Supporting Information

Enhanced photocatalytic performance of g-C_3N_4 by introducing gradient energy band structure and activated n-π* electronic transition for visible light hydrogen generation

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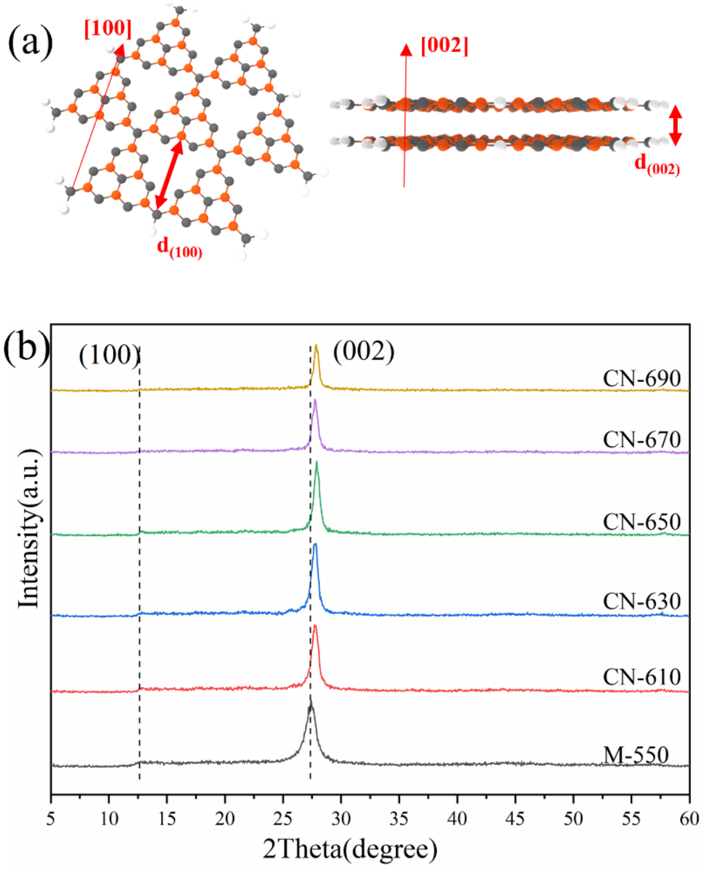


Fig. S1 (a) Ideal g-C_3N_4 structure constructed by stacking heptazine layers, (b) XRD patterns of M-550 and CN-x samples.

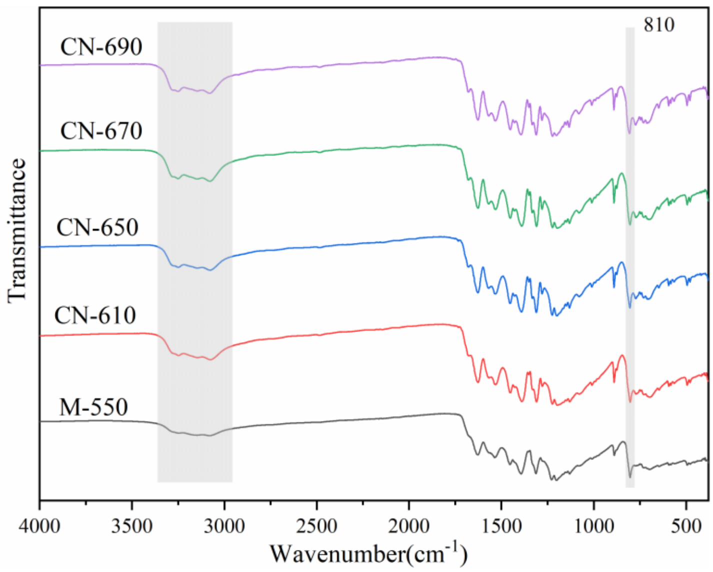


Fig. S2 FT-IR spectra of M-550 and CN-x samples.

Table. S1 Element contents in M-550, CN-670, KCN-30, KCN-75 and KCN105 samples estimated by elemental analysis.

Elemental analysis	C(wt%)	N(wt%)	H(wt%)	C/N(mol ratio)
M-550	35.4	62.4	2.23	0.662
CN-670	35.8	62.1	2.04	0.673
KCN-30	36.3	61.8	1.91	0.685
KCN-75	36.7	61.5	1.80	0.697
KCN-105	37.3	61.1	1.63	0.711

Table. S2 K element contents in CN-670, KCN-30, KCN-75 and KCN-105 samples estimated by ICP analysis.

