3D hierarchical g-C_3N_4 architectures assembled by ultrathin self-doped nanosheets: extremely facile HMTA activation and superior photocatalytic hydrogen evolution

Huihui Gao,† Ruya Cao,† Shouwei Zhang,* Hongcen Yang, Xijin Xu*

School of Physics and Technology, University of Jinan, Shandong, 250022, P. R. China. E-mail: sps_xuxj@ujn.edu.cn; sps_zhangsw@ujn.edu.cn

†These authors contributed equally to this work.

Figure S1 showed their typical N_2 adsorption-desorption isotherms, which show a similar shape of type IV for all samples. The specific surface areas calculated by the BET method (S_{BET}) are 101.48, 104.49, 102.56, 102.18, 101.14, 103.49 and 107.65 m^2/g, for pristine CNS, CCNS-30~CCNS-200, respectively. The results presented little effect on the surface area of the modified g-C_3N_4.

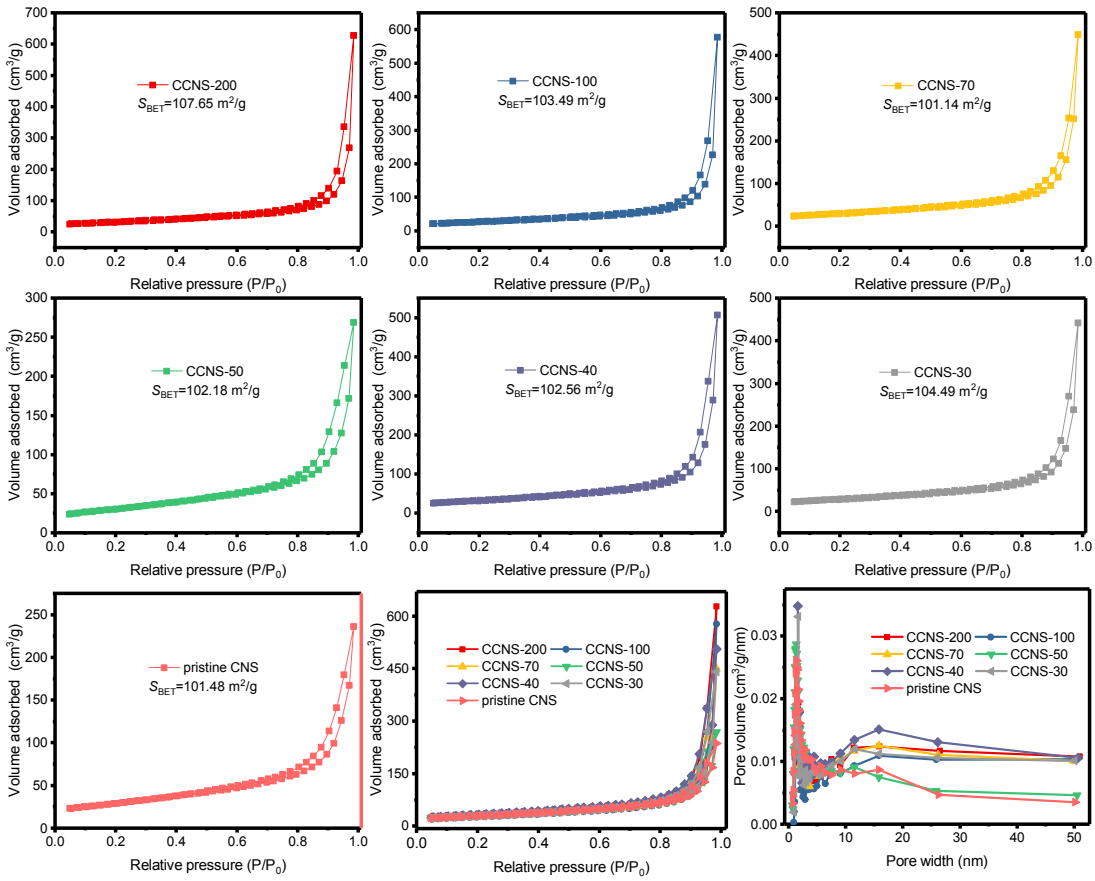

Figure S1. N_2 adsorption-desorption isotherms of all the samples.

CCNS was also prepared by direct one-step calcination of urea together with HMTA. Typically, ~50 mg HMTA was mixed with 15 g urea in the state of solid, and then the homogenous mixture was put into a crucible with a cover and annealed at 550 °C for 2 h at ramp rate of 5 °C/min in air atmosphere. After cooling to room temperature, a dark brown solid was obtained, defined as one step-CCNS. The TEM image of the

As we known, it is of great importance to absorb reactant molecule for photocatalyst to undergo the photocatalytic reaction on its surface. Thus, the water dispersibility is very important for CCNS. The Figure S5 showed the digital photograph of 25.0 mL of homogeneous CCNS-50 aqueous dispersion with the concentration of 10 mg/mL stockpiled for one week, demonstrating the uniform dispersion of CCNS-50 in water and the good stability. The excellent water dispersibility of CCNS-50 is beneficial to enhance water adsorption and the proton reduction reaction for hydrogen production.

