Supporting information

Ordered and carbon-doped porous polymeric graphitic carbon nitride nanosheets toward enhanced visible light absorption and efficient photocatalytic H_2 evolution

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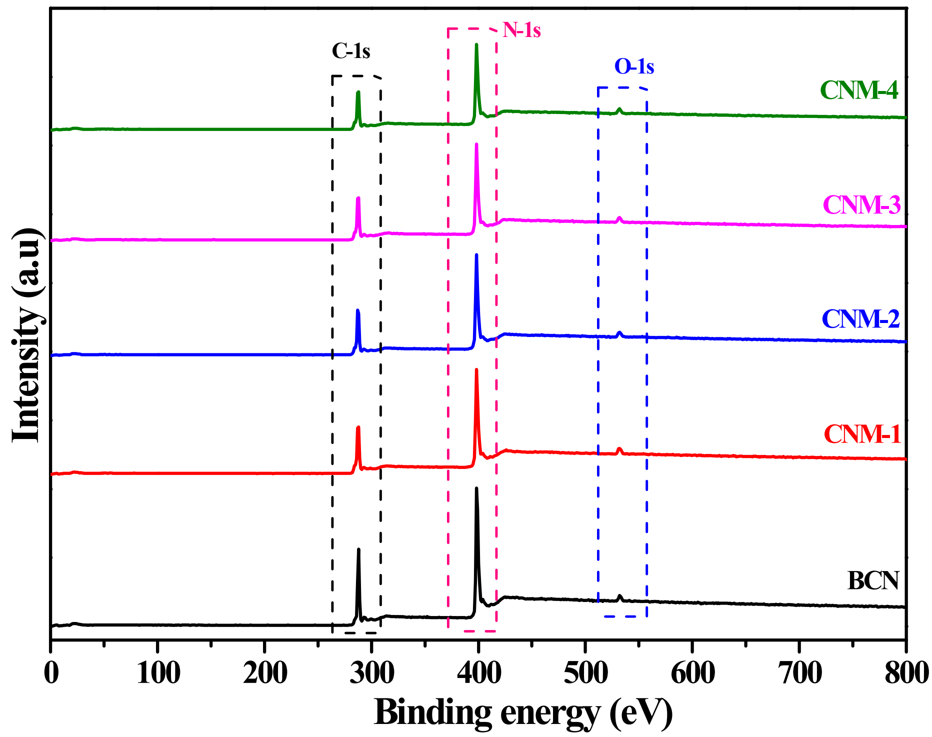

Figure S1. The XPS survey scan spectra of BCN and CNM samples.

Sample	**C-1s**	**N-1s**	**C/N**
BCN	**41.61**	**56.29**	**0.739**
CNM-1	**42.35**	**54.61**	**0.775**
CNM-2	**42.18**	**55.04**	**0.766**
CNM-3	**42.40**	**54.76**	**0.774**
CNM-4	**42.76**	**54.23**	**0.788**