ICP	CN-670	KCN-30	KCN-75	KCN-105
K(wt%)	Trace	2.26	5.37	7.92

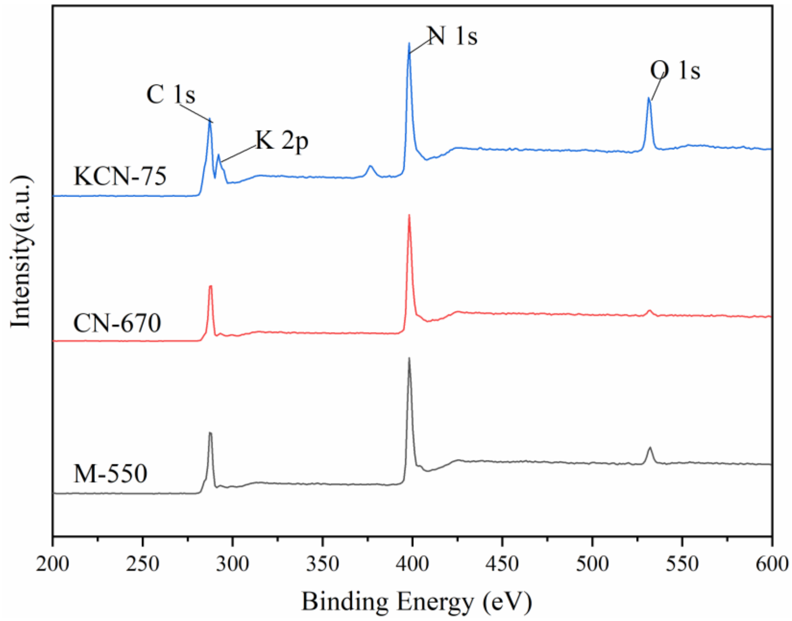


Fig. S3 XPS survey spectra of M-550, CN-670, and KCN-75 samples.

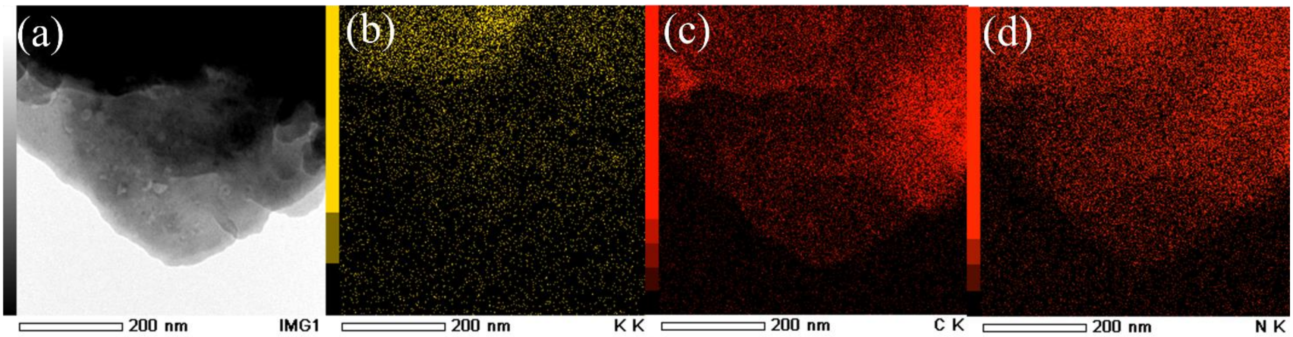


Fig. S4 EDX element mapping of KCN-75 samples.