Figure S2. Digital photographs of the photocatalysts aqueous dispersion

one step-CCNS is shown in Figure S2. Obviously, the one step-CCNS obviously displayed thicker nanosheets structures. The TEM result verified that ultrathin 3D CCNS nanosheets can be obtained by the several steps rather than one step. Meanwhile, it is obvious that one step-CCNS showws much lower H_2 production rates than CCNS-50.

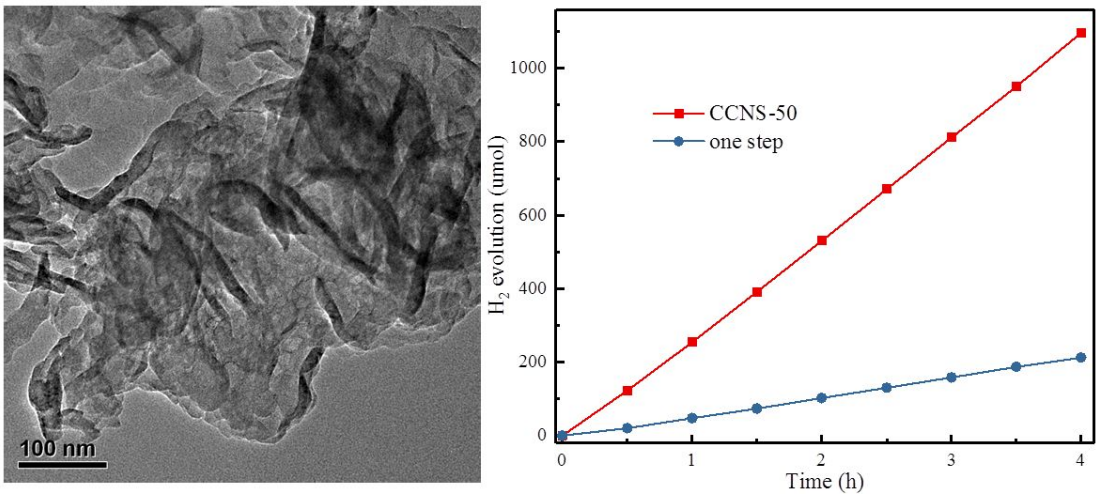

Figure S3. The TEM image of one-step calcination of urea together with HMTA (defined as one step-CNNS) and its hydrogen evolution rate.

To explore the thickness of as-synthesized CCNS nanosheets, the samples were investigated by means of Atomic force microscopy (AFM). As shown in Figure S3, the average thickness of GCN0.5 is around 5-6 nm, which directly prove the presence of ultrathin CCNS nanosheets.

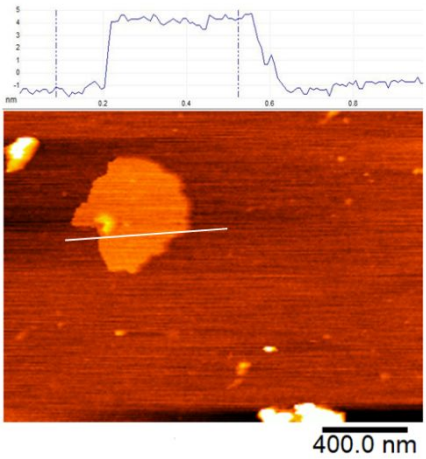

Figure S4. AFM image of as-prepared CCNS-50 nanosheets.

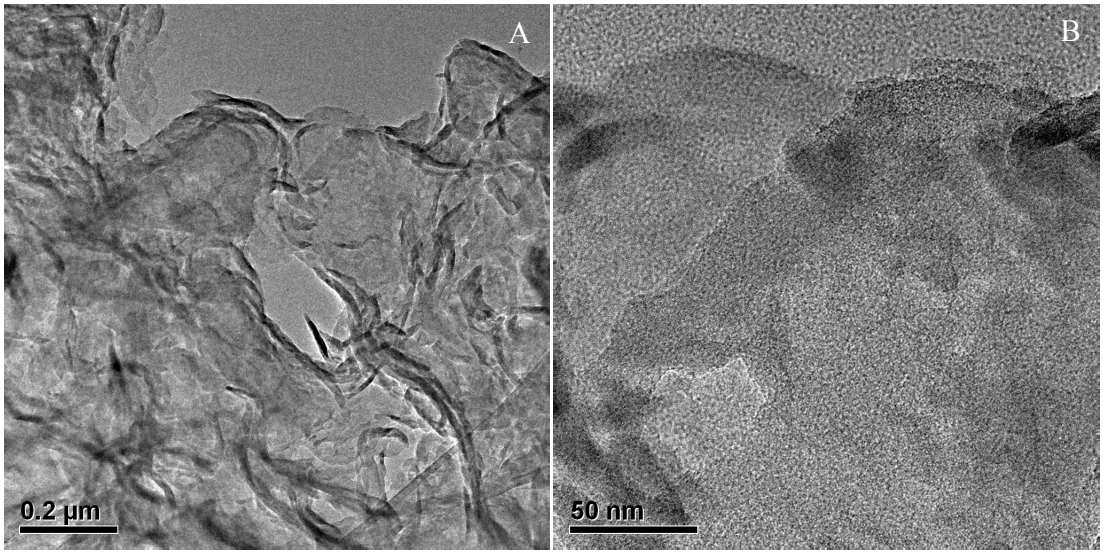

Figure S5. The TEM images of pristine CNS.

