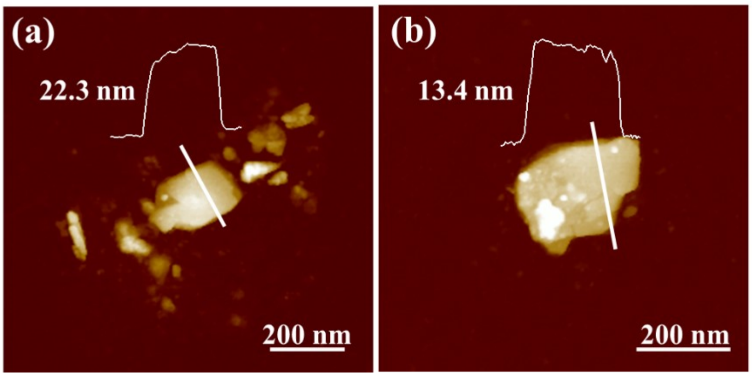

Fig. S5. AFM images of (a) CN and (b) DCN-3.

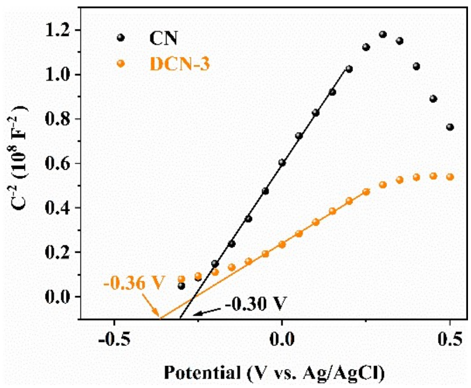

Fig. S6. Mott-Schottky plots of CN and DCN-3.

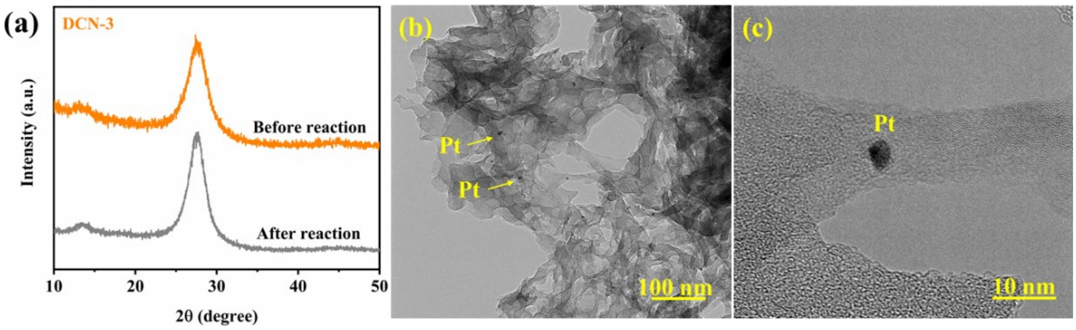

Fig. S7. (a) XRD patterns of DCN-3 before and after photocatalytic stability tests. (b, c) TEM images of DCN-3 after cyclic stability tests for 16 h, the black dots in (b) and (c) show the Pt nanoparticles.

Table S1. The element content and C/N atomic ratios based on XPS and elemental analysis results.

	XPS			elemental analysis		
	C	N	C/N	C	N	C/N
CN	47.2	48.3	0.98	35.13	59.91	0.586
DCN-3	53.6	37.9	1.41	35.59	60.21	0.591

Table S2. The ratio of peak areas for CN and DCN-3 based on XPS C 1s and N 1s results.

	C 1s			N 1s		
	C-C	C-NH_x	N-C=N	C-N=C	N-$(C)_3$	C-NH_x
CN	26.8%	7.8%	65.3%	60.9%	31.9%	7.2%
DCN-3	39.4%	7.5%	53.1%	55.5%	36.8%	7.7%

Table S3. The average PL lifetimes and relative percentages of photoinduced charge carriers in CN and DCN-3.

sample	τ (ns)	component	lifetime (ns)	percentage (%)
CN	6.15	τ_1	2.23	73.6
		τ_2	8.89	26.4
DCN-3	5.23	τ_1	1.48	81.9
		τ_2	8.27	18.1

Table S4. The comparisons of using different precursors and photocatalytic H_2 evolution performance with some C-doped g-C_3N_4 photocatalysts reported in recent years.

Precursors	Light source	HER (μmol h^{-1} g^{-1})	Enhanced factor	AQE (%)	Ref.
melamine + glucose	λ > 400 nm	305	3.1	/	[1]
urea + malondiamide	λ > 400 nm	2720	3.4	3.17	[2]
dicyandiamide + β-cyclodextrin	λ > 400 nm	360	4.8	2.05	[3]
dicyandiamide + uracil	λ > 420 nm	364	21	/	[4]
melamine + methyl-cyclodextrin	λ > 420 nm	125.1	10.4	6.8	[5]
melamine + ethanol	λ > 420 nm	/	1.42	/	[6]
dicyandiamide + dimethylformamide	λ > 400 nm	177.6	5.2	/	[7]
dicyandiamide + glucose	λ > 420 nm	1636	3.0	/	[8]
urea + D-mannitol	λ > 420 nm	3180	5.3	3.26	This work

References

1 G. Liu, M. Xue, Q. Liu, H. Yang and Y. Zhou, Int. J. Hydrogen Energy, 2019, **44**, 25671-25679.

2 Y. F. Li, S. Wang, W. Chang, L. H. Zhang, Z. S. Wu, R. X. Jin and Y. Xing, Appl. Catal. B-Environ., 2020, **274**, 10.

3 E. S. Da Silva, N. M. M. Moura, A. Coutinho, G. Drazic, B. M. S. Teixeira, N. A. Sobolev, C. G. Silva, M. Neves, M. Prieto and J. L. Faria, ChemSusChem, 2018, **11**, 2681-2694.

4 Y. Huang, D. Li, Z. Fang, R. Chen, B. Luo and W. Shi, Appl. Catal. B-Environ., 2019, **254**, 128-134.

5 Z. Chen, T.T. Fan, X. Yu, Q.-L. Wu, Q.H. Zhu, L.Z. Zhang, J.H. Li, W.P. Fang and X.D. Yi, J. Mater. Chem. A, 2018, **6**, 15310-15319.

6 G. Dong, K. Zhao and L. Zhang, Chem. Commun., 2012, **48**, 6178-6180.

7 J. Cao, H. Fan, C. Wang, J. Ma, G. Dong and M. Zhang, Ceram. Int., 2020, **46**, 7888-7895.

8 H. Wang, G. Huang, Z. Chen and W. Li, Catalysts, 2018, **8**, 366.