Supporting Information

Atmosphere-Dependent Crystallization of Carbon Nitride: Balancing Activity and Stability for Efficient Photocatalysis

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Table S1. A comparative list of hydrogen evolution activity for crystalline carbon nitride obtained under different experimental conditions.

Precursor	Atmosphere	Tem./ ºC	Time/h	Salt	Light	Cocatalysts	Sacrificial Agent	Reaction Tem./℃	H_2 evolution rate （$mmol \cdot g^{-1} \cdot h^{-1}$）	Ref.
Dicyandiamide	Vacuum	550	12	NaCl, KCl, LiCl	300 W Xe lamp λ>300 nm	0.5 wt% Co, 1 wt% Pt, 0.75 wt% Cr		12	6.1	1
Dicyandiamide	Vacuum	600	24	KCl, LiCl	300 W Xe lamp	1 wt% Pt and 9 wt% Co	10 vol% MeOH		0.649	2
BCN	Sealed	550	8	KCl, LiCl	300 W Xe lamp λ>300 nm	3 wt% Pt	10 vol% TEOA	15	5.062	3
P-CN	Ar	550	4	KCl, LiCl, $CoCl_2 \cdot 6H_2O$	300 W Xe lamp λ>420 nm	1 wt% Pt	10 vol% TEOA		3.538	4
Melon	Ar	400 °C 1 h then 500 °C 0.5 h		KSCN	300 W Xe lamp AM 1.5 G	8 wt% Pt	10 vol% MeOH	25	2.4	5
CN	Ar	550	2	KCl, ZnCl	300 W Xe lamp λ>420 nm	3 wt% Pt	10 vol% MeOH	15	1.5	6

MCA-x	Ar	550	4	KCl, LiCl	300 W Xe lamp AM 1.5G	2 wt% Pt	1.25 vol% benzyl alcohol	35	7.470	7
PCN	N_2	550	3	KCl	300 W Xe lamp λ>420 nm	1 wt% Pt	10 vol% TEOA	5	1.188	8
BCN	N_2	550	4	KCl, LiCl	300 W Xe lamp λ>420 nm	1 wt% Pt	20 vol% lactic acid		32.1	9
BCN	N_2	550	4	KCl, LiCl	3W LED light λ>420 nm	1 wt% Pt	10 vol% TEOA		2.457	10
g-C_3N_4	N_2	550	4	KCl, LiCl	300 W Xe lamp λ>420 nm	3 wt% Pt	10 vol% MeOH		1.060	11
HCN	N_2	520	4	NaSCN, NH_4Cl	300 W Xe lamp λ>420 nm	3 wt% Pt	10 vol% TEOA		3.550	12
Dicyandiamide		550	4	$NaHCO_3$	300 W Xe lamp λ>420 nm	3 wt% Pt	10 vol% TEOA	15	1.26	13
Melon	N_2	550	4	KCl, LiCl	300 W Xe lamp λ>420 nm	3 wt% Pt	10 vol% TEOA	12	6.970	14
GCN	N_2	550	4	KCl, LiCl	300 W Xe lamp λ>400 nm	3 wt% Pt	10 vol% MeOH		8.67	15
Co-CN	N_2	550	8	KCl, LiCl	300 W Xe lamp λ>400 nm	1 wt% Co, 3 wt% Pt			0.44	16
Bulk CN_T	N_2	550	4	KCl, LiCl	300 W Xe lamp	3 wt% Pt	10 vol% MeOH		0.660	17
Melem-based oligomer/PCN polymer	N_2	550	4	KCl, LiCl	300 W Xe lamp				/	18
Melamine	Air	550	3	KCl	300 W Xe lamp λ>420 nm	1 wt% Pt	10 vol% TEOA		1.356	19

Melamine	Air	550	3	KBr	500 W Xe lamp λ>280 nm	1 wt% Pd	16.7 vol% MeOH	20	1.6	20
CN	Air	600	0.5-4	KCl	300 W Xe lamp λ>420 nm	3 wt% Pt	20 vol% TEOA	15	5.238	21
Urea	Air	600	3	KCl, $CaCl_2$	300 W Xe lamp λ>420 nm	3 wt% Pt	10 vol% TEOA	5	5.19	22
Melamine	Air	600	3	KCl, $MnCl_2$	300 W Xe lamp λ>420 nm	3 wt% Pt	10 vol% benzyl alcohol	10	0.792	23
Dicyandiamide	Air	550	4	KCl	300 W Xe lamp λ>420 nm	3 wt% Pt	10 vol% TEOA		0.569	24
Urea	Air	600	3	KCl, KOH	300 W Xe lamp λ>420 nm	3 wt% Pt	10 vol% TEOA		4.008	25
C-CN	Air	550	2	KCl, NaCl, LiCl	300 W Xe lamp λ>420 nm	3 wt% Pt	10 vol% TEOA	5	0.182	26
Mel-T	Air	550	4	KCl, LiCl	350 W Xe lamp	3 wt% Pt	10 vol% TEOA		0.890	27
CM-CN	Air	550	4	KCl, LiCl	350 W Xe lamp	3 wt% Pt	4 wt% BPA		0.151	28
Urea	Air	600	6	KCl	300 W Xe lamp λ>500 nm	3 wt% Pt	20 vol% TEOA	15	0.922	29
Cu-CN	Air	550	4	KCl, LiCl					CO_2 Reduction	30