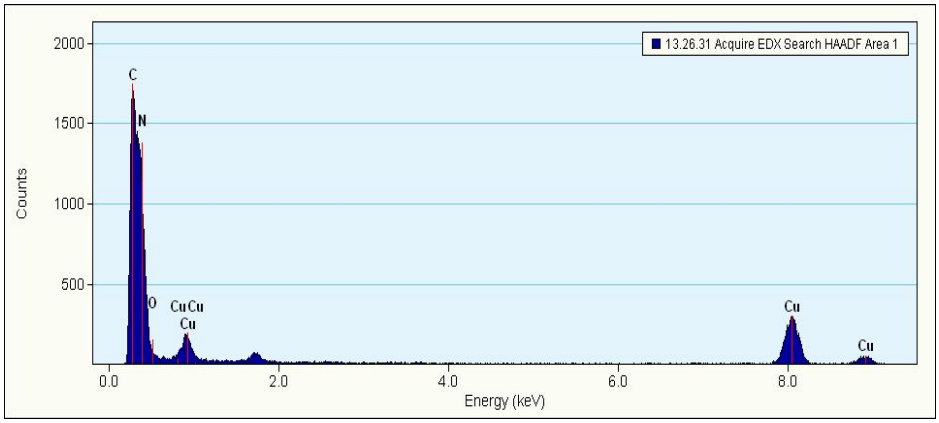

Figure S6. The EDS spectrum of CCNS-50.

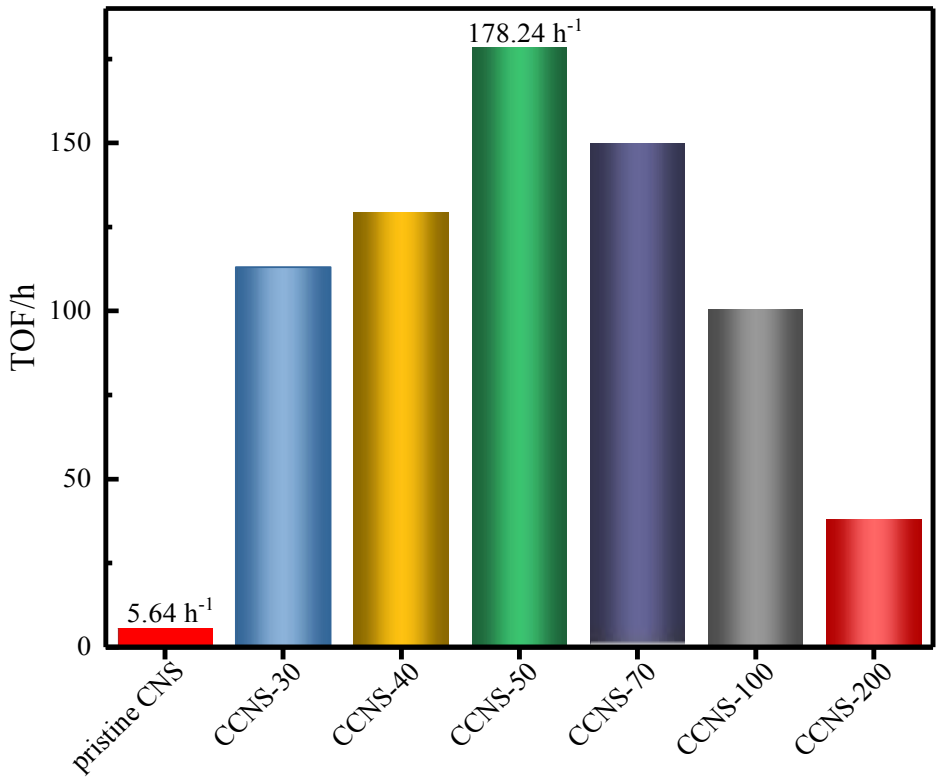

Figure S7. Turnover frequency of pristine CNS and CCNS-H.

