Electronic Supplementary Information

Purposefully designing novel hydroxylated and carbonylated melamine towards to the synthesis of targeted mesoporous oxygen-doped g-C_3N_4 nanosheets for highly enhanced photocatalytic hydrogen production

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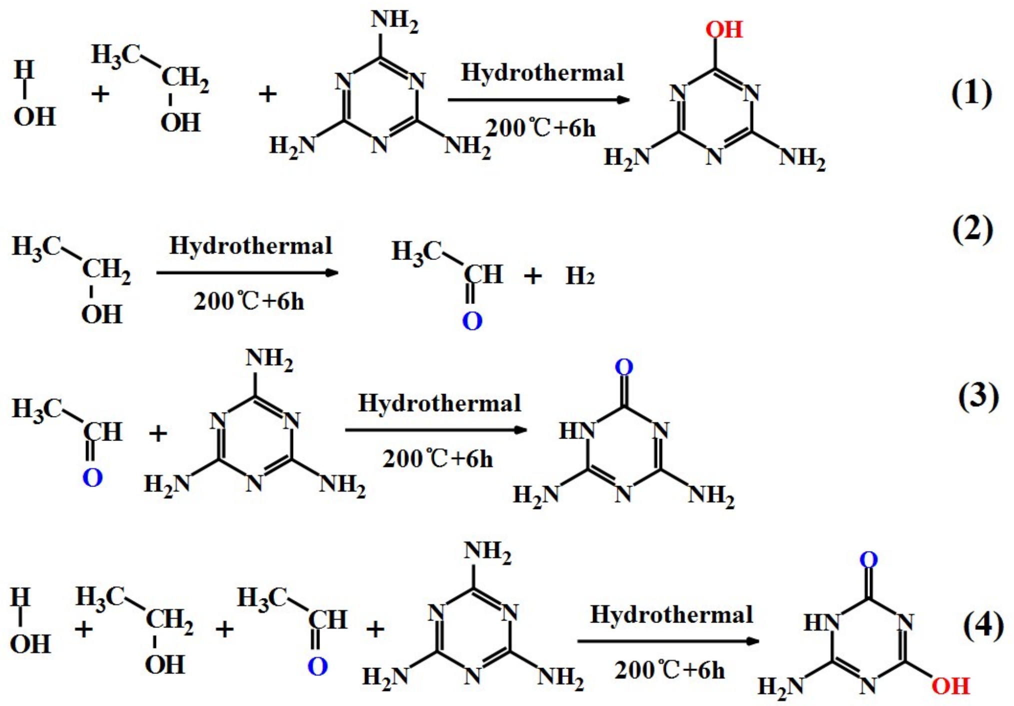

