Supplementary Information

Strengthen H_2O adsorption and photogenerated carrier separation: Surface C-coupled hydroxylation of g-C_3N_4 photocatalysts for the efficient H_2 production

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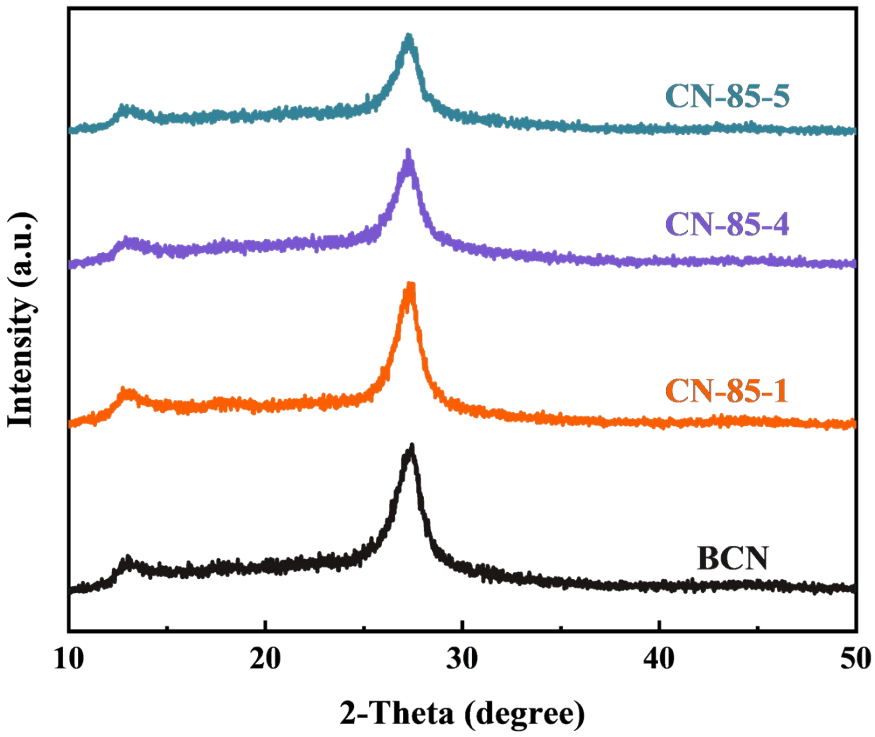

Figure S1. The XRD patterns of BCN, CN-85-1, CN-85-4, and CN-85-5.