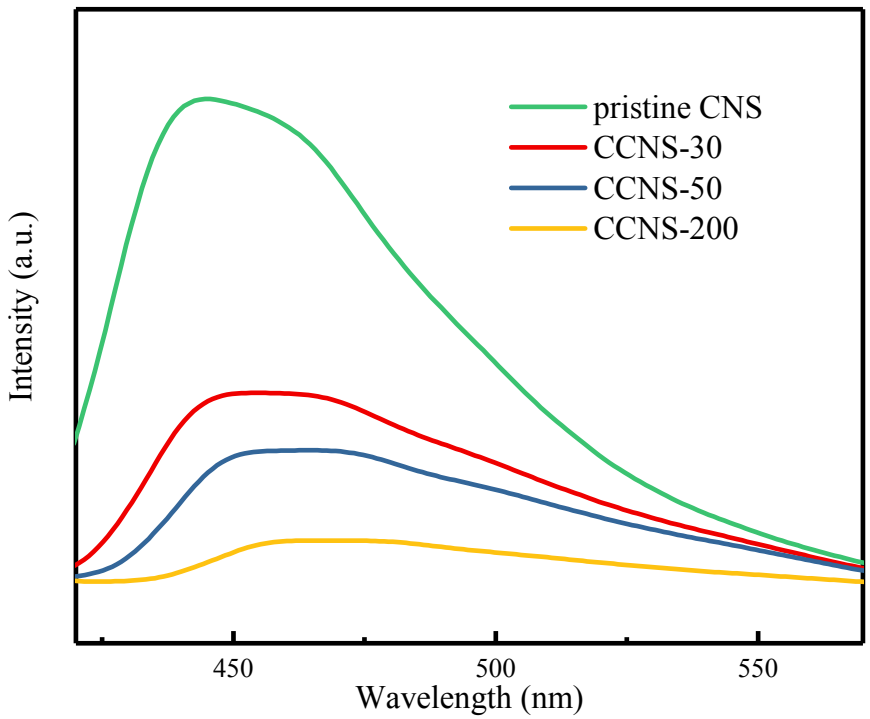

Figure S8. The photoluminescence emission spectra comparison of pristine CNS and CCNS-H.

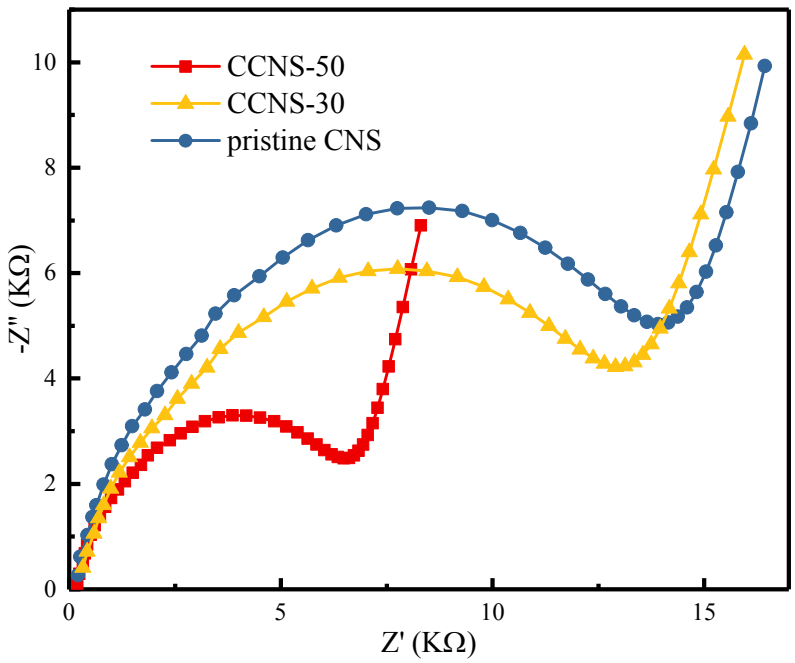

Figure S9. EIS spectra of pristine CNS, CCNS-30 and CCNS-50.

The elemental composition of pristine CNS and CCNS-H were analyzed by an Elementar Vario EL cube element analyzer. As detailed in Table S1, it is interesting to observe that the concentration of C was significantly higher in CCNS-H than pristine CNS, indicating that the C content had self-doped into the g-C_3N_4 matrix during the HMTA activation.

Table S1. C/N atomic ratios of pristine g-C3N4 and CCNS-H.

photocatalysts	Pristine CNS	CCNS-30	CCNS-40	CCNS-50	CCNS-70	CCNS-100	CCNS-200
C/N	0.637	0.672	0.703	0.726	0.739	0.776	0.867

Table S2. Recently published g-C_3N_4 based materials towards photocatalytic hydrogen generation.