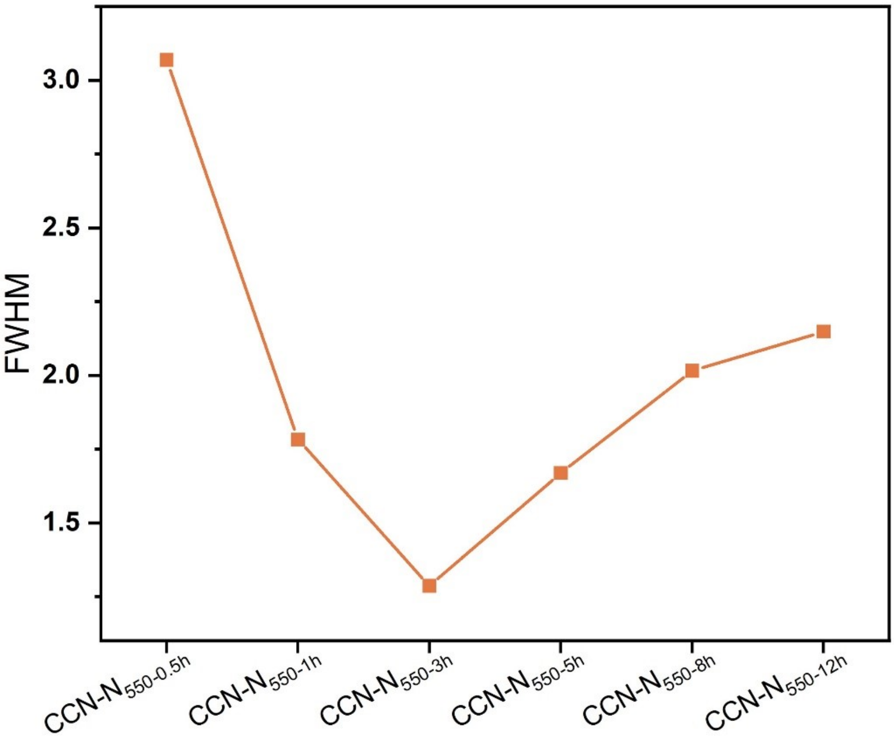

Figure S1. FWHM of the (002) peak as a function of calcination time.

Table S2. EPR-quantified nitrogen vacancy concentrations.

Concentrations	g-C_3N_4	CCN-N_{550}	CCN-A_{550}
Spins/mm^3（$\times 10^{16}$）	2.946	5.566	6.933

Table S3. Elemental composition of g-C_3N_4, CCN-N_{550}, and CCN-A_{550} determined by elemental analysis.

Elemental analysis	g-C_3N_4	CCN-N_{550}	CCN-A_{550}
C (%)	34.79	25.75	26.63
N (%)	61.59	42.81	44.67
H (%)	1.88	1.97	2.08
O (%)	1.10	15.41	14.89
C/N (mol ratio)	0.57	0.60	0.60

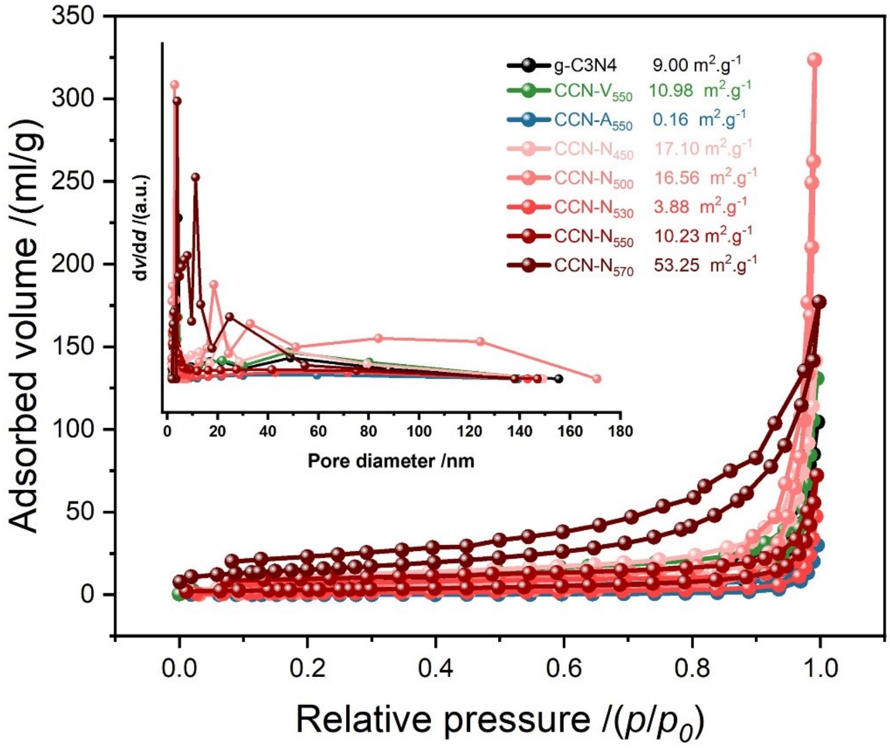

Figure S2. Nitrogen adsorption-desorption isotherms of the synthesized CCN catalysts.