Scheme S1 The formation process of the hydroxyl and carbonyl group in melamine

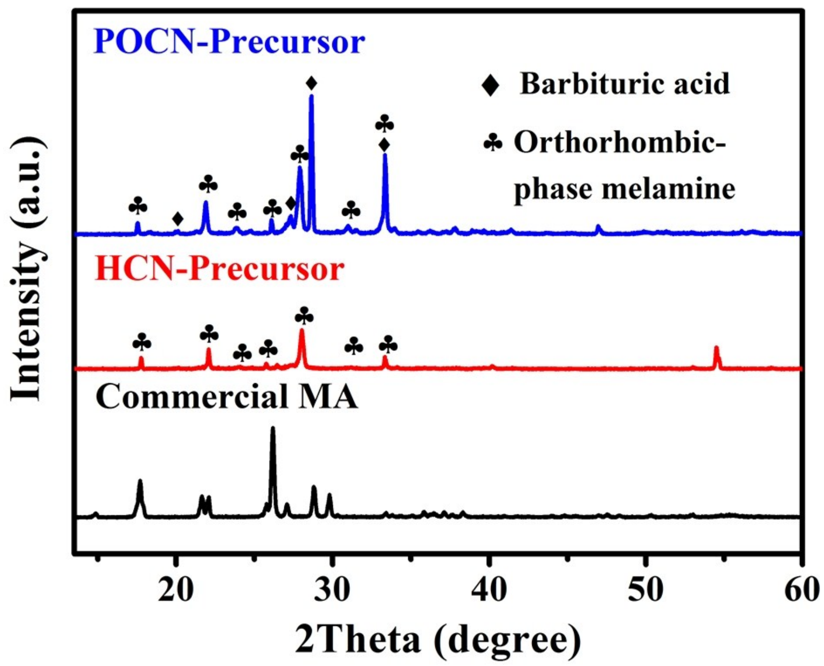

Fig.S1 XRD patterns of the commercial MA, HCN-precursor and POCN-precursor

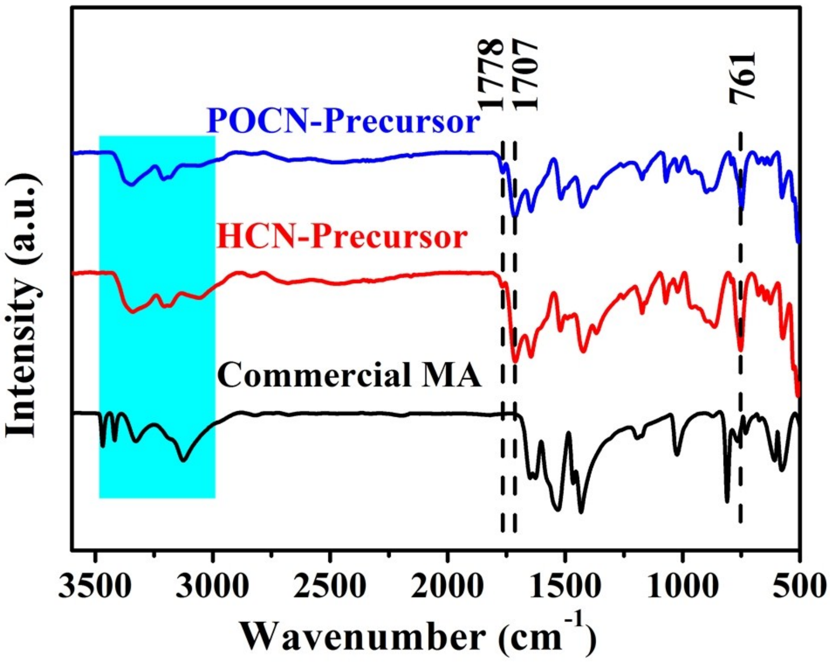

Fig.S2 FTIR spectra of the commercial MA, HCN-precursor and POCN-precursor