Photocatalysts	Cocatalysts	Hydrogen evolution rate (umol/g/h)	Ref.
0.5 wt.% MoS_2/mpg-CN	MoS_2	1030	S1
0.16wt% Pt-CN	Pt	6360	S2
α-Fe_2O_3/2D g-C_3N_4	Pt	31400	S3
ACN	Pt	157.9	S4
BD-C_3N_4	Pt	3167	S5
C_3N_{4+x}	Pt	553.5	S6
CCNNSs	Pt	1060	S7
CDots-C_3N_4	Pt	105	S8
CN-20	Pt	1280	S9
CNC0.1	Pt	212.8	S10
CNHS	Pt	2860	S11
CN-NS	Pt	18940	S12
CNSC	Pt	3960	S13
CN-SP	Pt	570	S14
CNUB	Pt	5560	S15
Co_1-phosphide/PCN	Pt	410.3	S16
CoP/g-C_3N_4	Pt	1924	S17
C-PDA-g-C_3N_4	Pt	811	S18
DCN-200	Pt	4020	S19
GC1.0	Pt	451	S20
g-C_3N_4 nanosheets	Pt	1860	S21
g-C_3N_4 nanosheets	Pt	3410	S22
g-C_3N_4-500-4	Pt	6334	S23

g-C_3N_4-Pt^{2+} (0.18 wt%)	Pt	605	S24
g-C_3Nx-0.01	Pt	6900	S25
HCNS	Pt	4480	S26
HGCN	Pt	8290	S27
HR-CN	Pt	3700	S28
IGCNSs	Pt	890	S29
LCN	Pt	598	S30
LCN180-96	Pt	122	S31
mpg-C_3N_4	Pt	1490	S32
nanomesh nanosheets	Pt	8510	S33
NS-g-C3N4	Pt	14350	S34
PCN	Pt	4009	S35
PCNM	Pt	2900	S36
PCN-S	Pt	1596	S37
PCN-U-AC nanosheets	Pt	5222	S38
P-PCNNS	Pt	3916	S39
P-TCN	Pt	670	S40
Pt/g-C_3N_4@C	Pt	46011	S41
PTI nanosheets	Pt	1750	S42
SAHEP-CNs-1	Pt	4200	S43
"seaweed"	Pt	9900	S44
thermally oxidized g-C_3N_4-500 ^oC	Pt	1430.1	S45
UGCNPs	Pt	1365	S46
UM3	Pt	1365	S47
Urea-based g-C_3N_4	Pt	19412	S48
urea-CNx	Pt	2810	S49
CCNS	Pt	27035	This work

Table S3. Summary of surface areas and the hydrogen evolution rate (HER) of photocatalysts as well as the photocatalytic activity enhancement times.

photocatalysts	BET (m^2/g)	HER (umol/g/h)	HER/BET
bulk g-C_3N_4	53.27	186.52	3.51
pristine CNS	101.48	864.47	8.52
Enhancement times	1.91	4.63	2.43
pristine CNS	101.48	864.47	8.52
CCNS-50	102.18	27035.23	264.58
Enhancement times	1.01	31.27	31.05

BET: the specific surface area of various photocatalysts; HER: the hydrogen evolution rate.

References

S1. Hou, Y. D.; Laursen, A. B.; Zhang, J. S.; Zhang, G. G.; Zhu, Y. S.; Wang, X. C.; Dahl, S.; Chorkendorff, I. Layered Nanojunctions for Hydrogen-Evolution Catalysis. *Angew. Chem. Int. Edit.* **2013,** *52* (13), 3621-3625.

S2. Li, X. G.; Bi, W. T.; Zhang, L.; Tao, S.; Chu, W. S.; Zhang, Q.; Luo, Y.; Wu, C. Z.; Xie, Y. Single-Atom Pt as Co-Catalyst for Enhanced Photocatalytic H_2 Evolution. *Adv. Mater.* **2016,** *28* (12), 2427-2431.

S3. She, X.; Wu, J.; Xu, H.; Zhong, J.; Wang, Y.; Song, Y.; Nie, K.; Liu, Y.; Yang, Y.; Rodrigues, M.-T. F.; Vajtai, R.; Lou, J.; Du, D.; Li, H.; Ajayan, P. M. High Efficiency Photocatalytic Water Splitting Using 2D α-Fe_2O_3/g-C_3N_4 Z-Scheme Catalysts. *Adv. Energy Mater.* **2017,** *7* (17), 1700025.

S4. Kang, Y.; Yang, Y.; Yin, L.-C.; Kang, X.; Liu, G.; Cheng, H.-M. An Amorphous Carbon Nitride Photocatalyst with Greatly Extended Visible-Light-Responsive Range for Photocatalytic Hydrogen Generation. *Adv. Mater.* **2015,** *27* (31), 4572-4577.

S5. Yu, Y.; Yan, W.; Gao, W. Y.; Li, P.; Wang, X. F.; Wu, S. M.; Song, W. G.; Ding, K. J. Aromatic ring substituted g-C_3N_4 for enhanced photocatalytic hydrogen evolution. *J. Mater. Chem. A* **2017,** *5* (33), 17199-17203.

S6. Fang, J.; Fan, H.; Li, M.; Long, C. Nitrogen self-doped graphitic carbon nitride as efficient visible light photocatalyst for hydrogen evolution. *J. Mater. Chem. A* **2015,** *3* (26), 13819-13826.

S7. Ou, H. H.; Lin, L. H.; Zheng, Y.; Yang, P. J.; Fang, Y. X.; Wang, X. C. Tri-s-triazine-Based Crystalline Carbon Nitride Nanosheets for an Improved Hydrogen Evolution. *Adv. Mater.* **2017,** *29* (22), .1700008.

