

Supporting Information

Salt-assisted activation of $n \rightarrow \pi^*$ electronic transition in orange carbon nitride for enhanced visible-light-driven H_2 generation

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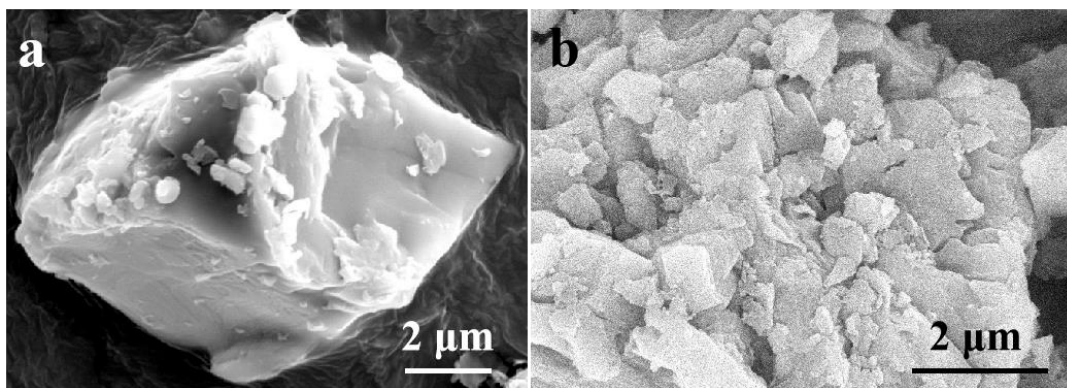


Fig. S1 SEM images of (a) NaCl particle and (b) melem.