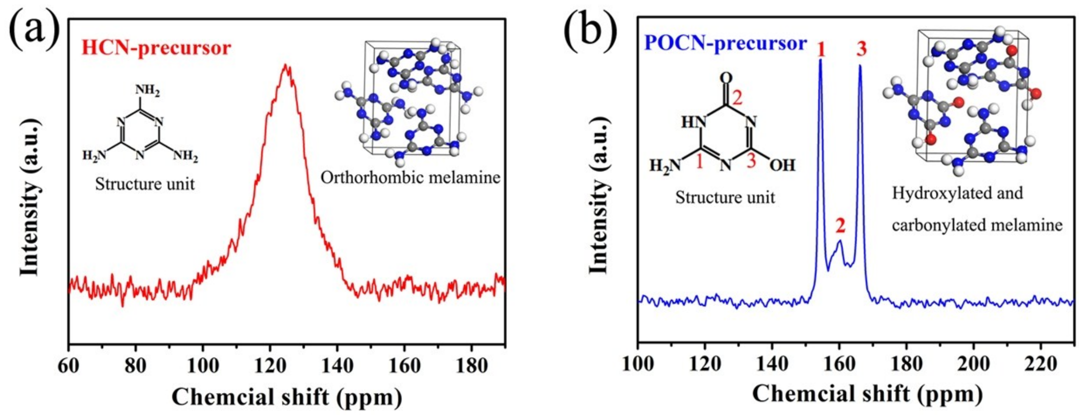

Fig.S3 Solid-state ^{13}C MAS NMR of (a) HCN- precursor and (b) POCN-precursor

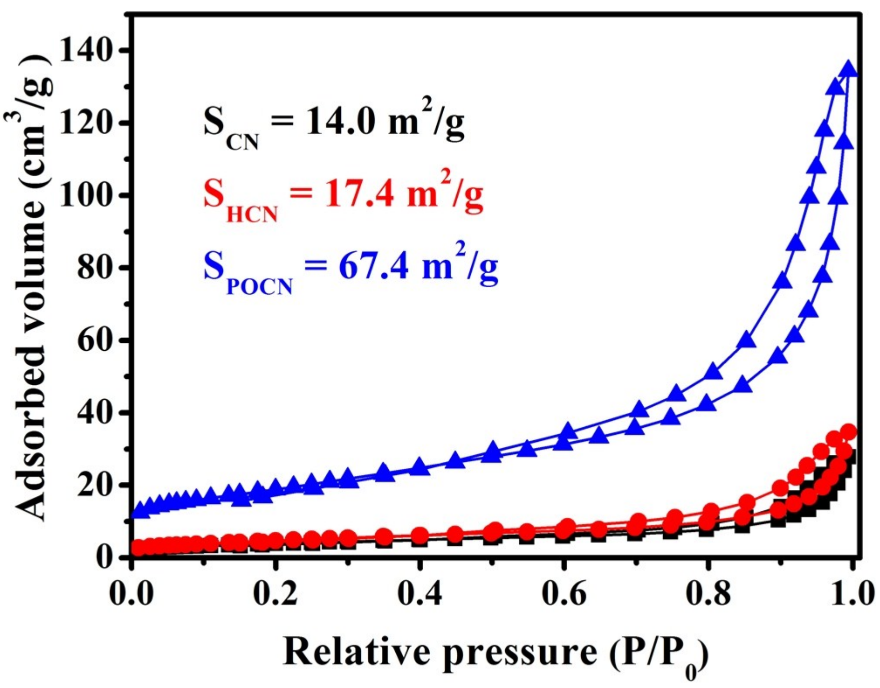

Fig.S4 N_2 adsorption/desorption isotherms of the CN, HCN and POCN samples

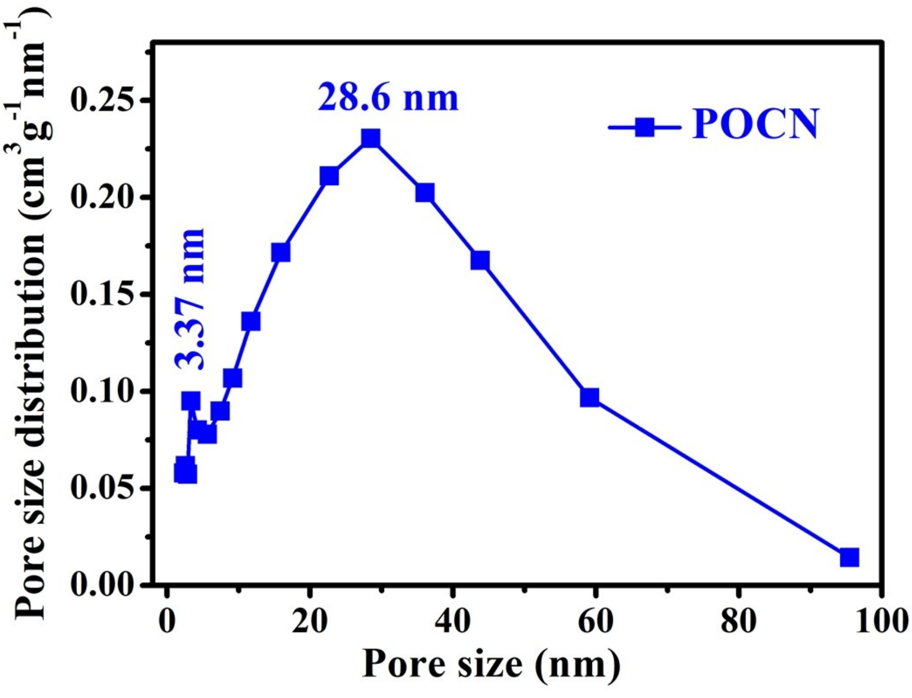