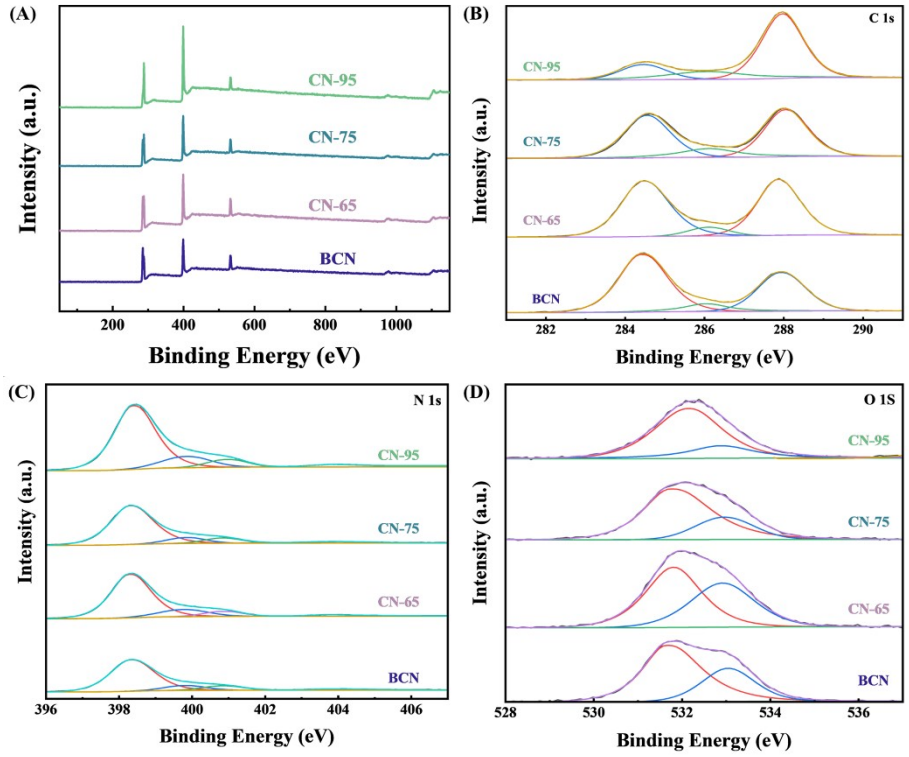

Figure S2. (A) XPS survey, (B) C 1s spectra, (C) N 1s spectra, and (D) O 1s spectra of BCN, CN-65, CN-75, and CN-95.

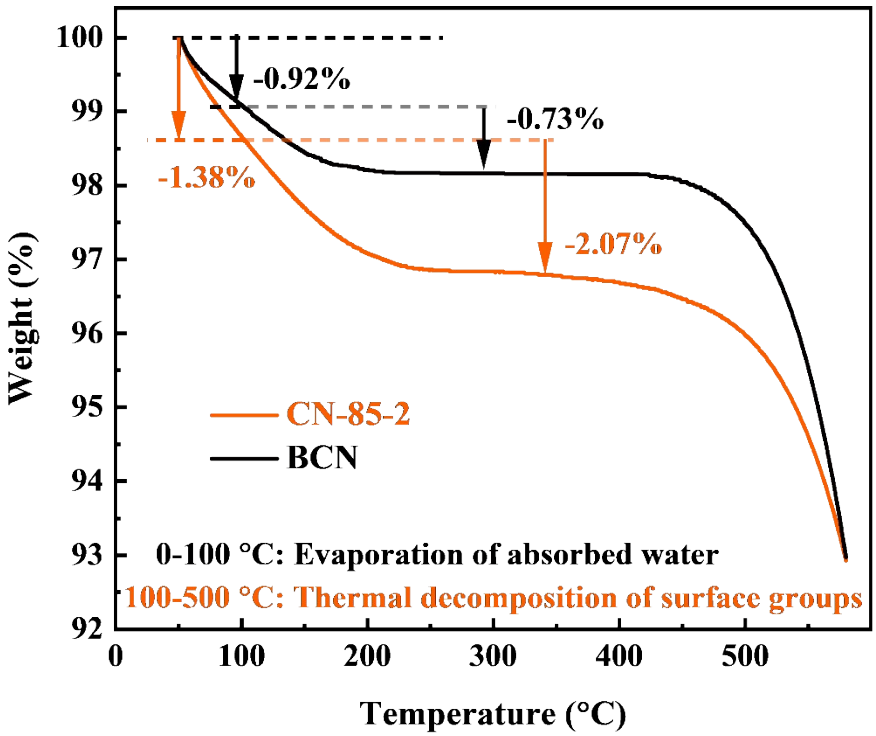

Figure S3. TGA curves of BCN and CN-85-2.