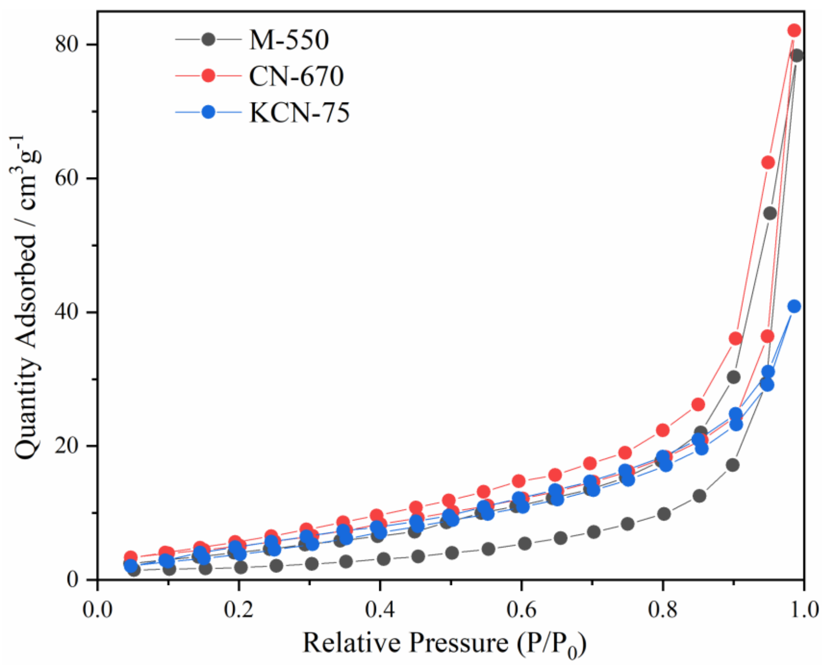
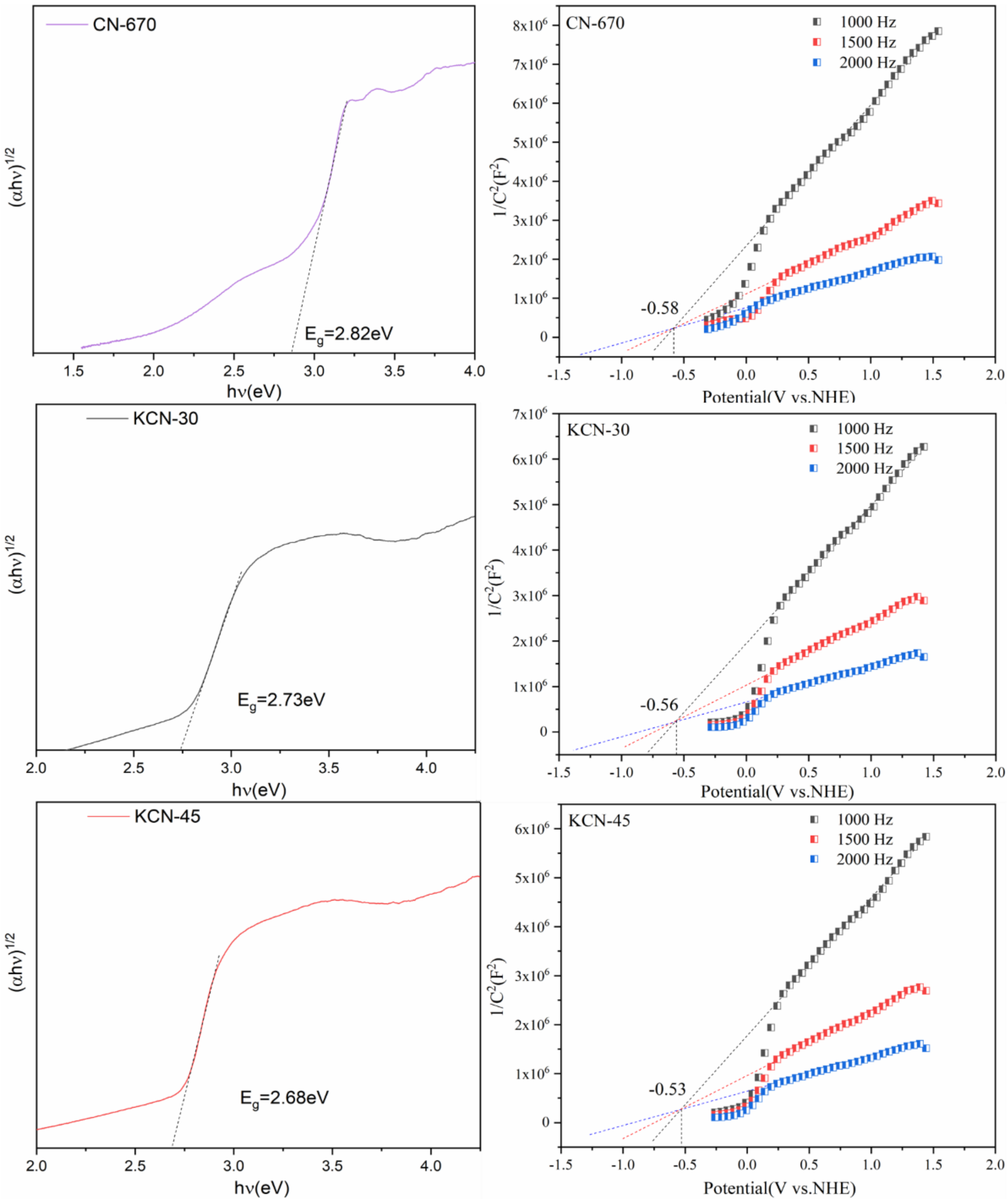