Table S1. Atomic ratios of C and N elements in the prepared GCN samples

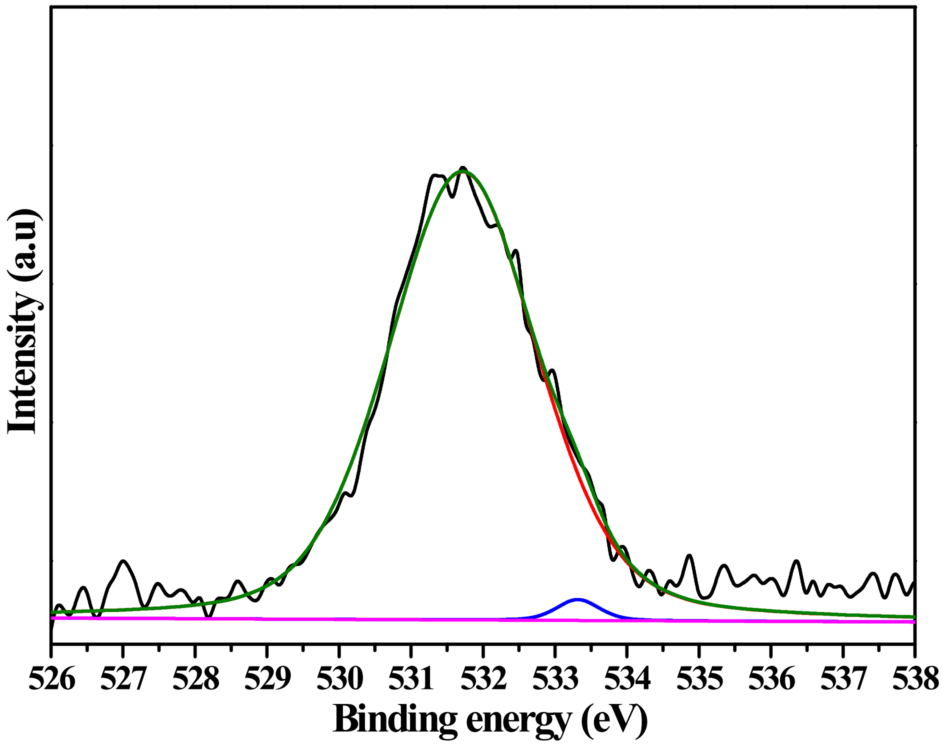

Figure S2. The XPS survey scan spectra of O-1s element in CNM-3 sample.