Fig.S5 Pore distribution centers of POCN

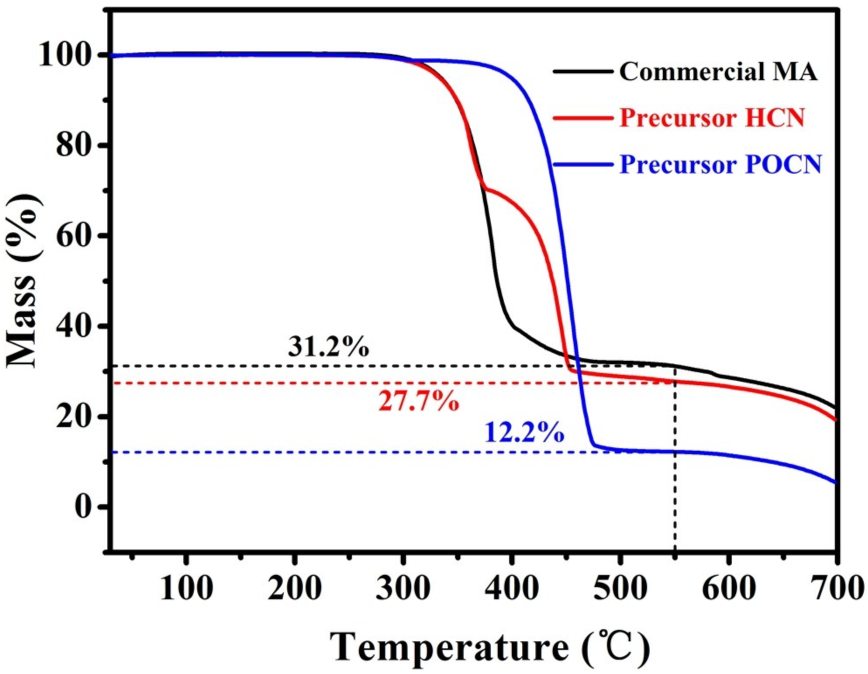

Fig.S6 TGA curves of the commercial MA, HCN-precursor and POCN-precursor

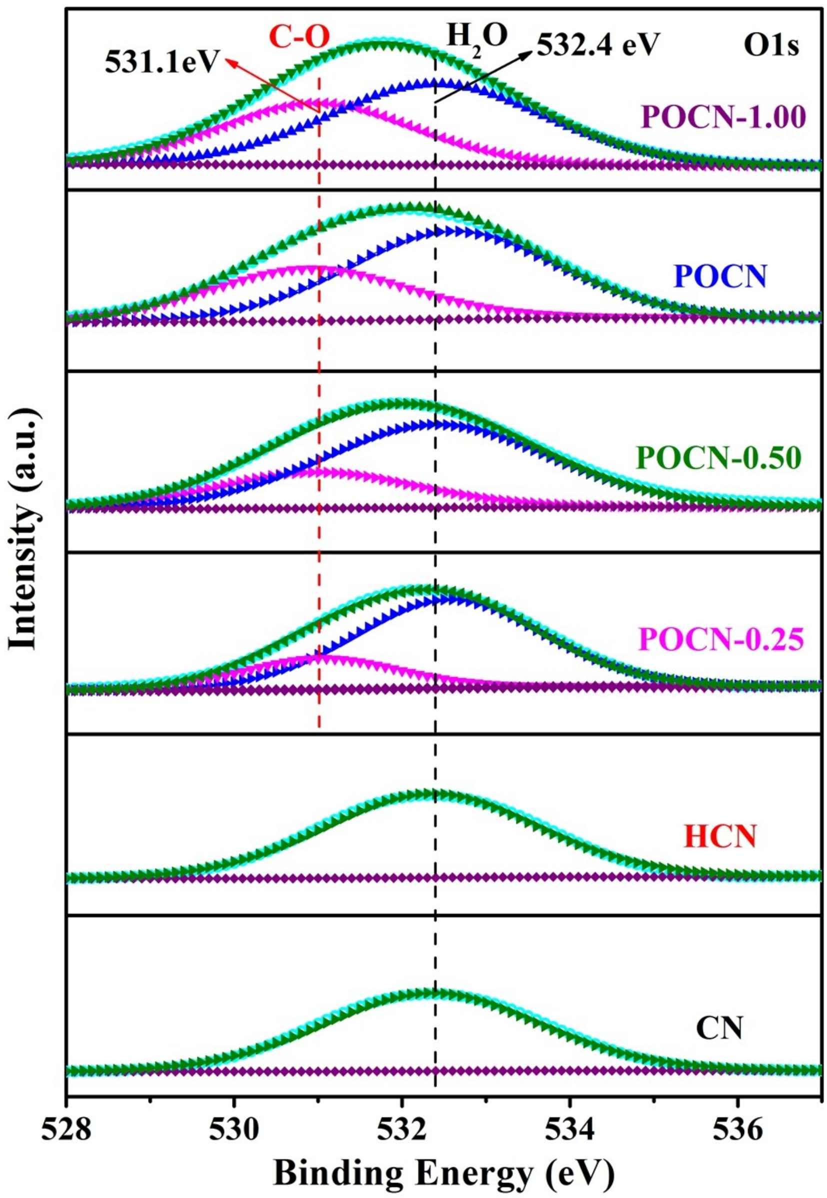

Fig.S7 The high-resolution O 1s spectra of CN, HCN, POCN-0.25, POCN-0.50, POCN and POCN-1.00 samples.