Fig. S5 N_2 adsorption-desorption isotherms of M-550, CN-670, and KCN-75 samples.


CN-670
E_g=2.82eV
(αhν)^1/2
hν(eV)
CN-670
1000 Hz
1500 Hz
2000 Hz
-0.58
1/C^2(F^2)
Potential(V vs.NHE)
KCN-30
E_g=2.73eV
(αhν)^1/2
hν(eV)
KCN-30
1000 Hz
1500 Hz
2000 Hz
-0.56
1/C^2(F^2)
Potential(V vs.NHE)
KCN-45
E_g=2.68eV
(αhν)^1/2
hν(eV)
KCN-45
1000 Hz
1500 Hz
2000 Hz
-0.53
1/C^2(F^2)
Potential(V vs.NHE)

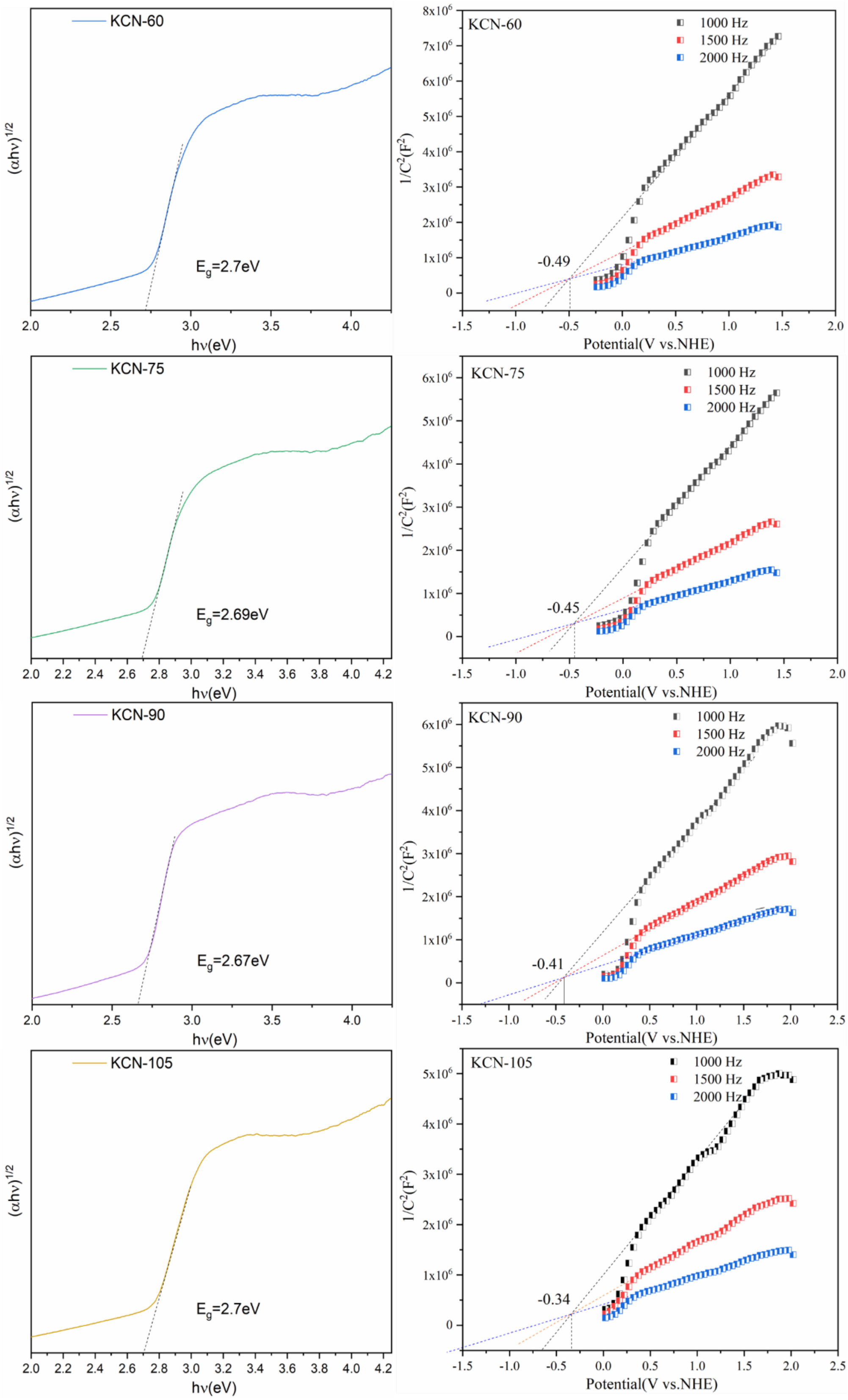


Fig. S6 Plots of transformed Kubelka-Munk function and Mott-Schottky plots for CM-670 and KCN-x samples

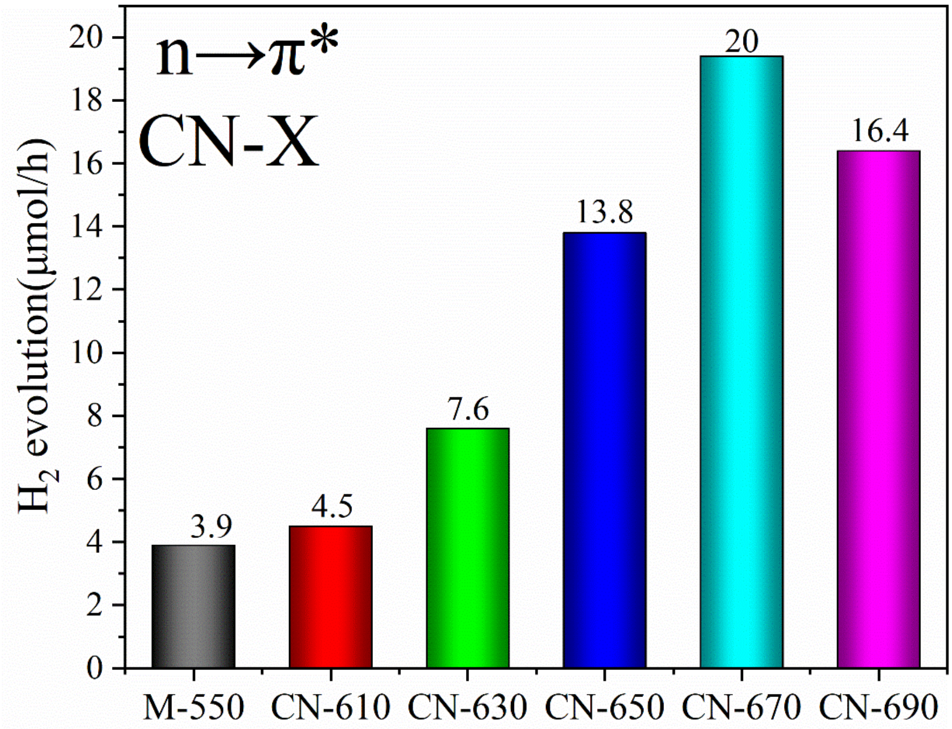


Fig. S7 H_2 production rates of M-550 and CN-x samples.