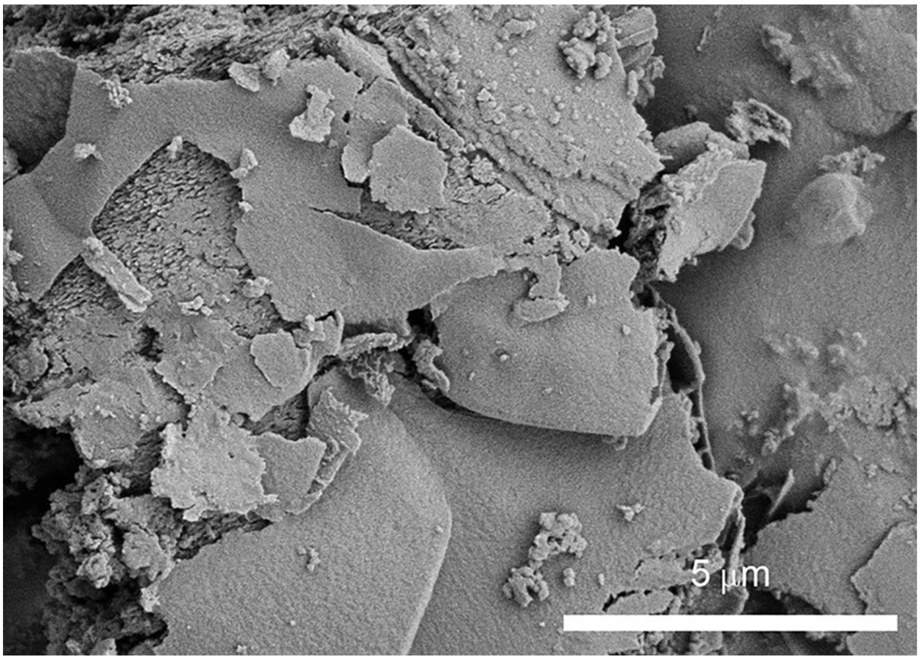

Figure S3. SEM images of g-C_3N_4.