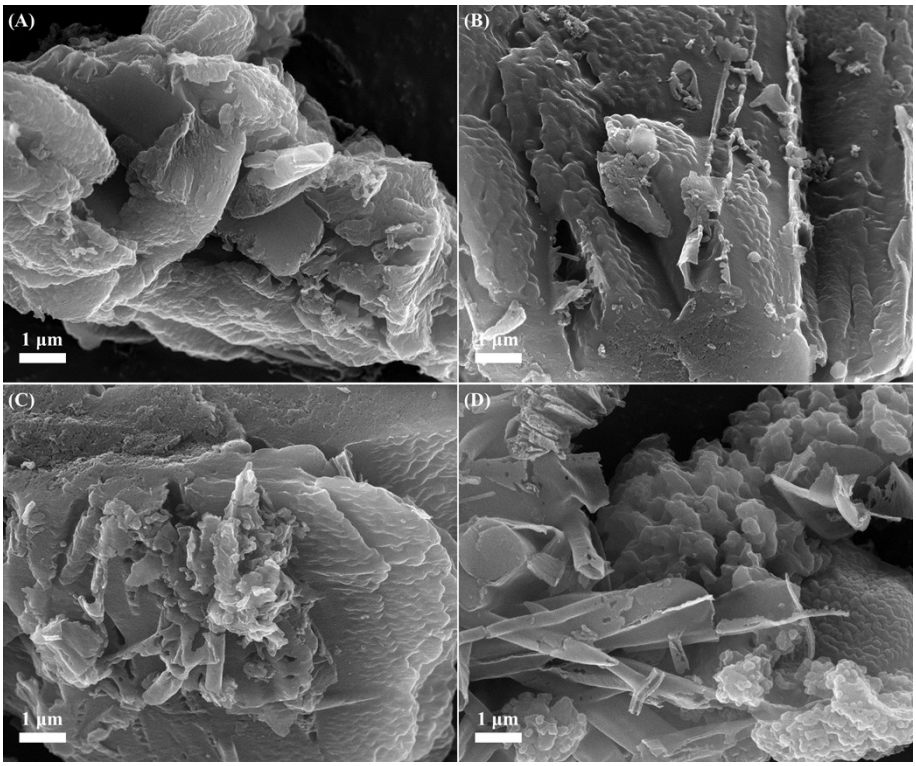

Figure S4. SEM images of (A) CN-65, (B) CN-75, (C) CN-85-3, and (D) CN-95.

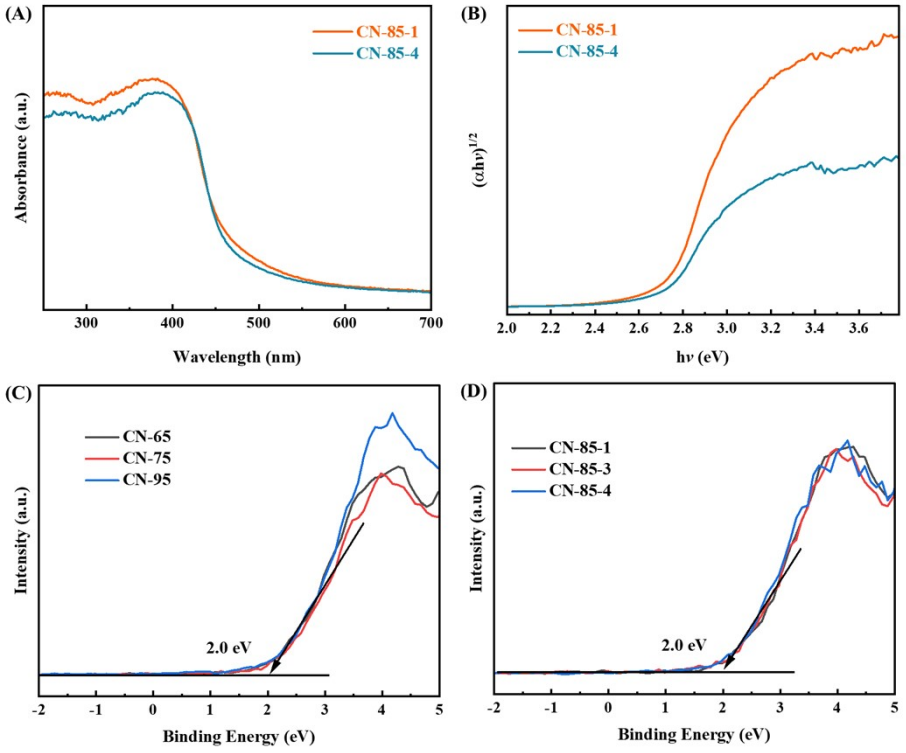

Figure S5. (A) UV-vis spectrum and (B) Tauc plots of CN-85-1 and CN-85-4. (C) XPS-VB curves of CN-65, CN-75, and CN-95. (D) XPS-VB spectra of CN-85-1, CN-85-3, and CN-85-4.