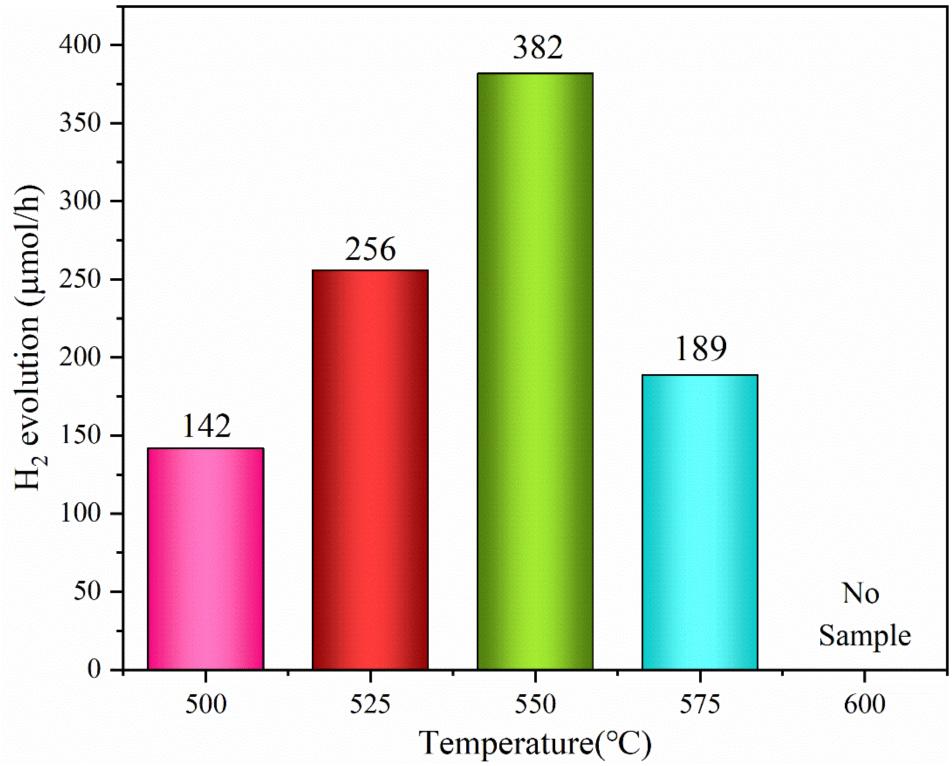


Fig. S8 H_2 production rates of samples with different temperature.

Table S3 Values of elements in equivalent circuit resulted from fitting the EIS data in Fig 7(b).

Sample	R_s(Ω cm^{-2})	R_{ct}(Ω cm^{-2})	CPE(F cm^{-2})
CN-670	11.5	2.67E5	3.23E-5
KCN-30	11.5	2.06E5	3.15E-5
KCN-45	10.3	1.85E5	2.88E-5
KCN-60	11.5	1.70E5	3.18E-5
KCN-75	9.34	1.43E5	3.04E-5
KCN-90	11.3	1.53E5	2.94E-5
KCN-105	10.4	1.56E5	3.01E-5

Table S4 Bandgap E_g, conduction band position E_c and valence band position E_v (vs. NHE) of CM-670 and KCN-x samples from Fig S6.

Sample	E_g(eV)	E_c(eV)	E_v(eV)
CN-670	2.82	-0.58	2.24
KCN-30	2.73	-0.56	2.17
KCN-45	2.68	-0.53	2.15
KCN-60	2.70	-0.49	2,21
KCN-75	2.69	-0.45	2.24
KCN-90	2.67	-0.41	2.26
KCN-105	2.70	-0.34	2.36

Table. S5 Summary table of H_2-evolution by different g-C_3N_4-based materials.

Catalysts	**Light Source**	**Reaction Conditions**	**H_2 evolution Rate (μmol h^{-1})**	**Reference**
KCN-75	**300 W Xenon lamp (λ>420 nm)**	**50 mg catalyst, 100 mL, 20 vol% TEOA, 3wt%Pt**	**382**	**This work**
CN-M-630	300 W Xenon lamp (λ>420 nm)	25 mg catalyst, 100 mL, 10 vol% TEOA, 3wt%Pt	132	[1]
K-CN 0.4	300 W Xenon lamp (λ>420 nm)	50 mg catalyst, 50 mL, 10 vol% TEOA, 3wt%Pt	200	[2]
UCN-670	300 W Xenon lamp (λ>420 nm)	10 mg catalyst, 30 mL, 10 vol% TEOA, 1.1wt%Pt	92	[3]
KCCN 2	300 W Xenon lamp (λ>420 nm)	50 mg catalyst, 50 mL, 20 vol% TEOA, 3wt%Pt	262	[4]
SA-Pt/g-C_3N_4-8.7	300 W Xenon lamp (λ>420 nm)	10 mg catalyst, 100 mL, 10 vol% TEOA, 8.7wt%Pt	227	[5]
Few-layer C_3N_4	300 W Xenon lamp (λ>420 nm)	20 mg catalyst, 100 mL, 20 vol% TEOA, 1wt%Pt	160	[6]
S-g-C_3N_4-D	300 W Xenon lamp (λ>420 nm)	20 mg catalyst, 100 mL, 10 vol% TEOA, 3wt%Pt	113	[7]
BPCN1.5	300 W Xenon lamp (λ>420 nm)	5 mg catalyst, 3 mL, 10 vol% TEOA, 1wt%Pt	23	[8]
CNV-mCN-Br	300 W Xenon lamp (λ>420 nm)	10 mg catalyst, 100 mL, 10 vol% TEOA, 1wt%Pt	222	[9]
DA-HM	300 W Xenon lamp (λ>420 nm)	50 mg catalyst, 100 mL, 10 vol% TEOA, 3wt%Pt	207	[10]
HcPCN	300 W Xenon lamp (λ>420 nm)	20 mg catalyst, 100 mL, 10 vol% TEOA, 3wt%Pt	190	[11]
cMel-5	200 W Xe lamp (λ ≥ 420 nm)	50 mg catalyst, 80 mL, 10 vol% TEOA, 3wt%Pt	324	[12]
Cu-Ni(OH)$_2$-C_3N_4	300 W Xe lamp (AM 1.5G)	20 mg in 100 mL 10 vol% TEOA	41	[13]
20-CNCo	300 W Xe lamp (AM 1.5G)	50 mg catalyst, 100 mL, 10 vol% TEOA, 3wt%Pt	7	[14]
K-I-CCN	300 W Xenon lamp (λ>400 nm)	50 mg catalyst, 100 mL, 10 vol% TEOA, 3wt%Pt	256	[15]