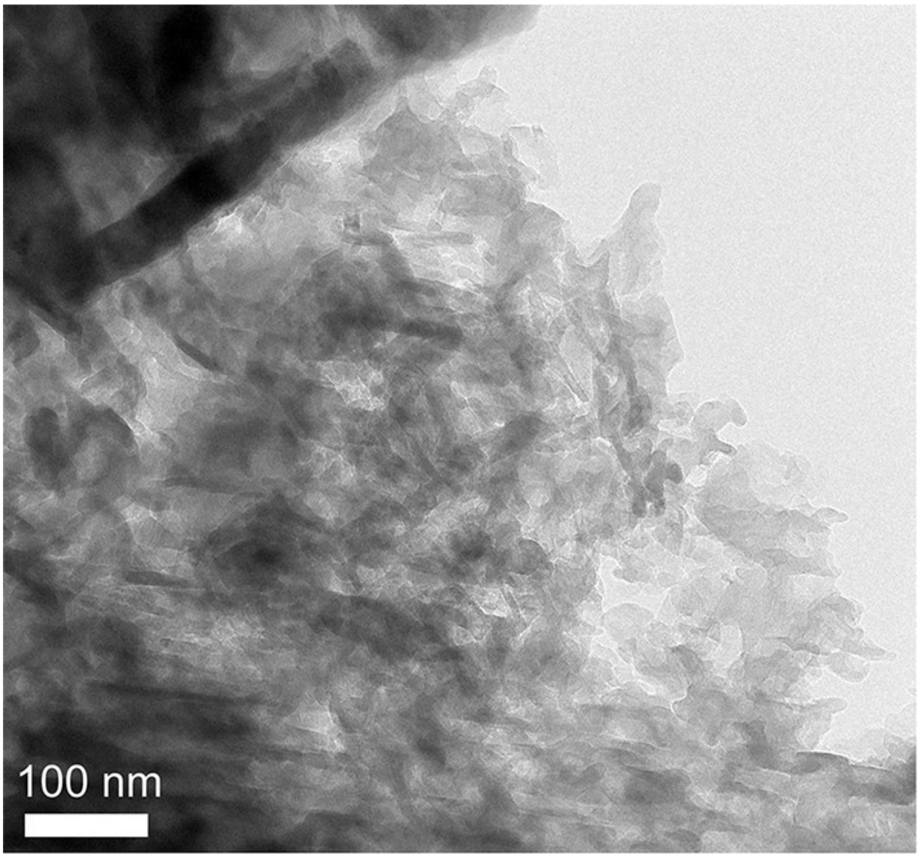

Figure S4. TEM images of CCN-V_{550}

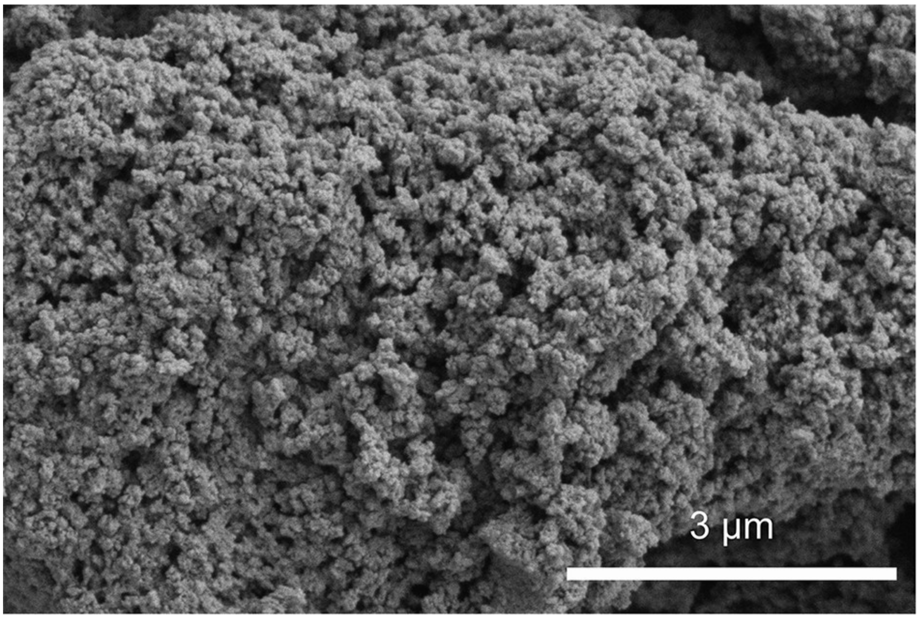

Figure S5. SEM images of CCN-N_{550}

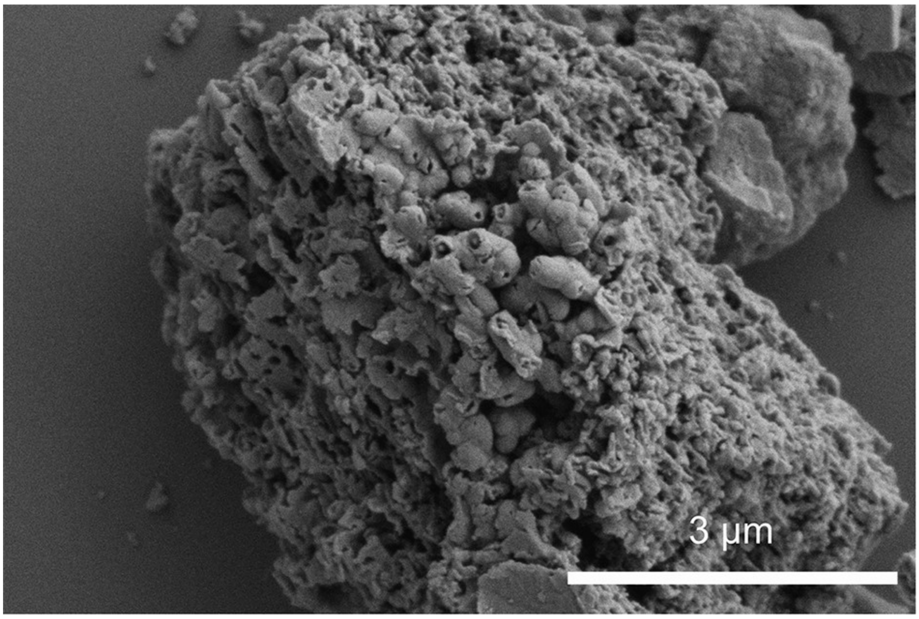

Figure S6. SEM images of CCN-A_{550}

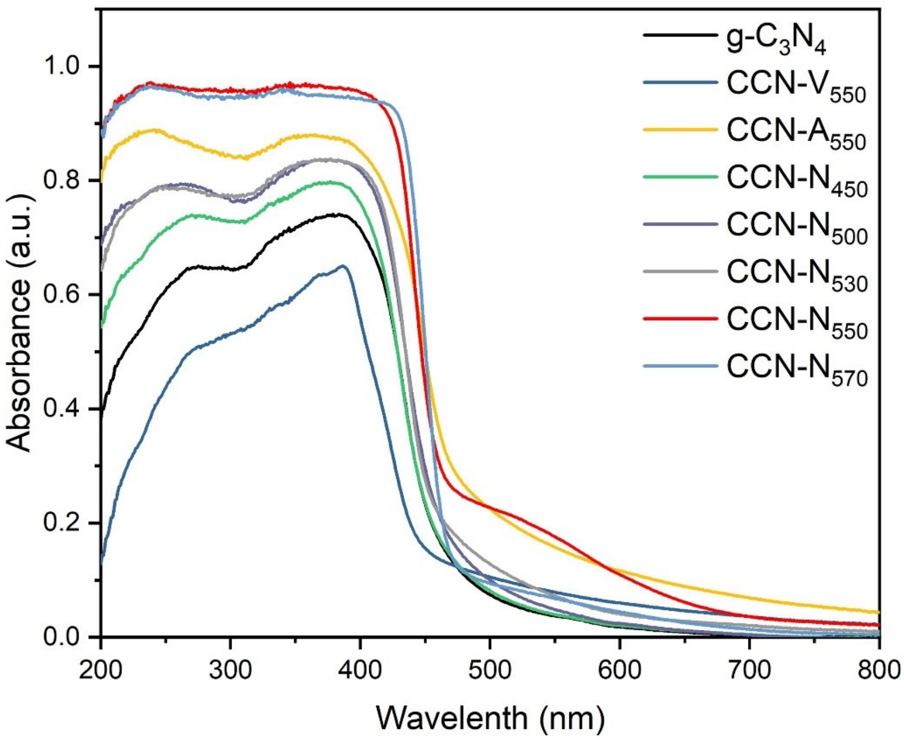

Figure S7. UV-vis diffuse reflectance spectra (DRS) of samples.