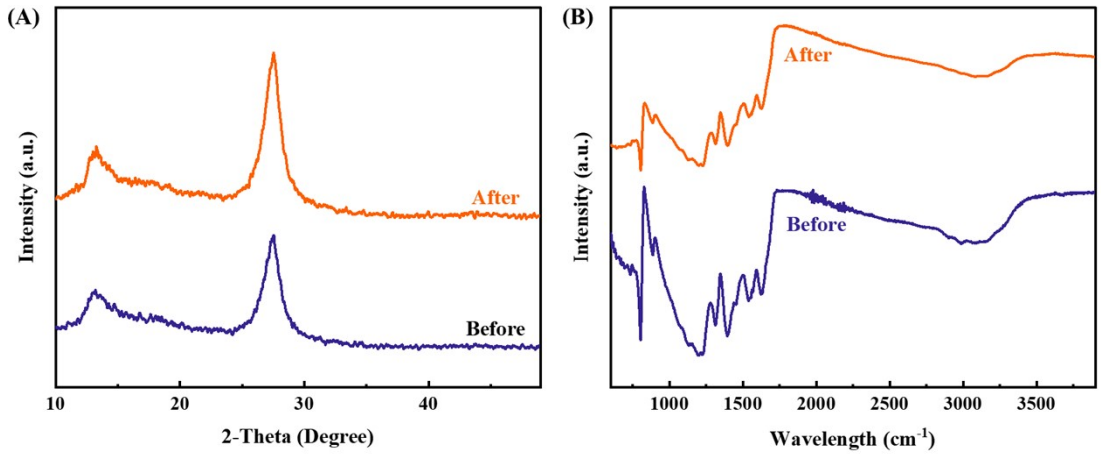

Figure S6. (A) XRD patterns and (B) FT-IR spectrum of the as-used CN-85-2 sample before and after four cycles of photocatalytic hydrogen evolution.

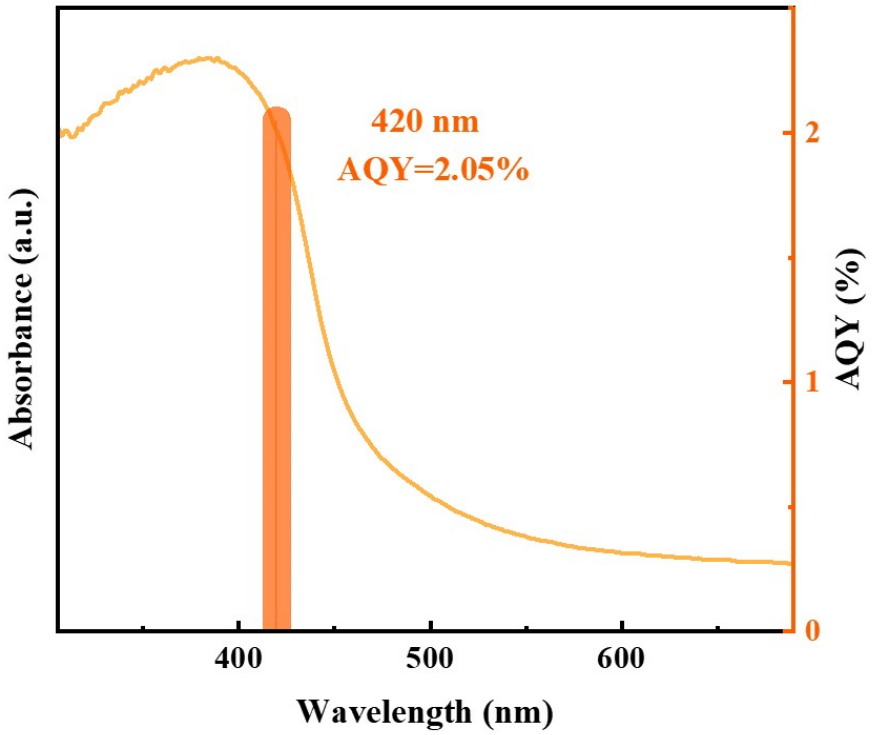

Figure S7. Apparent quantum yield of the CN-85-2 at a wavelength of 420 nm.