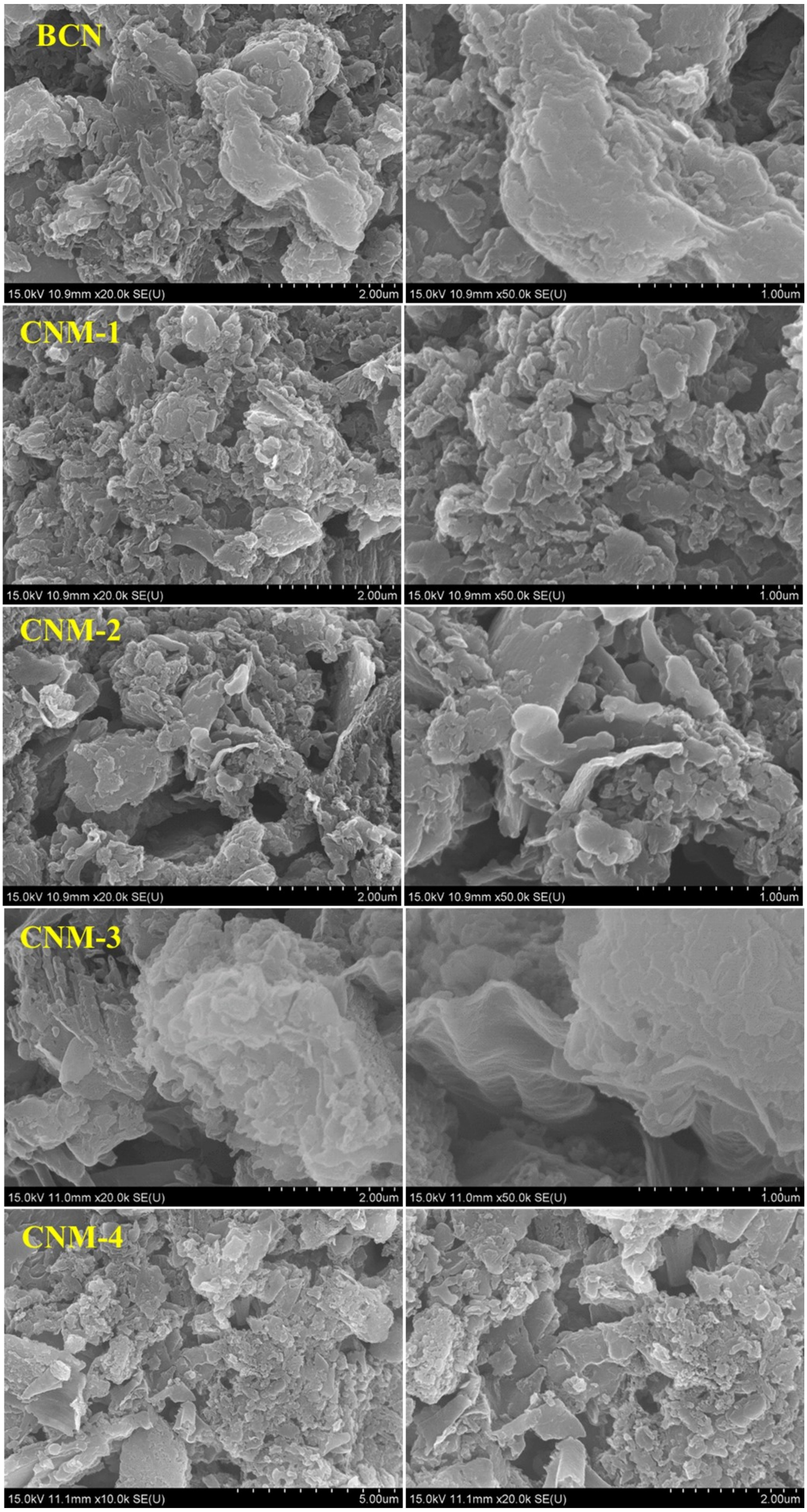

Figure S3. FE-SEM images of BCN and CNM photocatalyst samples

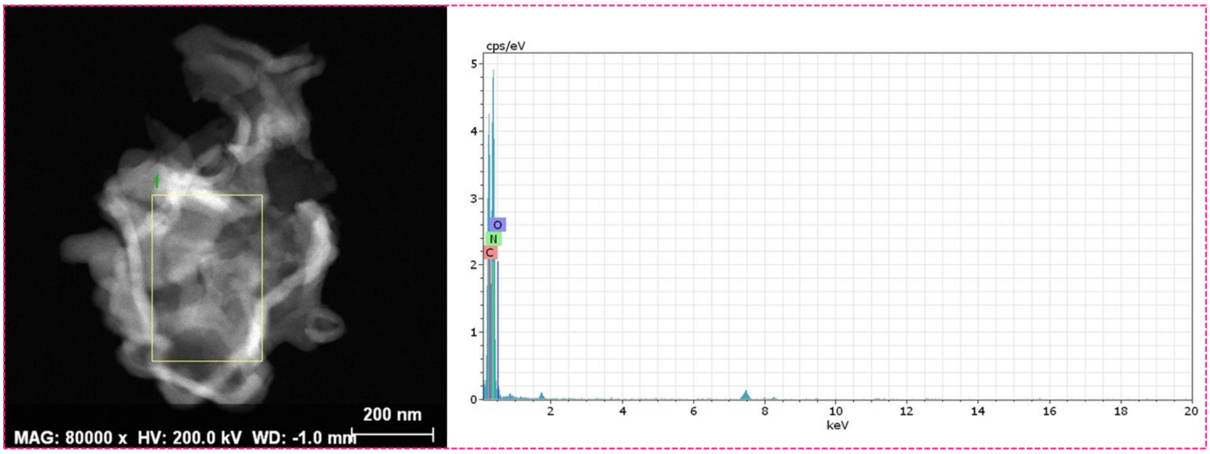

Figure S4. STEM-EDX spectral analysis of CNM-3 sample.