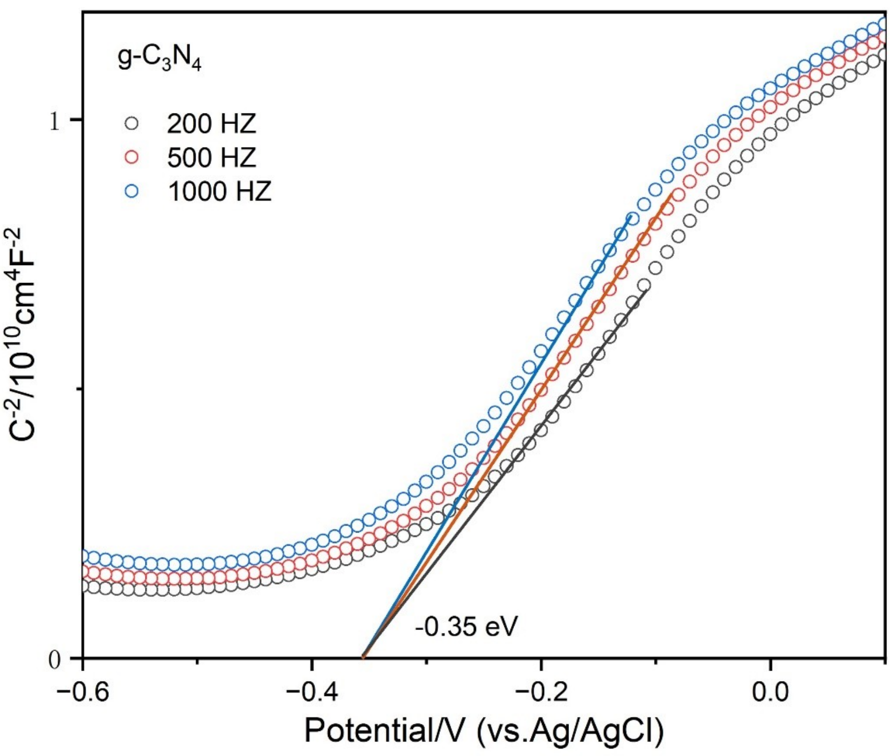

Figure S8. Mott-Schottky plots of g-C_3N_4.

Table S4. Electron transfer resistance values derived from the fitted EIS spectra in Figure 6f.

	R_1 / Ω ($g-C_3N_4$)	R_1 / Ω (CCN-A_{550})	R_1 / Ω (CCN-N_{550})	R_1 / Ω (CCN-V_{550})
Light off	23.37	28.54	25.55	26.50
Light on	15.83	12.82	10.88	19.73

R_1 represents the electron transfer impedance.

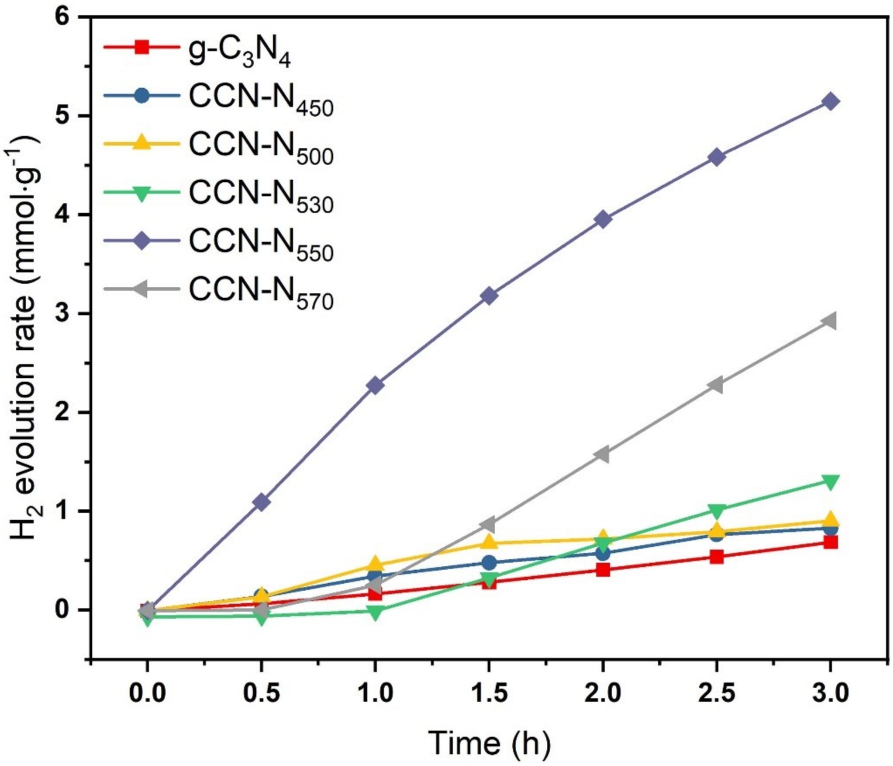

Figure S9. Photocatalytic performance of CCN-N_x and g-C_3N_4.