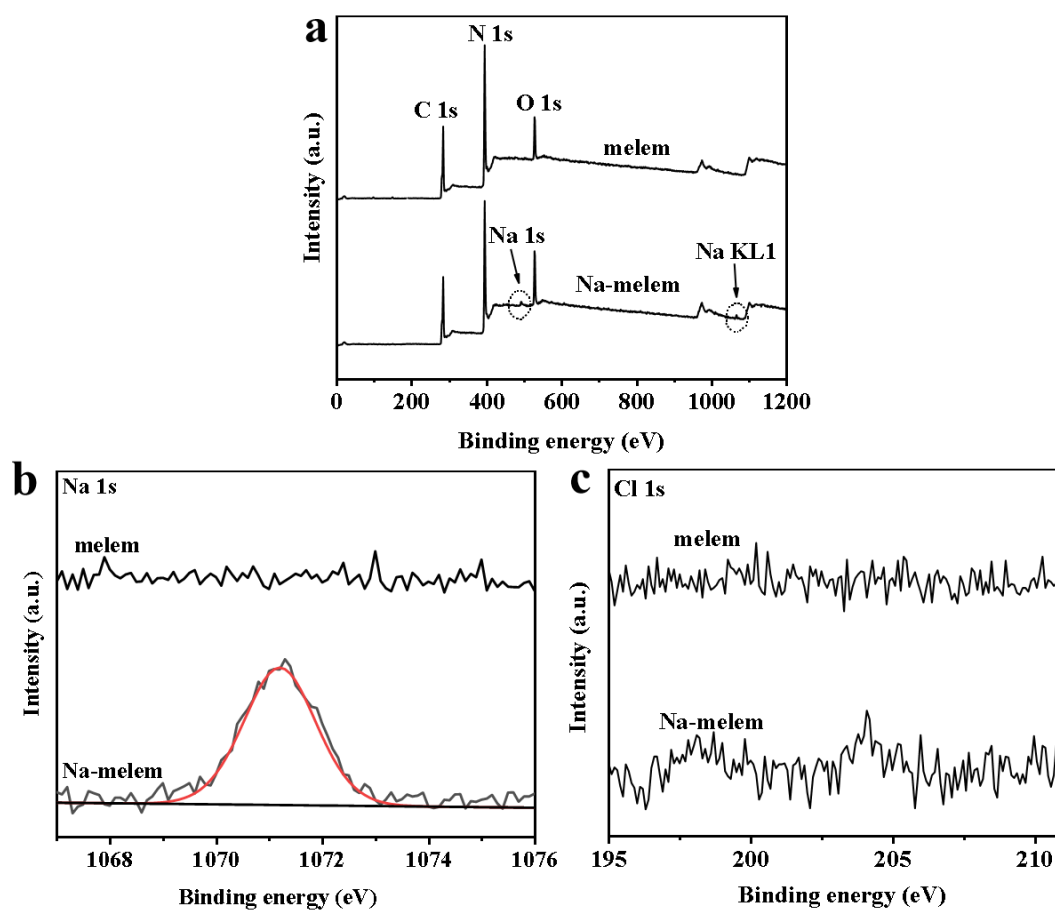


Fig. S2 (a) XPS survey, (b) Na 1s, and (c) Cl 1s spectra of melem and Na-melem.

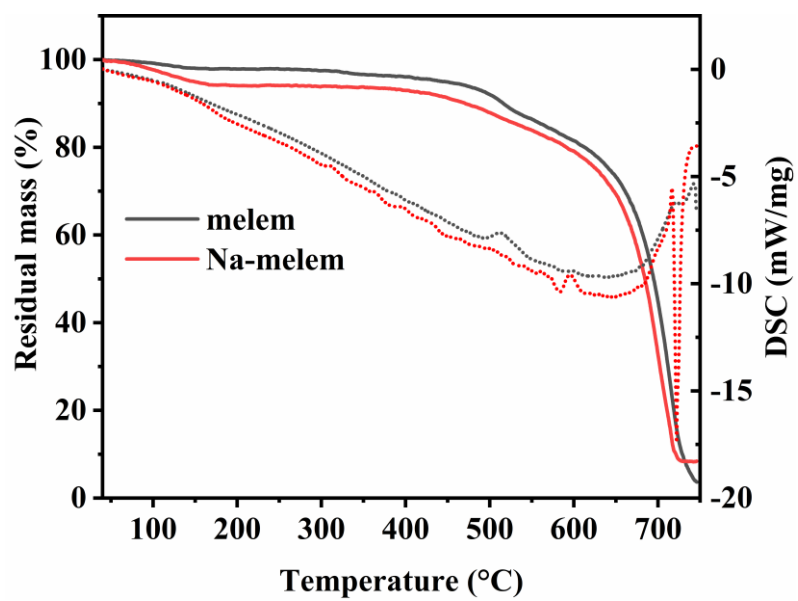


Fig. S3 TG-DSC curves of melem and Na-melem.