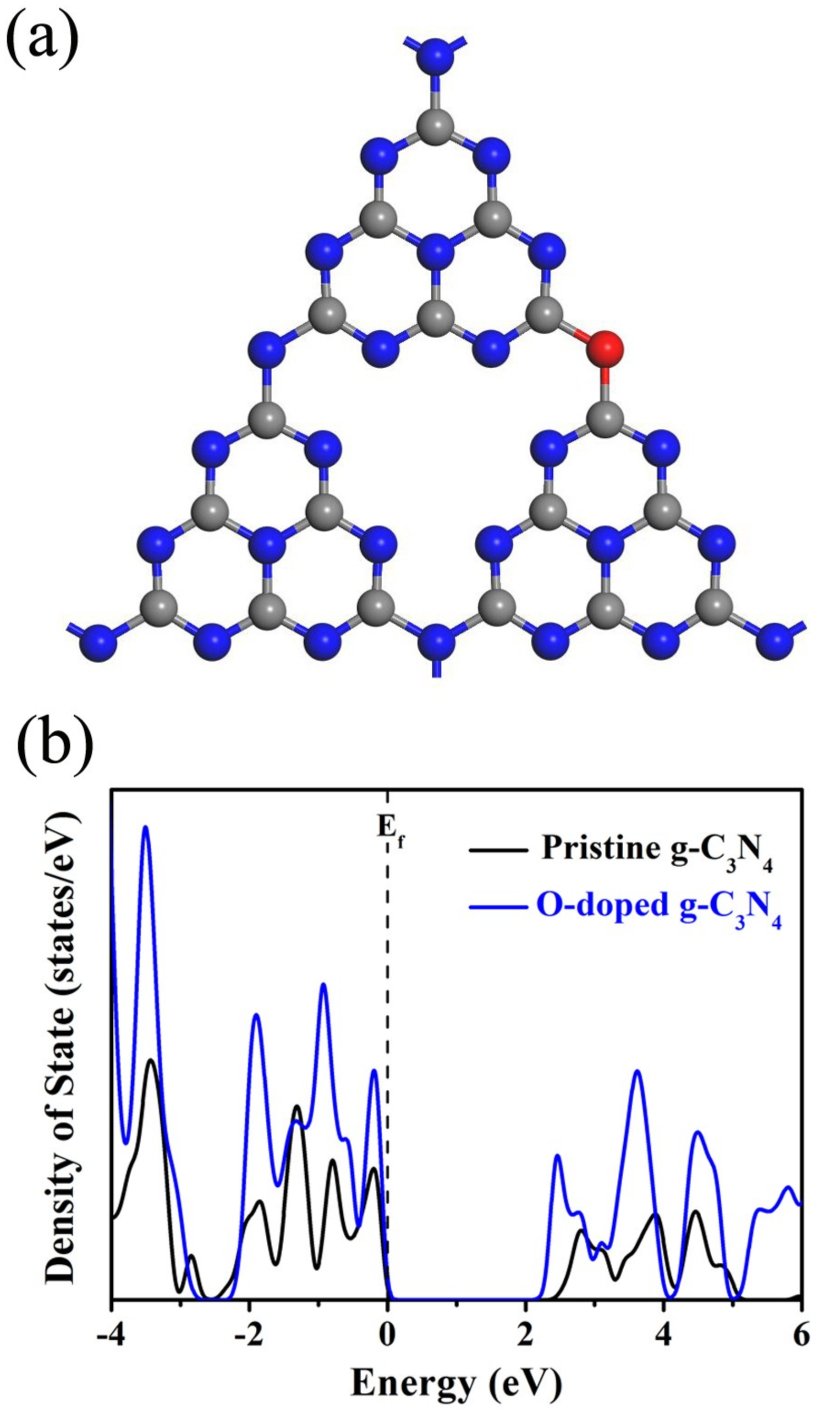

Fig.S8 (a) The geometry structure of O-doped g-C_3N_4. The gray, blue and red spheres represent the C, N and O atoms, respectively. (b) The DOS calculated for pristine g-C_3N_4 (black line) and O-doped g-C_3N_4 (blue line) using the HSE06 functional. The VBM of pristine g-C_3N_4 is chosen as the Fermi energy and is set to zero.

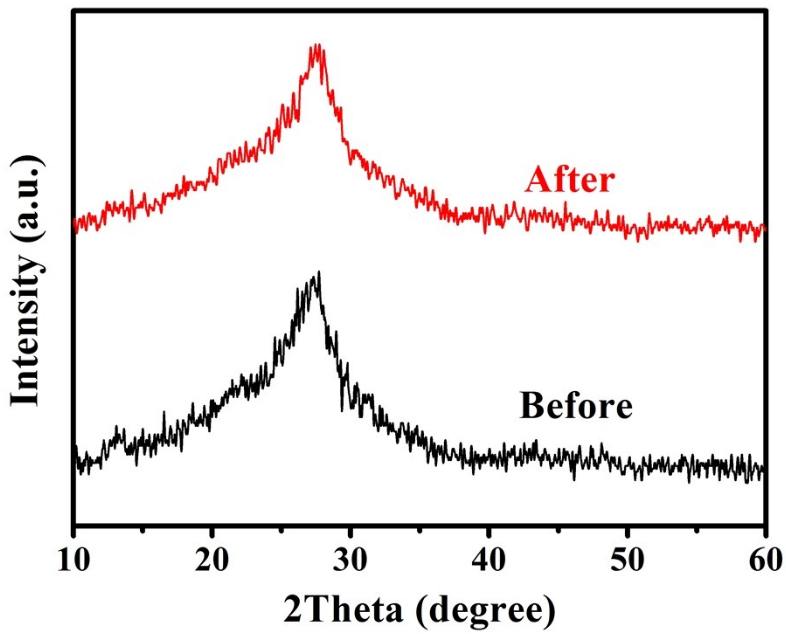

Fig. S9 XRD patterns of the recycled POCN sample

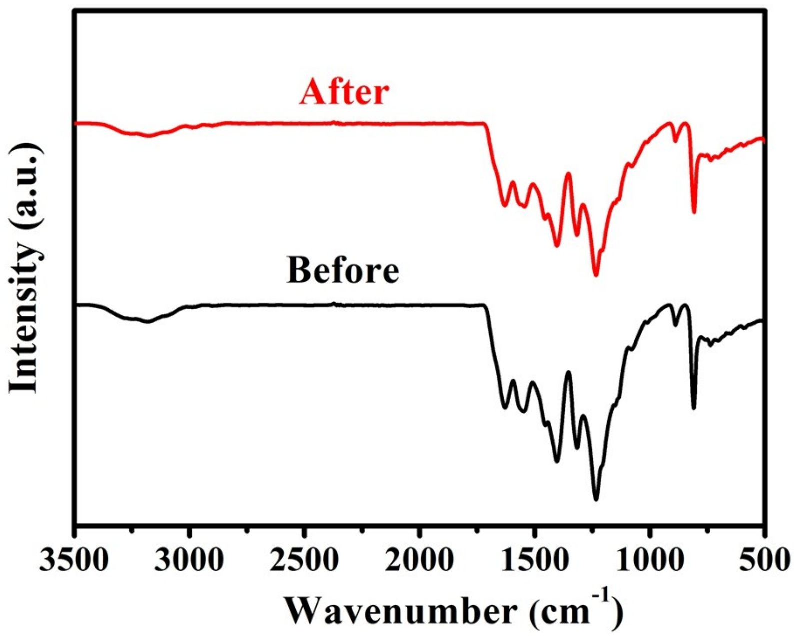

Fig.S10 FTIR patterns of the recycled POCN sample.