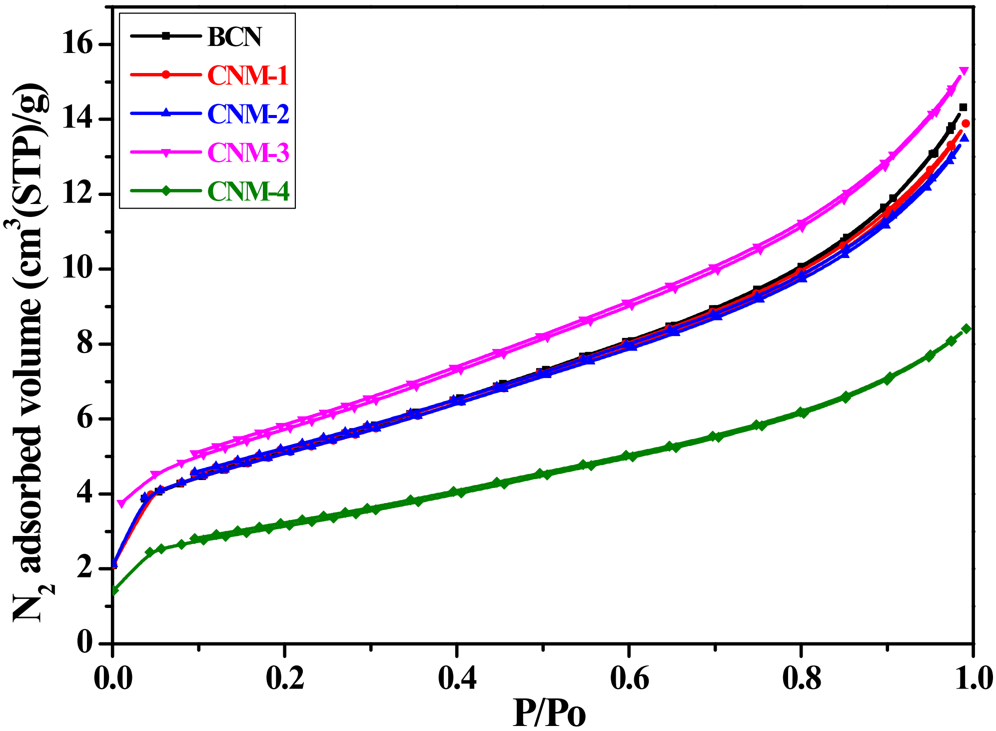

Figure S5. N2 adsorption-desorption isotherms of BCN and CNM samples.

Table S2. The comparison of photocatalytic H_2 evolution activity of g-C_3N_4 sample (CNM-3) derived from malonic acid treated melamine precursors with some previously reported g-C_3N_4-photocatalysts.

Photocatalyst	**H_2 evolution Activity**	**Light source**	**Reference**
3D g-C_3N_4	29 μmol/h	λ > 420 nm 300 W Xe lamp	1
Holey *g*-C_3N_4	82.9 μmol/h	λ > 420 nm 300 W Xe lamp	2
Porous g-C_3N_4	316.7 μmol/h	λ > 400 nm 300 W Xe lamp	3
Porous g-C_3N_4	1.8 μmol/h	λ > 420 nm 300 W Xe lamp	4
g-C_3N_4 nanosheets	170.5 μmol/h	λ > 400 nm 300 W Xe lamp	5
Carbon-rich g-C_3N_4	39.6 μmol/h 8.6 μmol/h	λ > 400 nm λ > 420 nm; 300 W Xe lamp	6
C-self doped g-C_3N_4	25.3 μmol/h	λ > 400 nm 300 W Xe lamp	7
C-rich g-C_3N_4	125.1μmol/h/g	λ > 420 nm 300 W Xe lamp	8
Porous crystalline g-C_3N_4	1010 μmol/h/g	λ > 420 nm 4 LEDs	9