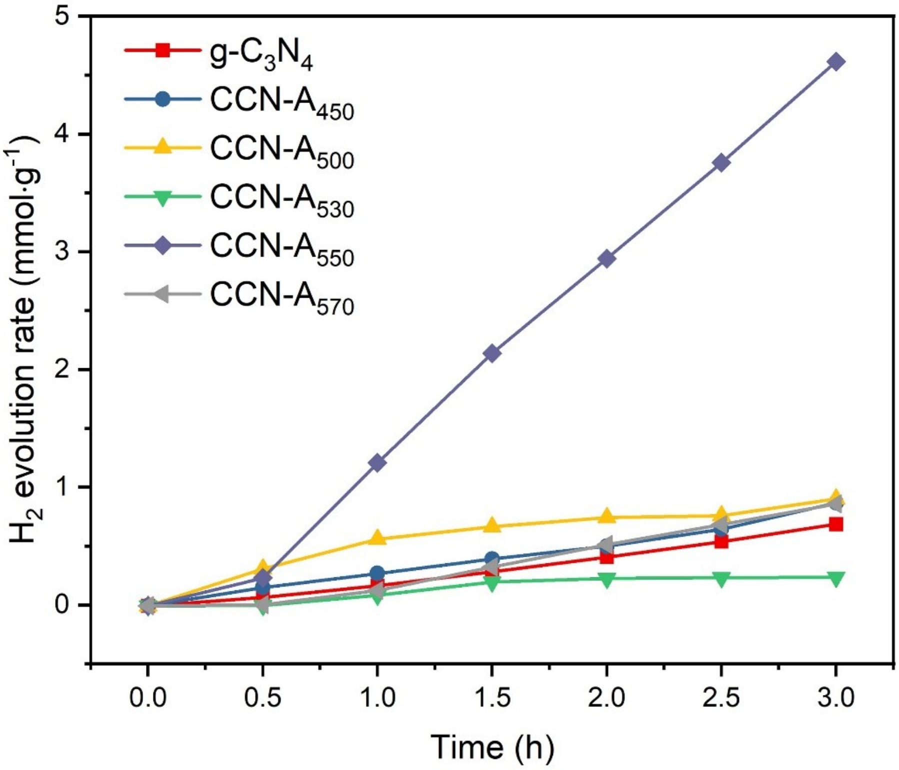

Figure S10. Photocatalytic performance of CCN-A_x and g-C_3N_4.

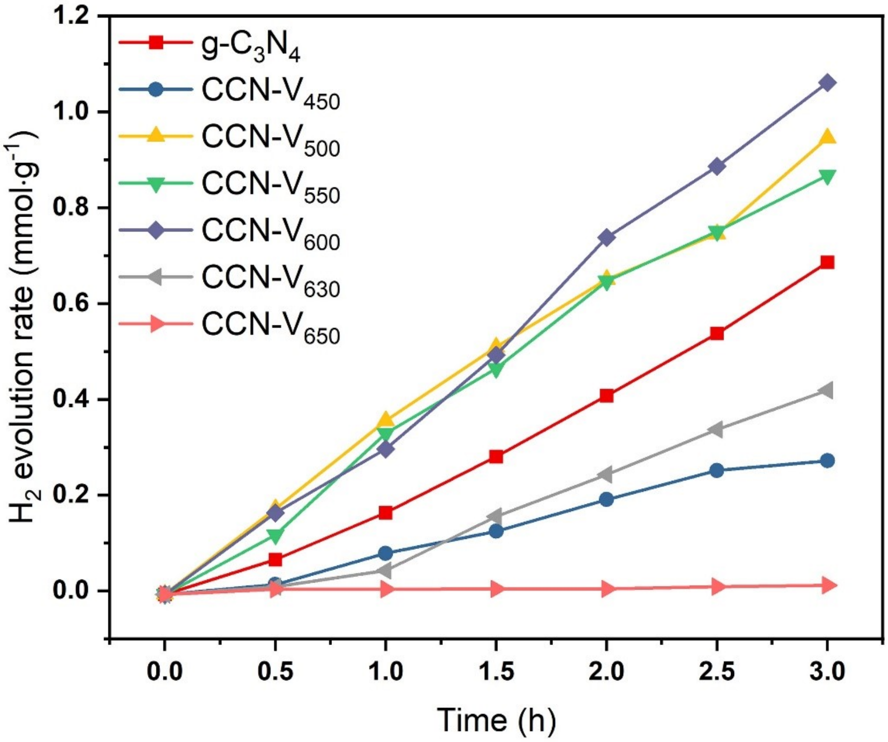

Figure S11. Photocatalytic performance of CCN-V_x and g-C_3N_4.