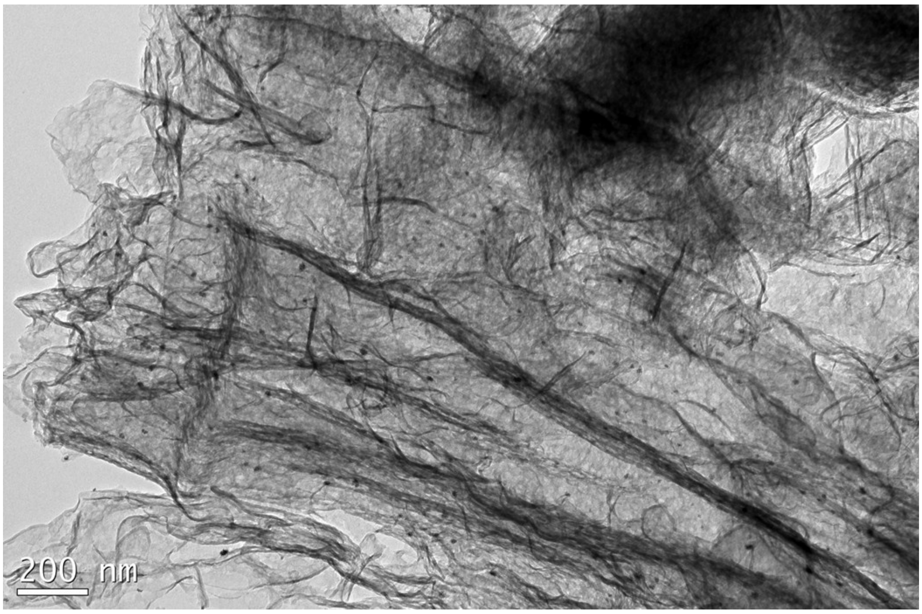

Fig.S11 TEM image of recycled POCN sample

Table S1 Relative content of various nitrogen species of CN, HCN and POCN

Sample	C=N-C	N-$(C)_3$	NH_X	C=N-C/ N-$(C)_3$	NH_X /N-$(C)_3$
POCN	73.28	23.46	3.25	3.12	0.139
HCN	67.31	27.08	5.61	2.48	0.207
CN	60.83	29.82	9.35	2.03	0.314

Table S2 The amount of C–O bond derived from the high-resolution O 1s spectra for CN, HCN, POCN-0.25, POCN-0.50, POCN and POCN-1.00.

Sample	CN	HCN	POCN-0.25	POCN-0.50	POCN	POCN-1.00
At. %(O)	none	none	0.9	1.32	2.36	3.25

Table S3 Comparison of the photocatalytic performance in hydrogen evolution of POCN with other recently reported carbon nitrides.

Catalyst	Light Source	Catalyst /Cocatalyst	Reactant Solution	HER (μmol ·h⁻¹· g⁻¹)	BET ($m^2·g^{-1}$)	AQE (%)	Reference
Porous O-doped $g-C_3N_4$ nanosheets	300W Xe lamp λ>420 nm	30 mg 3wt% Pt	90mL water +10mL TEOA	277	6.82	---	1
Porous O-doped $g-C_3N_4$ nanosheets	300W Xe lamp λ>420 nm	50 mg 3wt% Pt	40mL water +10mL TEOA	395.96	36.9	0.79	2
Porous O-doped $g-C_3N_4$ nanosheets	300W Xe lamp（λ>420 nm）	15mg 1wt% Pt	80mL water +20mL TEOA	533	41．2	----	3
Porous O-doped $g-C_3N_4$ nanorods	300W Xe lamp λ>400 nm	25mg 3wt% Pt	75mLwater +5mL TEOA	732	114.2	7.1	4
Porous O-doped $g-C_3N_4$ nanosheets	300W Xe lamp λ>420 nm	50 mg 3wt% Pt	108mL water +12mL TEOA	1204	36.1	7.8	5
Porous O-doped $g-C_3N_4$ nanosheets	300W Xe lamp λ>400 nm	50 mg 1wt% Pt	90mL water +10mL TEOA	1748.6	48.96	7.2	6
Porous K-Doped $g-C_3N_4$ nanosheets	300W Xe lamp λ>400 nm	50 mg 3wt% Pt	90mL water +10mL TEOA	1337．2	11	----	7
Mesoporous S-doped $g-C_3N_4$	300W Xe lamp λ>420 nm	100 mg 3wt% Pt	85mL water +15mL TEOA	1360	128.4	5.8	8
Porous S/W-doped g-C_3N_4 microrods	300W Xe lamp（λ>420 nm）	50 mg 3wt% Pt	20% Vol TEOA	857.3	45．2	----	**9**
Porous Na-doped $g-C_3N_4$ nanosheets	300W Xe lamp λ>420 nm	100 mg 3wt% Pt	90mL water +10mL TEOA	719	56.1	----	10
Mesoporous S-doped g-C_3N_4 spheres	300W Xe lamp λ>400 nm	10 mg 1wt% Pt	270mLwater +30mLTEOA	890.6	82.3	4.9	11
Porous P-doped $g-C_3N_4$ nanosheets	300W Xe lamp λ>400 nm	50 mg 1wt% Pt	20vol% TEOA	1596	122.6	3.56	12
Porous $g-C_3N_4$ nanosheets	300W Xe lamp λ>400 nm	100 mg 3wt% Pt	90mL water +10mL TEOA	1323.25	55.07	7.45	13
Porous $g-C_3N_4$ nanosheets	300W Xe lamp λ>420 nm	50mg 3wt% Pt	252mL water +28mL TEOA	1430.1	67.7	----	14
mesoporous $g-C_3N_4$	300W Xe lamp λ>420 nm	30mg 1wt% Pt	45mL water +5mL TEOA	1161.5	37.4	----	15
Porous $g-C_3N_4$ nanosheets	300W Xe lamp λ>420 nm	100mg 0.6wt% Pt	90mL water +10mL TEOA	1078	186.3	---	16