S8. Liu, J.; Liu, Y.; Liu, N. Y.; Han, Y. Z.; Zhang, X.; Huang, H.; Lifshitz, Y.; Lee, S. T.; Zhong, J.; Kang, Z. H. Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway. *Science* **2015,** *347* (6225), 970-974.

S9. Zhou, Y.; Zhang, L.; Huang, W.; Kong, Q.; Fan, X.; Wang, M.; Shi, J. N-doped graphitic carbon-incorporated g-C_3N_4 for remarkably enhanced photocatalytic H_2 evolution under visible light. *Carbon* **2016,** *99*, 111-117.

S10. Xu, Q.; Cheng, B.; Yu, J.; Liu, G. Making co-condensed amorphous carbon/g-C_3N_4 composites with improved visible-light photocatalytic H2-production performance using Pt as cocatalyst. *Carbon* **2017,** *118*, 241-249.

S11. Li, Y. F.; Jin, R. X.; Xing, Y.; Li, J. Q.; Song, S. Y.; Liu, X. C.; Li, M.; Jin, R. C. Macroscopic Foam-Like Holey Ultrathin g-C_3N_4 Nanosheets for Drastic Improvement of Visible-Light Photocatalytic Activity. *Adv. Energy Mater.* **2016,** *6* (24), 1601273.

S12. Liu, G. G.; Wang, T.; Zhang, H. B.; Meng, X. G.; Hao, D.; Chang, K.; Li, P.; Kako, T.; Ye, J. H. Nature-Inspired Environmental "Phosphorylation" Boosts Photocatalytic H_2 Production over Carbon Nitride Nanosheets under Visible-Light Irradiation. *Angew. Chem. Int. Edit.* **2015,** *54* (46), 13561-13565.

S13. Li, Y.; Yang, M.; Xing, Y.; Liu, X.; Yang, Y.; Wang, X.; Song, S. Preparation of Carbon-Rich g-C_3N_4 Nanosheets with Enhanced Visible Light Utilization for Efficient Photocatalytic Hydrogen Production. *Small* **2017,** *13* (33), 1701552.

S14. Guo, S. E.; Tang, Y. Q.; Xie, Y.; Tian, C. G.; Feng, Q. M.; Zhou, W.; Jiang, B. J. P-doped tubular g-C_3N_4 with surface carbon defects: Universal synthesis and

enhanced visible-light photocatalytic hydrogen production. *Applied Catalysis B-Environmental* **2017,** *218*, 664-671.

S15. Lin, Z. Z.; Wang, X. C. Nanostructure Engineering and Doping of Conjugated Carbon Nitride Semiconductors for Hydrogen Photosynthesis. *Angew. Chem. Int. Edit.* **2013,** *52* (6), 1735-1738.

S16. Liu, W.; Cao, L. L.; Cheng, W. R.; Cao, Y. J.; Liu, X. K.; Zhang, W.; Mou, X. L.; Jin, L. L.; Zheng, X. S.; Che, W.; Liu, Q. H.; Yao, T.; Wei, S. Q. Single-Site Active Cobalt-Based Photocatalyst with a Long Carrier Lifetime for Spontaneous Overall Water Splitting. *Angew. Chem. Int. Edit.* **2017,** *56* (32), 9312-9317.

S17. Li, C. M.; Du, Y. H.; Wang, D. P.; Yin, S. M.; Tu, W. G.; Chen, Z.; Kraft, M.; Chen, G.; Xu, R. Unique PCoN Surface Bonding States Constructed on g-C_3N_4 Nanosheets for Drastically Enhanced Photocatalytic Activity of H_2 Evolution. *Adv. Funct. Mater.* **2017,** *27* (4) 1604328.

S18. He, F.; Chen, G.; Yu, Y. G.; Zhou, Y. S.; Zheng, Y.; Hao, S. The synthesis of condensed C-PDA-g-C_3N_4 composites with superior photocatalytic performance. *Chem. Commun.* **2015,** *51* (31), 6824-6827.

S19. Liu, G. G.; Zhao, G. X.; Zhou, W.; Liu, Y. Y.; Pang, H.; Zhang, H. B.; Hao, D.; Meng, X. G.; Li, P.; Kako, T.; Ye, J. H. In Situ Bond Modulation of Graphitic Carbon Nitride to Construct p-n Homojunctions for Enhanced Photocatalytic Hydrogen Production. *Adv. Funct. Mater.* **2016,** *26* (37), 6822-6829.

S20. Xiang, Q. J.; Yu, J. G.; Jaroniec, M. Preparation and Enhanced Visible-Light Photocatalytic H_2 Production Activity of Graphene/C_3N_4 Composites. *J. Phys. Chem. C* **2011,** *115* (15), 7355-7363.

S21. Yang, S. B.; Gong, Y. J.; Zhang, J. S.; Zhan, L.; Ma, L. L.; Fang, Z. Y.; Vajtai, R.; Wang, X. C.; Ajayan, P. M. Exfoliated Graphitic Carbon Nitride Nanosheets as Efficient Catalysts for Hydrogen Evolution Under Visible Light. *Adv. Mater.* **2013,** *25* (17), 2452-2456.