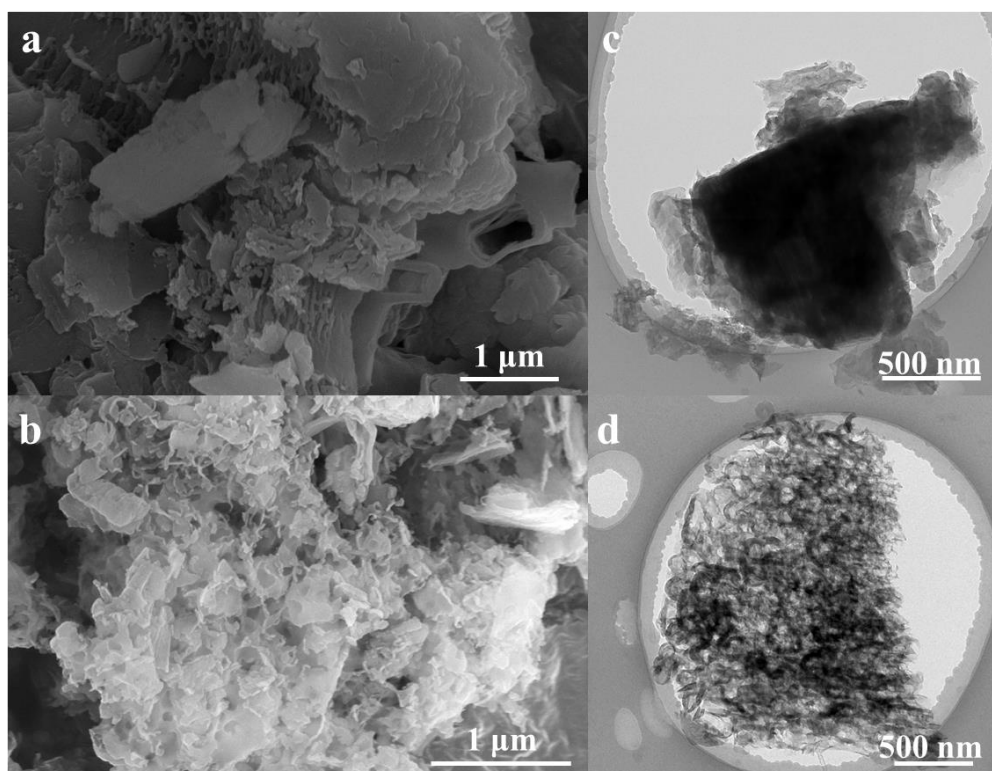


Fig. S4 SEM images of (a) PCN and (b) MCN. TEM images of (c) PCN and (d) MCN.

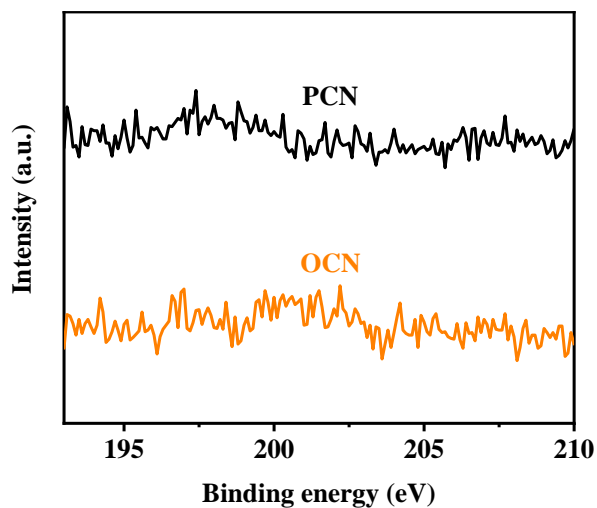


Fig. S5 XPS Cl 1s spectra of PCN and OCN.

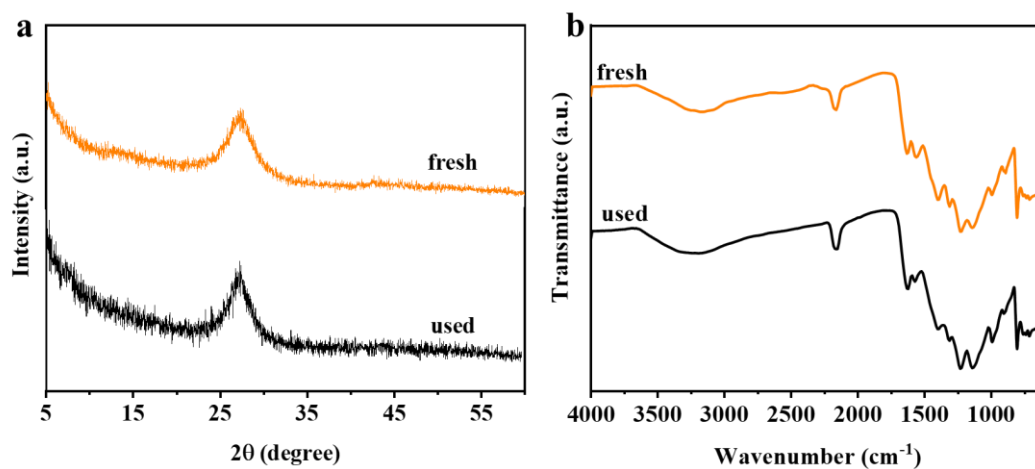


Fig. S6 (a) XRD patterns and (b) FTIR spectra of OCN before and after photocatalytic reaction.