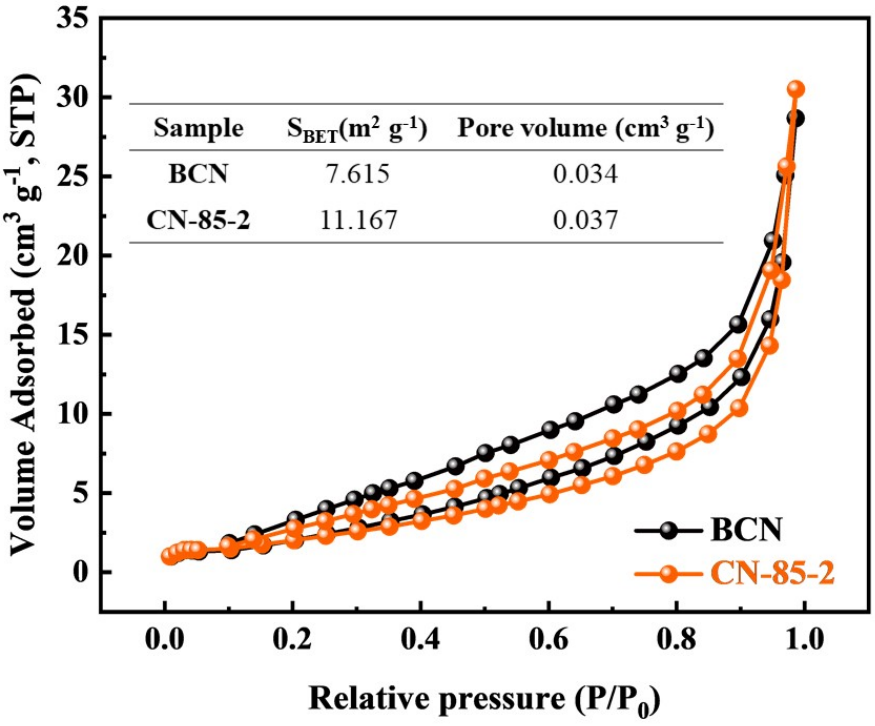

Figure S8. N_2 adsorption-desorption isotherms and specific surface areas of BCN and CN-85-2.

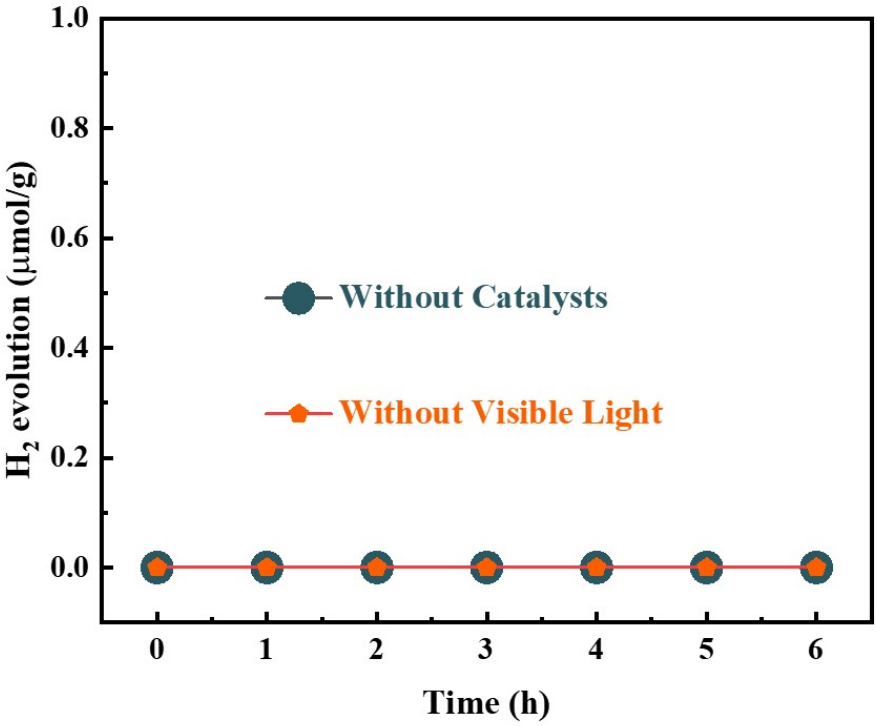

Figure S9. The hydrogen evolution efficiency without catalysts and without visible light irradiation.