Catalyst	Light Source	Catalyst /Cocatalyst	Reactant Solution	HER (μmol $\cdot h^{-1}\cdot g^{-1}$)	BET ($m^2\cdot g^{-1}$)	AQE (%)	Reference
Porous $g-C_3N_4$ nanosheets	300W Xe lamp λ>420 nm	50 mg 2wt% Pt	45mL water +5mL TEOA	1074.9	73.29	----	17
Porous $g-C_3N_4$ nanosheets	300W Xe lamp λ>420 nm	50 mg 1wt% Pt	20% Vol TEOA	991	44.2	----	18
Porous $g-C_3N_4$ nanosheets	150W Xe lamp λ>420 nm	50 mg 2wt% Pt	90mL water +10mL TEOA	387	160	21.3	19
Porous $g-C_3N_4$ nanosheets	300W Xe lamp λ>400 nm	2 mg 1wt% Pt	36mL water +4mL TEOA	198	193.98	----	20
Porous FeP /$g-C_3N_4$ nanosheets	300W Xe lamp λ>400 nm	60 mg 2.2wt% Fe	135mL water +15mL TEOA	177.9	----	1.57	21
Porous Ag/$g-C_3N_4$ Nanofibers	300W Xe lamp λ>420 nm	50 mg 1wt% Pt	90mL water +10mL TEOA	625	26	----	22
O-doped $g-C_3N_4$ nanosheets	300W Xe lamp λ>420 nm	30 mg 3wt% Pt	45mL water +5mL TEOA	1050.3	31.7	13.04	23
K-doped $g-C_3N_4$ nanosheets	300W Xe lamp λ>420 nm	30 mg 3wt% Pt	45mL water +5mL TEOA	919.5	46.0	6.98	24
Porous $g-C_3N_4$	350W Xe lamp λ>420 nm	40 mg 3wt% Pt	72mL water +8mL TEOA	1590	37	----	25
Porous $g-C_3N_4$	300W Xe lamp λ>400 nm	100 mg 1.5wt% Pt	270mL water +30mL TEOA	597.3	56.9	2.85	26
Porous $g-C_3N_4$	300W Xe lamp λ>420 nm	50 mg 0.5wt% Pt	80mLwater +20mL TEOA	1216	158.13	----	27
Amorphous $g-C_3N_4$	300W Xe lamp λ>440 nm	50 mg 6wt% Pt	270mL water +30mL TEOA	157.9	—	5.1	28
P-doped $g-C_3N_4$	300W Xe lamp λ>420 nm	100 mg 1wt% Pt	80mL water +20mL TEOA	670	22.95	5.68	29
Nitrogen self-doped $g-C_3N_4$	300W Xe lamp λ>400 nm	80 mg 3wt% Pt	90mL water +10mL TEOA	553.5	9.21	---	30
Porous O-doped $g-C_3N_4$ nanosheets	300W Xe lamp λ>420 nm	50 mg 1wt% Pt	90mL water +10mL TEOA	1285.7	67.4	12.06	This work

References

1 L. J. Fang, X. Wang, J. J. Zhao, Y. Li, Y. Wang, X. L. Du, Z. F. He, H. Zeng and H. Yang, *Chem. Commun.*, 2016, **52**, 14408–14411.

2 Y. B. Jiang, Z. Z. Sun, C. Tang, Y. X. Zhou, L. Zeng and L. M. Huang. *Appl. Catal. B-Environ.*, 2019, **240**, 30–38.

3 J. R. Bai, C. C. Yin, H. Y. Xu, G. Chen, Z. J. Ni, Z. L. Wang, Y. G. Li , S. F. Kang, Z. Zheng and X. Li, *J. Colloid. Interf. Sci.*, 2018, **532**, 280–286.

4 Y. X. Zeng, X. Liu, C. B. Liu, L. L. Wang, Y. C. Xia, S. Q. Zhang, S. L. Luo and Y. Pei, *Appl. Catal. B-Environ.*, 2018, **224**, 1–9.

5 Z. F. Huang, J. J. Song, L. Pan, Z. M. Wang, X. Q. Zhang, J. J. Zou, W. B. Mi, X. W. Zhang and L. Wang, *Nano Energy*, 2015, **12**, 646–656.

6 C. Wang, H. Q. Fan, X. H. Ren, J. W. Ma, J. W. Fang and W. J. Wang, *ChemSusChem*, 2018, **11**, 700–708.

7 Y. Y. Wang, S. Zhao, Y. W. Zhang, J. S. Fang, Y. M. Zhou, S. H. Yuan, C. Zhang and W. X. Chen, *Appl. Surf. Sci.*, 2018, **440**, 258–265.