Amine bridged g-C_3N_4	157 µmol/h/g	λ > 420 nm 300 W Xe lamp	10
Heptazine bridged g-C_3N_4	372 µmol/h	λ > 400 nm 300 W Xe lamp	11
Crystalline g-C_3N_4	150 µmol/h	White LED light 50 W	12
C-rich g-C_3N_4	551.5 µmol/h	λ > 400 nm 300 W Xe lamp	13
Defect- g-C_3N_4	504 µmol/h/g	λ > 420 nm 300 W Xe lamp	14
H-bond broken g-C_3N_4	580 µmol/h/g	λ > 440 nm 300 W Xe lamp	15
N-rich g-C_3N_4	15.5 µmol/h	λ > 420 nm 4 LEDs	16
O-doped g-C_3N_4	1748 µmol/h/g	λ > 400 nm 300 W Xe lamp	17
g-C_3N_4 with N-vacancies	652 µmol/h/g	λ > 420 nm 300 W Xe lamp	18
In-plane ordered g-C_3N_4	420 µmol/h	λ > 420 nm 300 W Xe lamp	19
g-C_3N_4 with cyanamide groups	8 µmol/h/g	λ > 400 nm 300 W Xe lamp	20
Porous C-rich g-C_3N_4	**663.6 µmol/h/g**	**λ > 420 nm 150 W Xe lamp**	**This work**

(1) Q. H. Liang, Z. Li, X. L. Yu, Z. H. Huang, F. Y. Kang, Q. H. Yang, Macroscopic 3D Porous Graphitic Carbon Nitride Monolith for Enhanced Photocatalytic Hydrogen Evolution, Adv. Mater. 2015, 27, 4634-4639.

(2) Q. H. Liang, Z. Li, Z. H. Huang, F. Y. Kang, Q. H. Yang, Holey Graphitic Carbon Nitride Nanosheets with Carbon Vacancies for Highly Improved Photocatalytic Hydrogen Production, Adv. Funct. Mater. 2015, 25, 6885-6892.

(3) P. J. Yang, J. H. Zhao, W. Qiao, L. Li, Z. P. Zhu, Ammonia-induced robust photocatalytic hydrogen evolution of graphitic carbon nitride, Nanoscale 2015, 7, 18887-18890.

(4) Q. Gu, Y. S. Liao, L. S. Yin, J. L. Long, X. X. Wang, C. Xue, Template-free synthesis of porous graphitic carbon nitride microspheres for enhanced photocatalytic hydrogen generation with high stability, Appl. Catal. B 2015, 165, 503-510.

(5) P. Niu, L. L. Zhang, G. Liu, H. M. Cheng, Graphene-Like Carbon Nitride Nanosheets for Improved Photocatalytic Activities, Adv. Funct. Mater. 2012, 22, 4763-4770

(6) Li, Y. F.; Yang, M.; Xing, Y.; Liu, X. C.; Yang, Y.; Wang, X.; Song, S. Y. Preparation of Carbon-Rich g-C_3N_4 Nanosheets with Enhanced Visible Light Utilization for Efficient Photocatalytic Hydrogen Production. Small 13, 2017, 1701552.

(7) Guohui Dong, Kun Zhao and Lizhi Zhang, Carbon self-doping induced high electronic conductivity and photoreactivity of g-C_3N_4, Chem. Commun., 2012, 48, 6178–6180.

(8) Zhou Chen, Ting-Ting Fan, Xiang Yu, Qiu-Ling Wu, Qiu-Hui Zhu, Li-Zhong Zhang, Jian-Hui Li, Wei-Ping Fang and Xiao-Dong Yi, Gradual carbon doping of graphitic carbon nitride towards metal-free visible light photocatalytic hydrogen evolution, J. Mater. Chem. A, 2018, 6, 15310–15319.

(9) Xinhe Wu, Haiqin Ma, Wei Zhong, Jiajie Fan, Huogen Yu, Porous crystalline g-C3N4: Bifunctional NaHCO3 template-mediated synthesis and improved photocatalytic H2-evolution rate, Applied Catalysis B: Environmental 271 (2020) 118899.