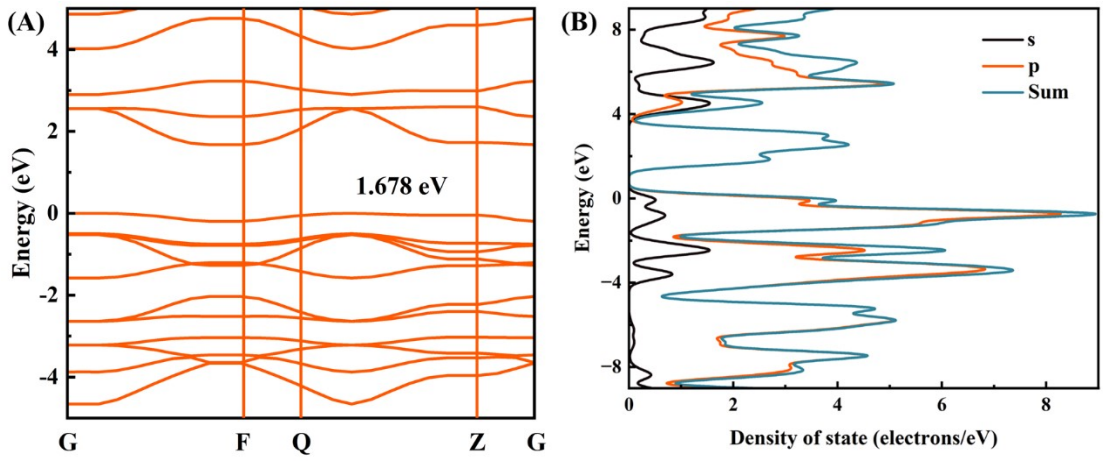

Figure S10. Band structure (A) and PDOS analysis (B) of BCN.

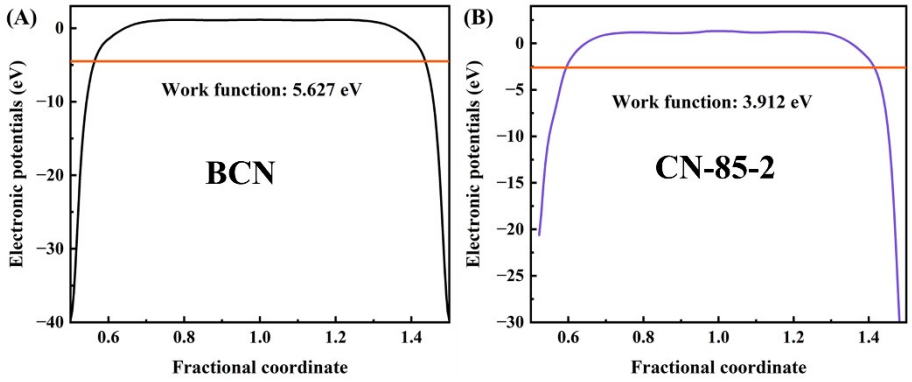

Figure S11. Work function of BCN (A) and CN-85-2 (B).

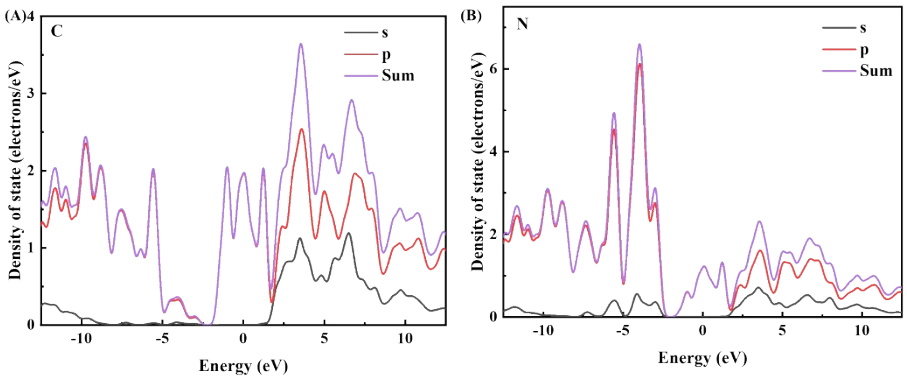

Figure S12. Corresponding PDOS of C and N over g-C_3N_4-85-2.