8 J. D. Hong, X. Y. Xia, Y. S. Wang and R. Xu, *J. Mater. Chem.*, 2012, **22**, 15006–15012.

9 K. Wu, D. D. Chen, J. Z. Fang, S. X. Wu, F. Yang, X. M. Zhu and Z. Q. Fang, *Appl. Surf. Sci.*, 2018, **462**, 991–1001.

10 Z. Shu, Y. Wang, W. B. Wang, J. Zhou, T. T. Li, X. Q. Liu, Y. G. Tan and Z. L. Zhao, *Int. J. Hydrogen. Energ.,* 2019, **44**, 748–756.

11 Y. D. Li, Z. H. Ruan, Y. Z. He, J. Z. Li, K. Q. Li, Y. L.Yang, D. B. Xia, K. F. Lin and Y. Yuan, *Int. J. Hydrogen. Energ.,* 2019, **44**, 707–719.

12 R. J. Ran, T. Y. Ma, G. Gao, X. Du and S. Qiao, *Energy Environ. Sci.*, 2015, **8**, 3708–3717.

13 W. Xing, G. Chen, C. Li, Z. Han, Y. Hu and Q. Meng*, Nanoscale*, 2018, **10**, 5239–5245.

14 L. Q. Yang, J. F. Huang, L.Shi, L. Y. Cao, Q. Yu, Y. N. Jie, J. Fei, H. B. Ouyang and J. H. Ye, *Appl. Catal. B-Environ.*, 2017, **204**, 335–345.

15 S. Sun, X. Gou, S. Tao, J. Li, J. Cui, Q. Yang, S. Liang and Z. Yang*, Mater. Chem.*

Front., 2019, **3**, 597–605.

16 L. T. Ma, H. Q. Fan, J. Wang, Y. W. Zhao, H. L. Tian and G. Z. Dong. *Appl. Catal. B-Environ.*, 2016, **190**, 93–102.

17 Q. Y. Yan, C. C. Zhao, L. Zhang, Y. L. Hou, S. J. Wang, P. Dong, F. F. Lin and Y. Q. Wang, *ACS Sustainable Chem. Eng.*, 2019, **74**, 3866–3874.

18 .H. Huang, K. Xiao,N. Tian, F. Dong, T. Zhang, X. Du and Y. Zhang, *J. Mater. Chem. A*, 2017, **5**, 17452–17463.

19 M. R. Gholipour, F. Beland and T. O. Do, *ACS Sustainable Chem. Eng.*, 2017, **5**, 213–220.

20 R. C. Pawar, S. Kang, H. Han, H. Choi and C. S. Lee, *Catal. Sci. Technol.*, 2019, **9**, 1004–1012.

21 D. Q. Zeng, T. Zhou, W. J. Ong, M. D. Wu, X. G. Duan, W. J. Xu, Y. Z. Chen, Y. A. Zhu and D. L. Peng, *ACS Appl. Mater. Interfaces*, 2019, **11**, 6, 5651–5660.

22 J. P. Wang, J. K. Cong, H. Xu, J. M. Wang, H. Liu, M. Liang, J. K. Gao, Q. Q. Ni and J. M. Yao, *ACS Sustainable Chem. Eng.*, 2017, **5**, 10633–10639.

23 S. D. Sun, J. Li, J. Cui, X. F. Gou, Q. Yang, S. H. Liang, Z. M. Yang and J. M. Zhang, *Inorg. Chem. Front.,* 2018, **5**, 1721–1727.

24 S. D. Sun, J. Li, J. Cui, X. F. Gou, Q. Yang, Y. H. Jiang, S. H. Liang and Z. M. Yang, *Int. J. Hydrogen. Energ.*, 2019, **44**, 778–787.

25 Z. Chen, S. Lu, Q. Wu, F. He, N. Zhao, C. He and C. Shi, *Nanoscale*, 2018, **10**, 3008–3013.

26 Y. D. Li, Z. H. Ruan, Y. Z. He, J. Z. Li, K. Q. Li, Y. Q. Jiang, X. Z. Xu, Y. Yuan and K. F. Lin, *Appl. Catal. B-Environ.*, 2018, **236**, 64–75.

27 C. Y. Liu, Y. H. Zhang, F. Dong, X. Du and H. W. Huang, *J. Phys. Chem. C*, 2016, 120, 19, 10381–10389.

28 Y. Y. Kang, Y. Q. Yang, L. C. Yin , X. D. Kang, G. Liu and H. M. Cheng, *Adv. Mater.*, 2015, **27**, 4572–4577.

29 S. E. Guo, Z. P. Deng, M. X. Li, B. J. Jiang, C. G. Tian, Q. J. Pan and H. G. Fu, *Angew. Chem. Int. Ed.*, 2016, **55**, 1830–1834.

30 J. W. Fang, H. Q. Fan, M. M.Li and C. B. Long*, J. Mater. Chem. A*, 2015, **3**, 13819–13826.