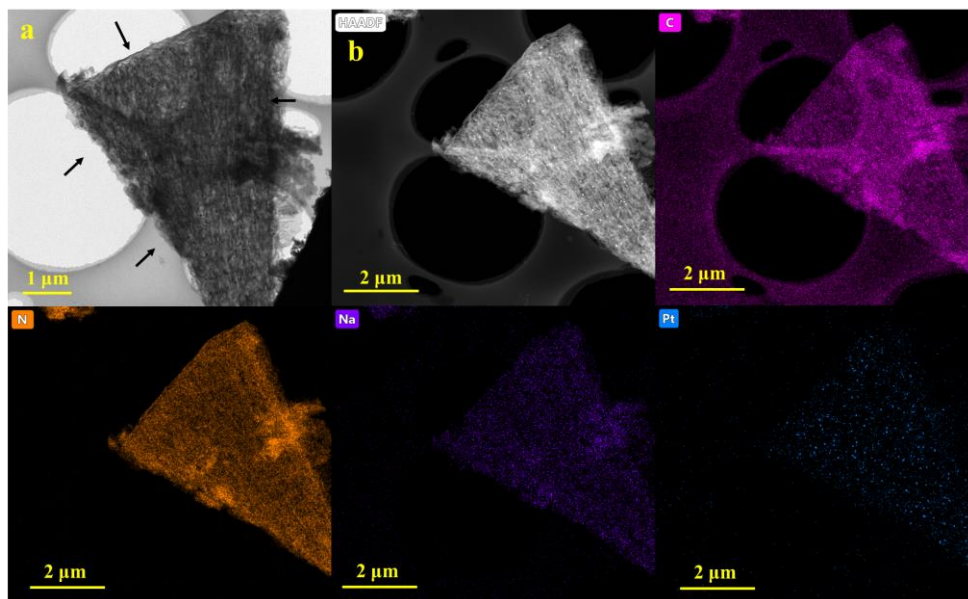


Fig. S7 (a) TEM image and (b) HAADF image with corresponding elemental mappings of C, N, Na, and Pt distribution of OCN after photocatalytic reaction.