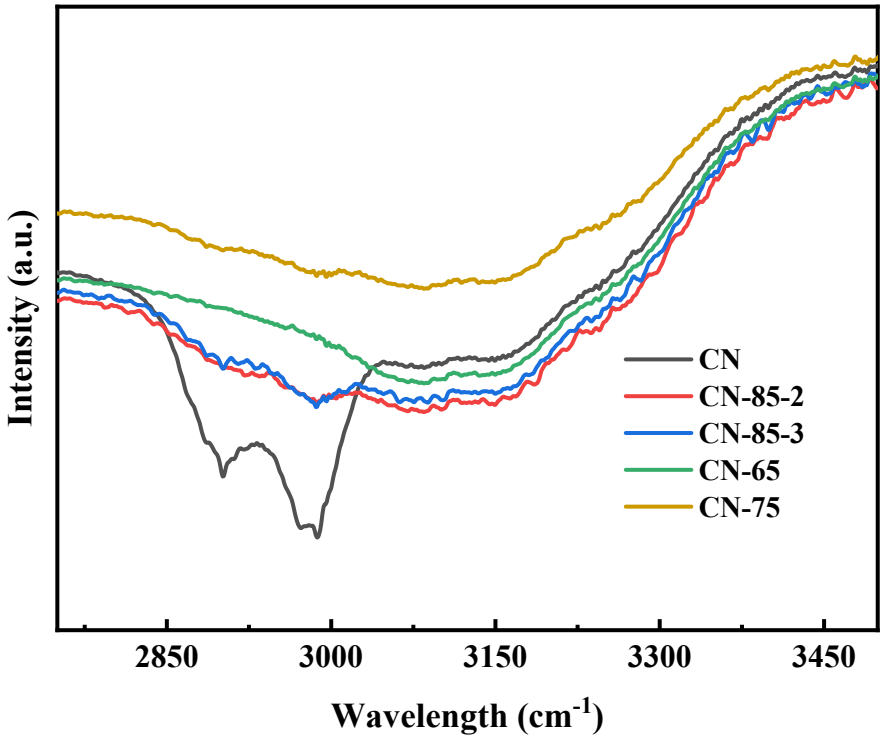

Figure S13. FT-IR spectra of materials between 2750 to 3500 cm^{-1}.

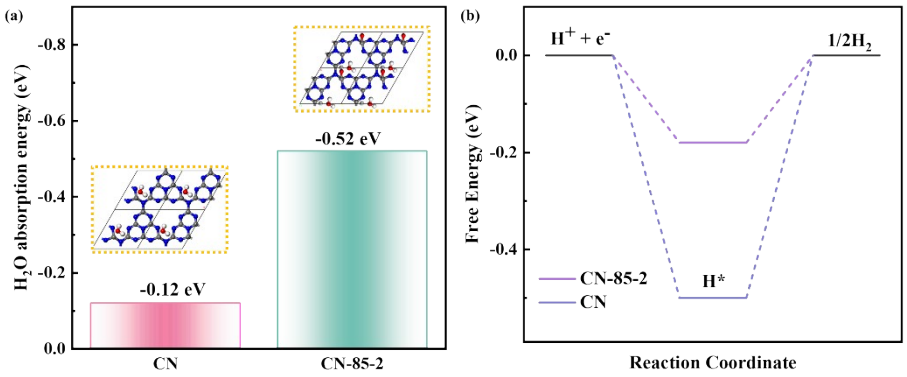

Figure S14. (a) The adsorption energies of H_2O on CN and CN-85-2 surface, and (b) free energy profiles for H adsorption at CN and CN-85-2 samples.