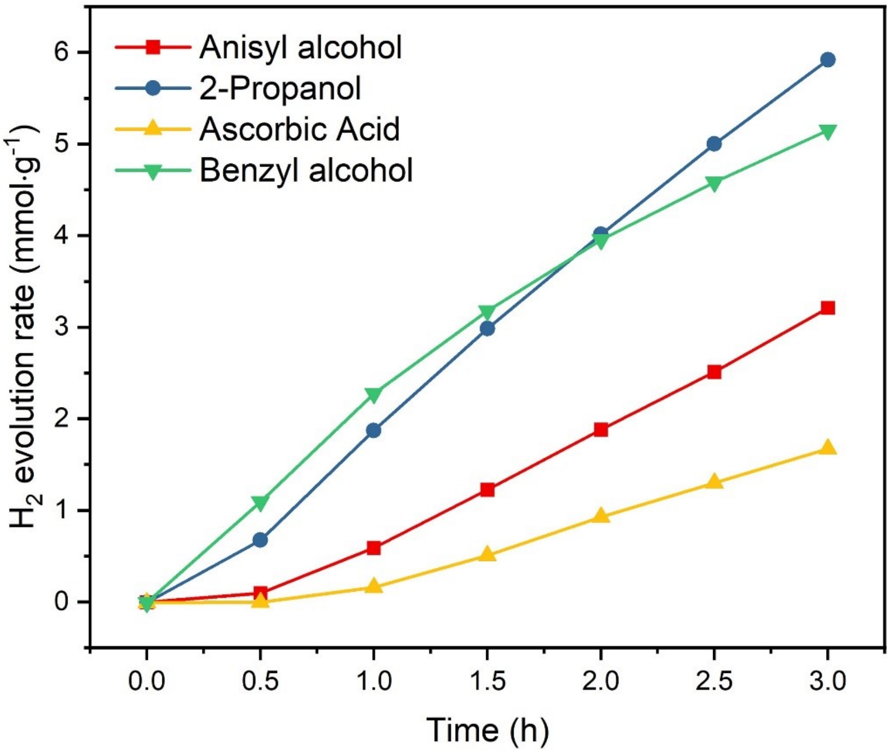

Figure S12. Hydrogen evolution activity of CCN-N_{550} over different organic substrates.

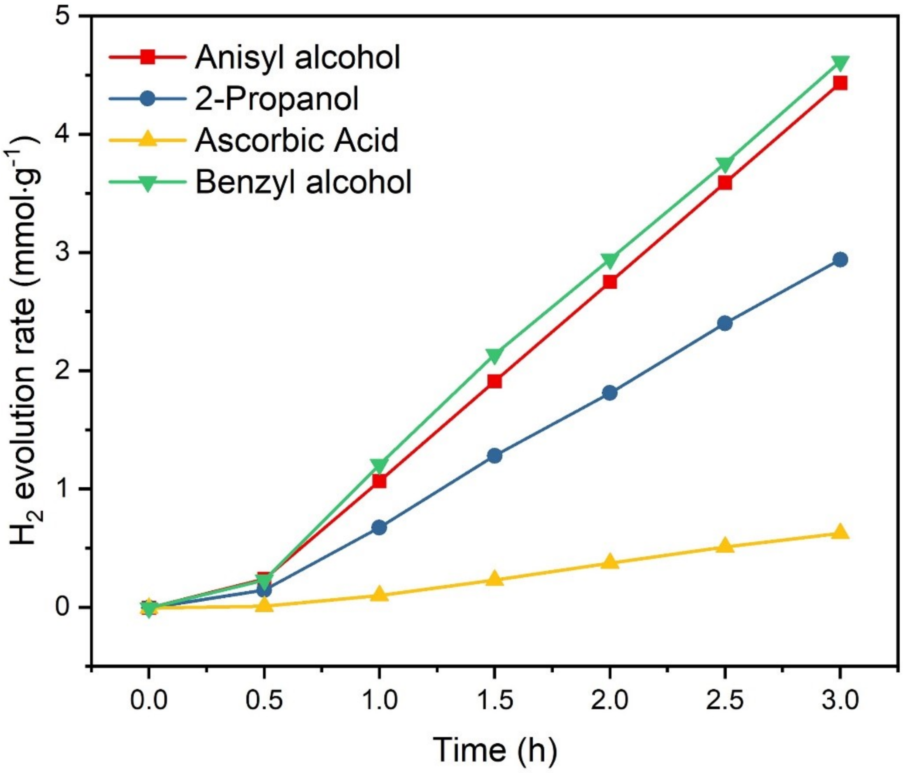

Figure S13. Hydrogen evolution activity of CCN-A_{550} over different organic substrates.

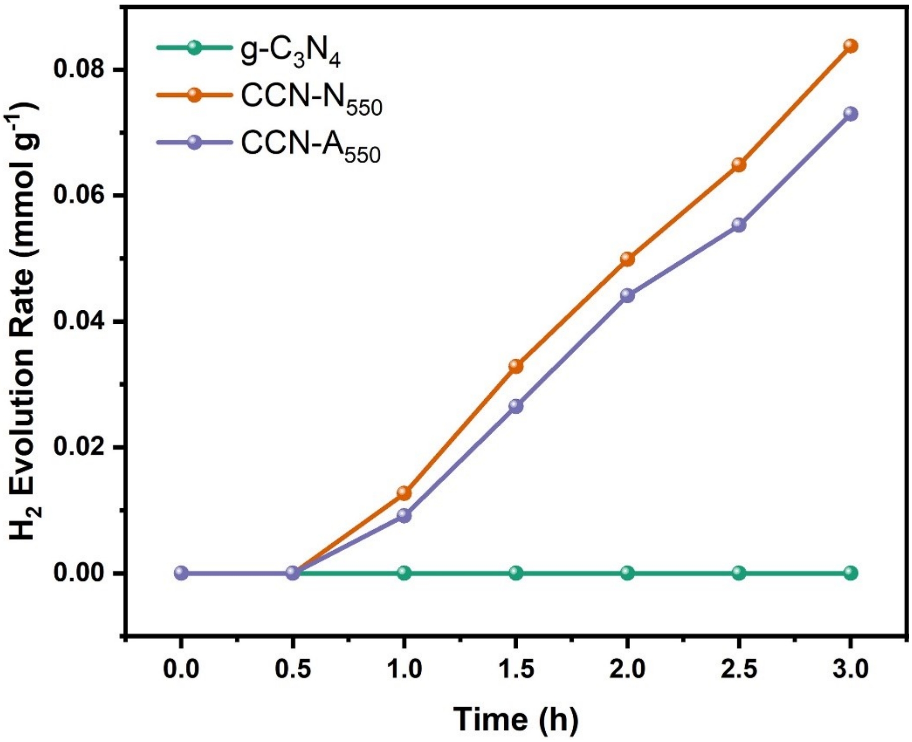

Figure S14. Hydrogen evolution activity of CCN-N_{550}, CCN-A_{550} and g-C_3N_4 without the addition of organic substrates.