References

1. W. Li, Z. Wei, K. Zhu, W. Wei, J. Yang, J. Jing, D. L. Phillips and Y. Zhu, *Applied Catalysis B: Environmental*, 2022, **306**, 121142.
2. G. Zhang, J. Zhu, Y. Xu, C. Yang, C. He, P. Zhang, Y. Li, X. Ren and H. Mi, *ACS Catalysis*, 2022, **12**, 4648-4658.
3. S. An, G. Zhang, K. Li, Z. Huang, X. Wang, Y. Guo, J. Hou, C. Song and X. Guo, *Advanced Materials*, 2021, **33**, 2104361.
4. G. Zhang, Y. Xu, D. Yan, C. He, Y. Li, X. Ren, P. Zhang and H. Mi, *ACS Catalysis*, 2021, **11**, 6995-7005.
5. Z. Zeng, Y. Su, X. Quan, W. Choi, G. Zhang, N. Liu, B. Kim, S. Chen, H. Yu and S. Zhang, *Nano Energy*, 2020, **69**, 104409.
6. Y. Xiao, G. Tian, W. Li, Y. Xie, B. Jiang, C. Tian, D. Zhao and H. Fu, *Journal of the American Chemical Society*, 2019, **141**, 2508-2515.
7. H. Wang, J. Jiang, L. Yu, J. Peng, Z. Song, Z. Xiong, N. Li, K. Xiang, J. Zou and J. P. Hsu, *Small*, 2023, **19**, 2301116.
8. F. Gao, H. Xiao, J. Yang, X. Luan, D. Fang, L. Yang, J. Zi and Z. Lian, *Applied Catalysis B: Environmental*, 2024, **341**, 123334.
9. M. Guo, M. Chen, J. Xu, C. Wang and L. Wang, *Chemical Engineering Journal*, 2023, **461**, 142046.
10. H. Ou, X. Chen, L. Lin, Y. Fang and X. Wang, *Angewandte Chemie International Edition*, 2018, **57**, 8729-8733.
11. Z. Liang, X. Zhuang, Z. Tang, H. Li, L. Liu and W. Kang, *Journal of Materials Chemistry A*, 2021, **9**, 6805-6810.
12. T. Huo, Q. Deng, F. Yu, G. Wang, Y. Xia, H. Li and W. Hou, *ACS Applied Materials & Interfaces*, 2022, **14**, 13419-13430.
13. D. Zhan, J. Tian, Q. Fu, P. Liu, Y. Zhao, W. Liu, D. Li, Y. Huang and C. Han, *Applied Surface Science*, 2023, **641**, 158463.
14. S. Chen, W. Wang, Y. Hou, Y. Hao, Y. Zhao, S. Wang, J. Meng and H. Xu, *ACS Applied Nano Materials*, 2023, **6**, 8717-8725.
15. Y. Cui, X. Li, C. Yang, B. Xiao and H. Xu, *International Journal of Hydrogen Energy*, 2022, **47**, 12569-12581.