(10) Dawoon Jang, Seungjoo Choi, Nam Hee Kwon, Kyung Yeon Jang, Suyeon Lee, Tae-Woo Lee, Seong-Ju Hwang, Hyungjun Kim, Jeongho Kim, Sungjin Park, Water-assisted formation of amine-bridged carbon nitride: A structural insight into the photocatalytic performance for H_2 evolution under visible light, Applied Catalysis B: Environmental 310 (2022) 121313.

(11) Dong Liu, Shengtao Chen, Yuexing Zhang, Renjie Li, Tianyou Peng, Modulating the bridging units of carbon nitride for highly efficient charge separation and visible-light-

responsive photocatalytic H_2 evolution, Applied Catalysis B: Environmental 333 (2023) 122805.

(12) Guigang Zhang, Guosheng Li, Zhi-An Lan, Lihua Lin, Aleksandr Savateev, Tobias Heil, Spiros Zafeiratos, Xinchen Wang, and Markus Antonietti, Optimizing Optical Absorption, Exciton Dissociation, and Charge Transfer of a Polymeric Carbon Nitride with Ultrahigh Solar Hydrogen Production Activity, Angew. Chem. Int. Ed. 2017, 56, 13445 –13449.

(13) Shuo Zhao, Yuepeng Liu, Yanyun Wang, Liying Xie, Jiasheng Fang, Yiwei Zhang, Yuming Zhou, and Shuping Zhuo, C-Rich Graphitic Carbon Nitride with Cross Pore Channels: A VisibleLight-Driven Photocatalyst for Water Splitting, ACS Appl. Energy Mater. 2021, 4, 1784−1792.

(14) Huihui Deng, Yushuai Jia, Wenquan Wang, Shengliang Zhong, Renqin Hao, Linjie Fan, and Xin Liu, Defect and Crystallinity-Mediated Charge Separation in Carbon Nitride for Synergistically Boosted Solar-Driven Hydrogen Evolution, ACS Sustainable Chem. Eng. 2023, 11, 13736−13746.

(15) Yuyang Kang, Yongqiang Yang, Li-Chang Yin, Xiangdong Kang, Lianzhou Wang, Gang Liu and Hui-Ming Cheng, Selective Breaking of Hydrogen Bonds of Layered Carbon Nitride for Visible Light Photocatalysis, Adv. Mater. 2016, 28, 6471–6477.

(16) Xinhe Wu, Duoduo Gao, Ping Wang, Huogen Yu, Jiaguo Yu, NH_4Cl-induced low-temperature formation of nitrogen-rich g-C_3N_4 nanosheets with improved photocatalytic hydrogen evolution, Carbon 2019, 153, 757-766.

(17) Chao Wang, Huiqing Fan, Xiaohu Ren, Jiangwei Ma, Jiawen Fang, and Weijia Wang, Hydrothermally Induced Oxygen Doping of Graphitic Carbon Nitride with a Highly Ordered Architecture and Enhanced Photocatalytic Activity, ChemSusChem 2018, 11, 700–708.

(18) Zhengdong Xu, Yang Chen, Binghao Wang, Yu Ran, Junbo Zhong, Minjiao Li, Highly selective photocatalytic CO_2 reduction and hydrogen evolution facilitated by oxidation induced nitrogen vacancies on g-C_3N_4, Journal of Colloid and Interface Science 651 (2023) 645–658.

(19) Guixia Zhao, Guigao Liu, Hong Pang, Huimin Liu, Huabin Zhang, Kun Chang, Xianguang Meng, Xiaojun Wang, and Jinhua Ye, Improved Photocatalytic H2 Evolution over G-Carbon Nitride with Enhanced In-Plane Ordering, Small, 2016, 12, 6160-6166.

(20) Vincent Wing-hei Lau, Igor Moudrakovski, Tiago Botari, Simon Weinberger, Maria B. Mesch, Viola Duppel, Jürgen Senker, Volker Blum, Bettina V. Lotsch, Rational design of carbon nitride photocatalysts by identification of cyanamide defects as catalytically relevant sites, Nat. Commun. 2016, 7, 12165.