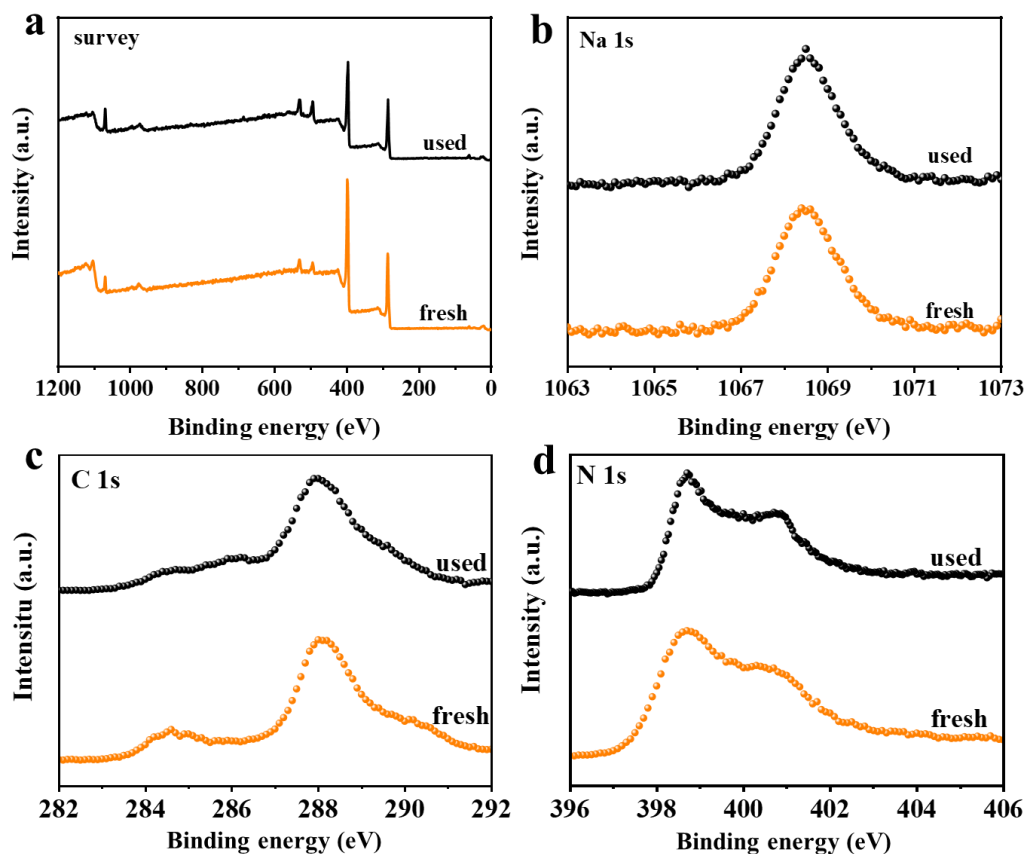


Fig. S8 (a) XPS survey spectra, high-resolution (b) Na 1 s, (c) C 1 s, and (d) N 1 s spectra of OCN before and after photocatalytic reaction.

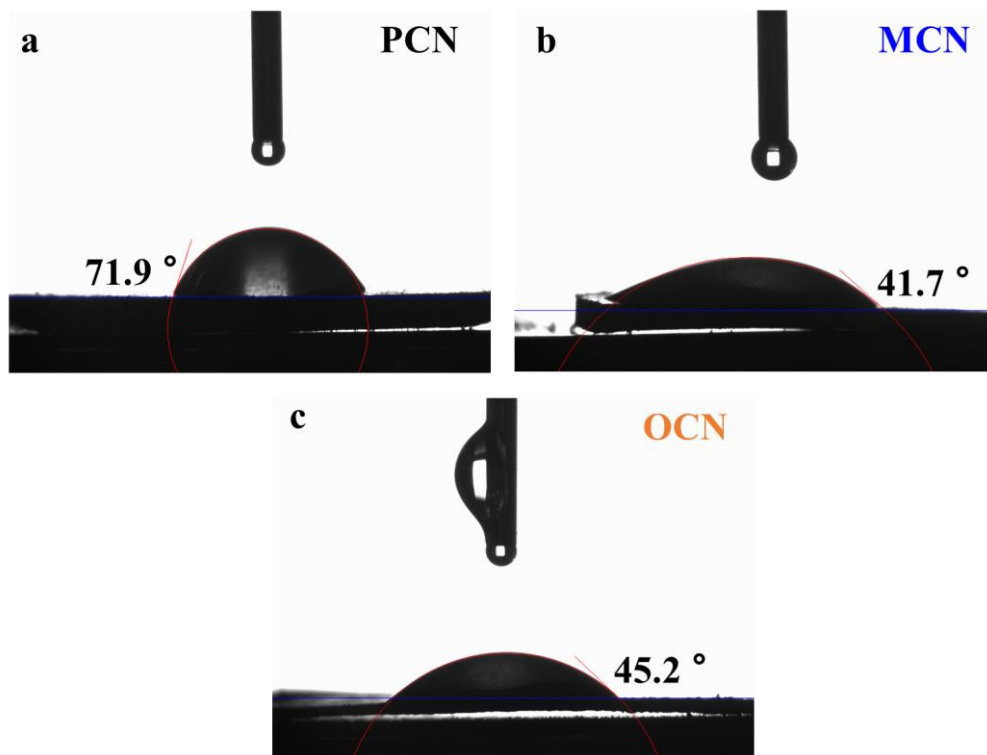


Fig. S9 The static water contact-angle measurement of (a) PCN, (b) MCN, and (c) OCN.