S22. Niu, P.; Zhang, L. L.; Liu, G.; Cheng, H. M. Graphene-Like Carbon Nitride Nanosheets for Improved Photocatalytic Activities. *Adv. Funct. Mater.* **2012,** *22* (22), 4763-4770.

S23. Yang, P. J.; Zhao, J. H.; Qiao, W.; Li, L.; Zhu, Z. P. Ammonia-induced robust photocatalytic hydrogen evolution of graphitic carbon nitride. *Nanoscale* **2015,** *7* (45), 18887-18890.

S24. Li, Y. R.; Wang, Z. W.; Xia, T.; Ju, H. X.; Zhang, K.; Long, R.; Xu, Q.; Wang, C. M.; Song, L.; Zhu, J. F.; Jiang, J.; Xiong, Y. J. Implementing Metal-to-Ligand Charge Transfer in Organic Semiconductor for Improved Visible-Near-Infrared Photocatalysis. *Adv. Mater.* **2016,** *28* (32), 6959-6965.

S25. Yu, H. J.; Shi, R.; Zhao, Y. X.; Bian, T.; Zhao, Y. F.; Zhou, C.; Waterhouse, G. I. N.; Wu, L. Z.; Tung, C. H.; Zhang, T. R. Alkali-Assisted Synthesis of Nitrogen Deficient Graphitic Carbon Nitride with Tunable Band Structures for Efficient Visible-Light-Driven Hydrogen Evolution. *Adv. Mater.* **2017,** *29* (16), 1605148.

S26. Sun, J. H.; Zhang, J. S.; Zhang, M. W.; Antonietti, M.; Fu, X. Z.; Wang, X. C. Bioinspired hollow semiconductor nanospheres as photosynthetic nanoparticles. *Nat. Commun.* **2012,** *3*, 1139.

S27. Liang, Q. H.; Li, Z.; Huang, Z. H.; Kang, F. Y.; Yang, Q. H. Holey Graphitic Carbon Nitride Nanosheets with Carbon Vacancies for Highly Improved Photocatalytic Hydrogen Production. *Adv. Funct. Mater.* **2015,** *25* (44), 6885-6892.

S28. Zheng, Y.; Lin, L.; Ye, X.; Guo, F.; Wang, X. Helical Graphitic Carbon Nitrides with Photocatalytic and Optical Activities. *Angew. Chem. Int. Edit.* **2014,** *53* (44), 11926-11930.

S29. Han, Q.; Hu, C.; Zhao, F.; Zhang, Z.; Chen, N.; Qu, L. One-step preparation of iodine-doped graphitic carbon nitride nanosheets as efficient photocatalysts for visible light water splitting. *J. Mater. Chem. A* **2015,** *3* (8), 4612-4619.

S30. Kang, Y.; Yang, Y.; Yin, L.-C.; Kang, X.; Wang, L.; Liu, G.; Cheng, H.-M. Selective Breaking of Hydrogen Bonds of Layered Carbon Nitride for Visible Light Photocatalysis. *Adv. Mater.* **2016,** *28* (30), 6471-6477.

S31. Cui, Y. J.; Ding, Z. X.; Fu, X. Z.; Wang, X. C. Construction of Conjugated Carbon Nitride Nanoarchitectures in Solution at Low Temperatures for Photoredox Catalysis. *Angew. Chem. Int. Edit.* **2012,** *51* (47), 11814-11818.

S32. Wang, X.; Maeda, K.; Chen, X.; Takanabe, K.; Domen, K.; Hou, Y.; Fu, X.; Antonietti, M. Polymer Semiconductors for Artificial Photosynthesis: Hydrogen Evolution by Mesoporous Graphitic Carbon Nitride with Visible Light. *J. Am. Chem. Soc.* **2009,** *131* (5), 1680-1681.

S33. Han, Q.; Wang, B.; Gao, J.; Cheng, Z. H.; Zhao, Y.; Zhang, Z. P.; Qu, L. T. Atomically Thin Mesoporous Nanomesh of Graphitic C_3N_4 for High-Efficiency Photocatalytic Hydrogen Evolution. *ACS Nano* **2016,** *10* (2), 2745-2751.

S34. Zhang, J. S.; Zhang, M. W.; Yang, C.; Wang, X. C. Nanospherical Carbon Nitride Frameworks with Sharp Edges Accelerating Charge Collection and Separation at a Soft Photocatalytic Interface. *Adv. Mater.* **2014,** *26* (24), 4121-4126.

S35. Hong, J. D.; Yin, S. M.; Pan, Y. X.; Han, J. Y.; Zhou, T. H.; Xu, R. Porous carbon nitride nanosheets for enhanced photocatalytic activities. *Nanoscale* **2014,** *6* (24), 14984-14990.