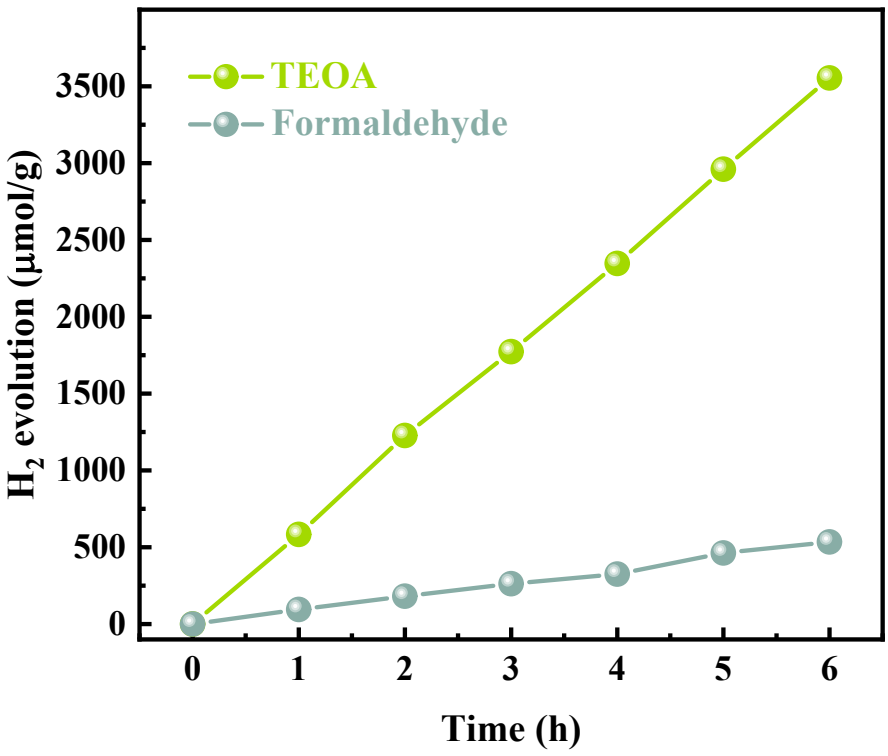

Figure S15. The photocatalytic hydrogen evolution of CN-85-2 sample in TEOA and formaldehyde solution.

Table S1. Zeta potential of BCN, CN-65, CN-75, CN-85-2, and CN-95.

Samples	**BCN**	**CN-65**	**CN-75**	**CN-85-**	**CN-95**
Zeta potential (mV)	-24.4	-25.6	-28	-28	-28.7

Table S2. The weight ratios in BCN, CN-65, CN-75. CN-85-2, and CN-95 according to the EDS analysis.

Samples	C (wt. %)	N (wt. %)	O (wt. %)
BCN	43.73	53.84	2.42
CN-65	42.76	52.72	4.53
CN-75	43.73	51.84	4.42
CN-85-2	41.91	52.77	5.32
CN-95	42.23	54.10	3.67

Table S3. The atomic ratios in pristine BCN and formaldehyde-treated g-C_3N_4 at 85 °C for 2 h.

Samples	C (atom %)	N (atom%)	O (atom%)
CN	42.62	54.82	2.56
CN-85-2	40.35	54.69	4.96

Table S4. Comparison of the present photocatalytic hydrogen evolution to the other CN-based photocatalysts in previous literatures.

Catalysts	**Light Source**	**Reaction Conditions**	**AQY**	**H_2 Evolution Rate ($\mu mol\ g^{-1}\ h^{-1}$)**	**Reference**
CN/Formaldehyde-85-2	300 W Xe lamp, λ> 400 nm	Aqueous (100 mL, 10 vol.% TEOA), 3 wt% Pt	2.05% (420 nm)	592	This work
PC-CN	300 W Xe lamp, λ> 420 nm	Aqueous (100 mL, 10 vol.% TEOA)	4.83% (420 nm)	1010	[S1]
C-Ti/CN	300 W Xe lamp, λ> 420 nm	Aqueous (100 mL, 10 vol.% TEOA), 2 wt% Pt	6.14% (420 nm)	1409	[S2]
GD/g-C_3N_4	350 W Xe lamp (λ > 420 nm)	Aqueous (80 mL, 15 vol.% ethanol), 1 wt% Pt	3.47% (420 nm)	792	[S3]
g-C_3N_4	300 W Xe lamp, λ> 420 nm	Aqueous (100 mL, 10 vol.% TEOA), 3 wt% Pt	6.10% (420 nm)	1391	[S4]
Co/P/CN-sc	300 W Xe lamp, λ> 420 nm	Aqueous (100 mL, 10 vol.% TEOA), 3 wt% Pt	1.53% (420 nm)	350	[S5]
UNU-C_3N_4	300 W Xe lamp, λ> 420 nm	Aqueous (100 mL, 10 vol.% TEOA), 3 wt% Pt	3.64% (420 nm)	830	[S6]

N-vacancies CN	300 W Xe lamp, λ> 420 nm	Aqueous (100 mL, 10 vol.% TEOA), 3 wt% Pt	8.25% (420 nm)	1880	[S7]
2D-2D g-C_3N_4/ MoS_2	300 W Xe lamp (λ > 420 nm)	Aqueous (250 mL, 0.1 M TEOA)	5.04% (420 nm)	1155	[S8]
$Ba_5Nb_4O_{15}$ / g-C_3N_4	3W LEDs, λ> 420 nm	Aqueous (100 mL, 0.025 M oxalic acid), 2 wt% Pt	11.71% (420 nm)	2673	[S9]

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S6. L. Jing, D. Wang, Y. Xu, M. Xie, J. Yan, M. He, Z. Song, H. Xu and H. Li, *J. Colloid Interface Sci.*, 2020, **566**, 171-182.

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