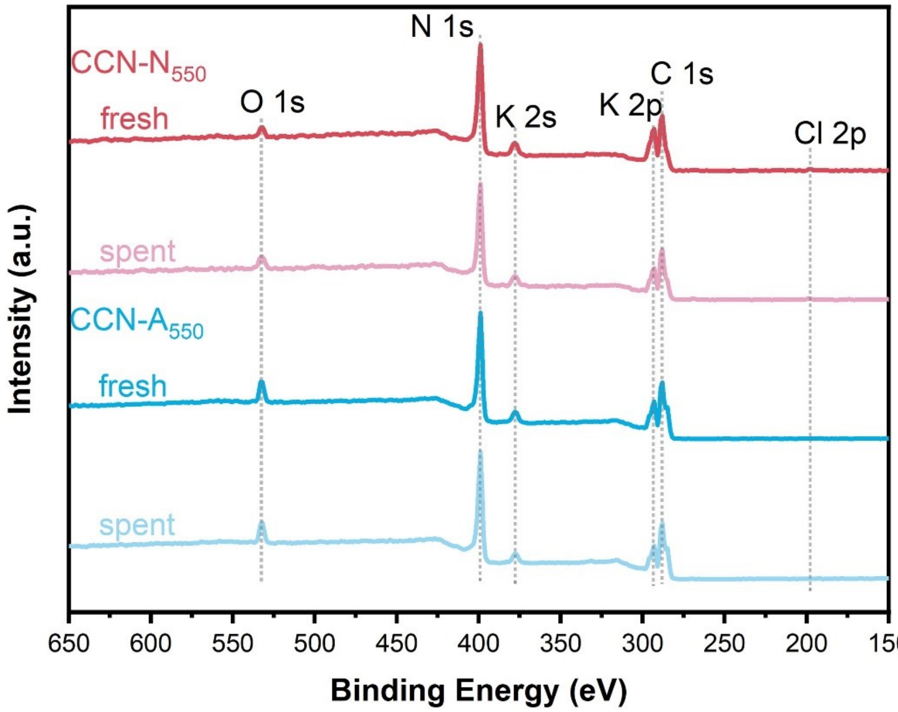

Figure S15. XPS survey spectra of fresh and spent catalysts.

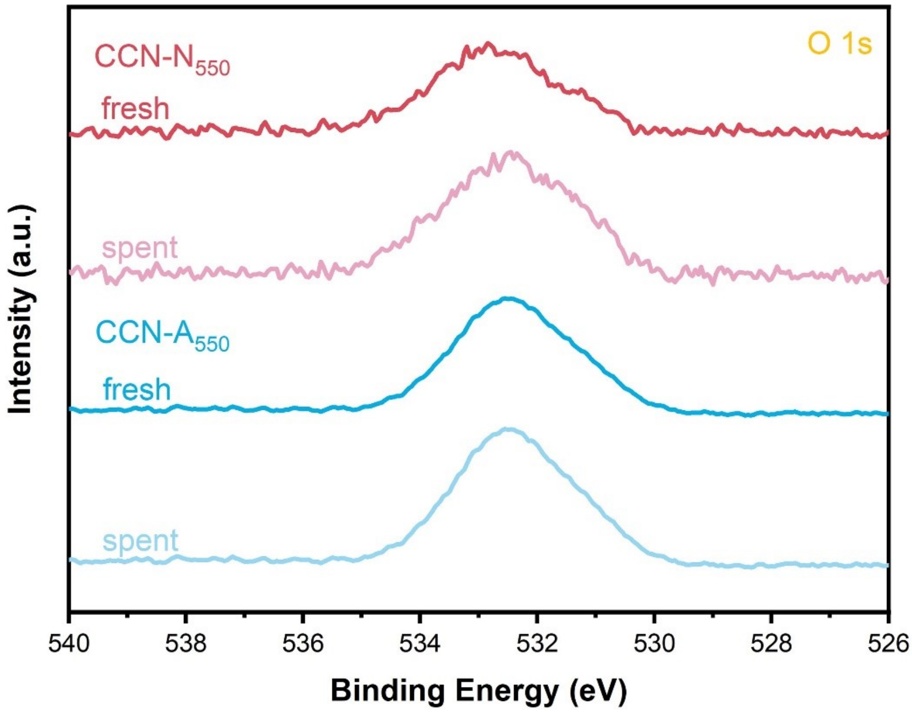

Figure S16. The high-resolution O 1s XPS spectra of fresh and spent catalysts.

Table S5. Comparative K and O contents of CCN-N_{550} and CCN-A_{550} pre- and post-photocatalysis.

Sample		K Content (%)	Relative Change (%)	O Content (%)	Relative Change (%)
CCN-N_{550}	Fresh	6.53	25	2.92	85
	Spent	4.88		5.40	
CCN-A_{550}	Fresh	5.50	15	3.48	35
	Spent	4.67		4.70	

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