S36. Liang, Q. H.; Li, Z; Yu, X. L.; Huang, Z. H.; Kang, F. Y. Yang, Q. H. Macroscopic 3D Porous Graphitic Carbon Nitride Monolith for Enhanced Photocatalytic Hydrogen Evolution, *Adv. Mater.* **2015**, *27*(31), 4634-4639.

S37. Ran, J. R.; Ma, T. Y.; Gao, G. P.; Du, X. W.; Qiao, S. Z. Porous P-doped graphitic carbon nitride nanosheets for synergistically enhanced visible-light photocatalytic H_2 production. *Energy Environ. Sci.* **2015,** *8* (12), 3708-3717.

S38. Yang, P. J.; Ou, H. H.; Fang, Y. X.; Wang, X. C. A Facile Steam Reforming Strategy to Delaminate Layered Carbon Nitride Semiconductors for Photoredox Catalysis. *Angew. Chem. Int. Edit.* **2017,** *56* (14), 3992-3996.

S39. Shi, L.; Chang, K.; Zhang, H. B.; Hai, X.; Yang, L. Q.; Wang, T.; Ye, J. H. Drastic Enhancement of Photocatalytic Activities over Phosphoric Acid Protonated Porous g-C_3N_4 Nanosheets under Visible Light. *Small* **2016,** *12* (32), 4431-4439.

S40. Guo, S. E.; Deng, Z. P.; Li, M. X.; Jiang, B. J.; Tian, C. G.; Pan, Q. J.; Fu, H. G. Phosphorus-Doped Carbon Nitride Tubes with a Layered Micro-nanostructure for Enhanced Visible-Light Photocatalytic Hydrogen Evolution. *Angew. Chem. Int. Edit.* **2016,** *55* (5), 1830-1834.

S41. Han, Q.; Wang, B.; Gao, J.; Qu, L. Graphitic Carbon Nitride/Nitrogen-Rich Carbon Nanofibers: Highly Efficient Photocatalytic Hydrogen Evolution without Cocatalysts. *Angew. Chem. Int. Edit.* **2016,** *55* (36), 10849-10853.

S42. Schwinghammer, K.; Mesch, M. B.; Duppel, V.; Ziegler, C.; Senker, J.; Lotsch, B. V. Crystalline Carbon Nitride Nanosheets for Improved Visible-Light Hydrogen Evolution. *J. Am. Chem. Soc.* **2014,** *136* (5), 1730-1733.

S43. Zhao, G. X.; Liu, G. G.; Pang, H.; Liu, H. M.; Zhang, H. B.; Chang, K.; Meng, X. G.; Wang, X. J.; Ye, J. H. Improved Photocatalytic H_2 Evolution over G-Carbon Nitride with Enhanced In-Plane Ordering. *Small* **2016,** *12* (44), 6160-6166.

S44. Han, Q.; Wang, B.; Zhao, Y.; Hu, C.; Qu, L. A Graphitic-C_3N_4 "Seaweed" Architecture for Enhanced Hydrogen Evolution. *Angew. Chem. Int. Edit.* **2015,** *127* (39), 11595-11599.

S45. Yang, L.; Huang, J.; Shi, L.; Cao, L.; Yu, Q.; Jie, Y.; Fei, J.; Ouyang, H.; Ye, J. A surface modification resultant thermally oxidized porous g-C_3N_4 with enhanced photocatalytic hydrogen production. *Appl. Catal. B: Environ.* **2017,** *204*, 335-345..

S46. Han, Q.; Zhao, F.; Hu, C. G.; Lv, L. X.; Zhang, Z. P.; Chen, N.; Qu, L. T. Facile production of ultrathin graphitic carbon nitride nanoplatelets for efficient visible-light water splitting. *Nano Res.* **2015,** *8* (5), 1718-1728.

S47. Tian, N.; Zhang, Y. H.; Li, X. W.; Xiao, K.; Du, X.; Dong, F.; Waterhouse, G. I. N.; Zhang, T. R.; Huang, H. W. Precursor-reforming protocol to 3D

mesoporous g-C_3N_4 established by ultrathin self-doped nanosheets for superior hydrogen evolution. *Nano Energy* **2017,** *38*, 72-81.

S48. Martin, D. J.; Qiu, K. P.; Shevlin, S. A.; Handoko, A. D.; Chen, X. W.; Guo, Z. X.; Tang, J. W. Highly Efficient Photocatalytic H_2 Evolution from Water using Visible Light and Structure-Controlled Graphitic Carbon Nitride. *Angew. Chem. Int. Edit.* **2014,** *53* (35), 9240-9245.

S49. Lau, V. W. H.; Yu, V. W. Z.; Ehrat, F.; Botari, T.; Moudrakovski, I.; Simon, T.; Duppel, V.; Medina, E.; Stolarczyk, J. K.; Feldmann, J.; Blum, V.; Lotsch, B. V. Urea-Modified Carbon Nitrides: Enhancing Photocatalytic Hydrogen Evolution by Rational Defect Engineering. *Adv. Energy Mater.* **2017,** *7* (12), 1602251.