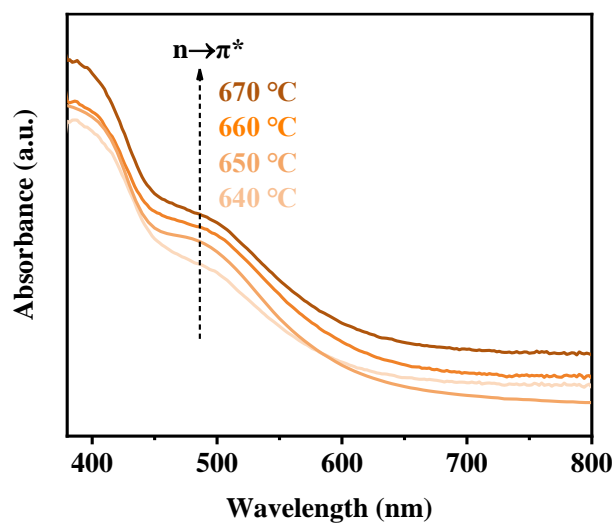


Fig. S10 UV-Vis DRS spectra of OCN synthesized at different temperatures.

Table S1 The average PL lifetimes and relative percentages of photoinduced charge carriers in PCN, MCN, and OCN.

Sample	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{av} (ns)
PCN	1.50	72.6	8.31	27.4	6.11
MCN	0.77	78.6	5.25	21.4	3.68
OCN	0.45	96.6	5.14	3.4	1.80

^{a)} The fitted PL lifetime decay curves $[I(t)-t]$ are based on biexponential decay function (Eq. 1).

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

where τ_1 and τ_2 are the lifetimes of radiative and nonradiative decay components, A_1 and A_2 are the amplitudes of radiative and nonradiative decay components.

The average PL lifetime decay (τ_{av}) is calculated by Eq. 2.

$$\tau_{av} = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 + A_2) \quad (2)$$

Table S2 Comparison of the HER and AQE from some Na⁺-doped carbon nitride photocatalysts reported in recent literature.

Photocatalysts	Conditions	HER ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	AQE $\lambda=420 \text{ nm}$	Refs.
honeycomb-like g-C ₃ N ₄	3 wt% Pt, 25 % lactic acid	459 ($\lambda > 420 \text{ nm}$)	2.2 %	1
Na ⁺ -doped g-C ₃ N ₄	1 wt% Pt, 10 % TEOA	374 ($\lambda > 400 \text{ nm}$)	/	2
g-C ₃ N ₄ -D	1 wt% Pt, 10 % lactic acid	667.8 ($\lambda > 420 \text{ nm}$)	1.8 %	3
MC-CN	3 wt% Pt, 10 % TEOA	215.8 ($\lambda > 420 \text{ nm}$)	1.56 %	4
NaCCNB	1 wt% Pt, 10 % TEOA	758 ($\lambda > 420 \text{ nm}$)	1.03 %	5
g-C ₃ N ₄ -Na	3 wt% Pt, /	37.2 ($\lambda > 420 \text{ nm}$)	/	6
PC-CN0.1	1 wt% Pt, 10 % lactic acid	1010 (420 nm)	/	7
OCN	1 wt% Pt, 10 % TEOA	1043 ($\lambda > 420 \text{ nm}$)	3.17 %	This work

Reference

1. F. Yang, D. Liu, Y. Li, L. Cheng and J. Ye, *Appl. Catal. B Environ.*, 2019, **240**, 64-71.
2. J. Jiang, S. Cao, C. Hu and C. Chen, *Chinese J. Catal.*, 2017, **38**, 1981-1989.
3. Y. Shao, X. Hao, S. Lu and Z. Jin, *Chem. Eng. J.*, 2023, **454**, 140123.
4. B. Zhai, H. Li, G. Gao, Y. Wang, P. Niu, S. Wang and L. Li, *Adv. Funct. Mater.*, 2022, **32**, 2207375.
5. W. Wang, Z. Shu, J. Zhou, D. Meng, Z. Zhao and T. Li, *J. Mater. Chem. A*, 2020, **8**, 6785-6794.
6. H. Luo, Y. Jia, Z. Xie and W. Shi, *Chem. Eng. Sci.*, 2024, **299**, 120409.
7. X. Wu, H. Ma, W. Zhong, J. Fan and H. Yu, *Appl. Catal. B Environ.*, 2020, **271**, 118899.