

Supporting Information

**Molten salt-assisted synthesis of boron-doped carbon nitride for photocatalytic
hydrogen evolution**

Xingzhou Li ^{a,1}, Yongkang Quan ^{a,1}, Rongxing Chen ^a, Guorong Wang ^b, Yingzhen Zhang ^a,
Jiaying Huang ^{a,*}, Yuekun Lai ^{a,*}

^a College of Chemical Engineering, Fuzhou University, Fuzhou 350116, P. R. China

^b School of Chemistry and Chemical Engineering, North Minzu University, Yinchuan 750021,
P.R.China

* Corresponding authors at: College of Chemical Engineering, Fuzhou University, Fuzhou 350116,
P. R. China.

E-mail: jyhuang@fzu.edu.cn, yklai@fzu.edu.cn.

¹ These authors contributed equally to this work.

1. Experiments and Methods

1.1. Materials

Melamine ($C_3H_6N_6$), potassium chloride (KCl), sodium chloride (NaCl), boric acid (H_3BO_3), sodium sulfate electrolyte (Na_2SO_4), chloroplatinic acid (H_2PtCl_6), triethanolamine (TEOA), methanol (CH_3OH), sodium sulfide (Na_2S), sodium sulfite (Na_2SO_3), lactic acid ($C_3H_6O_3$), anhydrous ethanol (C_2H_6O), etc. All the chemicals involved in this experiment were obtained from China National Pharmaceutical Chemical Reagent Co. Ltd. and were of analytical grade and did not require further purification.

1.2. Synthesis of CN

5 g of melamine was directly pyrolyzed in a muffle furnace at $550^\circ C$ for 4 h under air atmosphere with a ramp rate of $2^\circ C\ min^{-1}$ to obtain a lumpy yellow product, which was ground into a yellow powder and named CN.

1.3. Synthesis of BCN

0.1 g of H_3BO_3 , 1 g of melamine and 50 mL of deionized water were stirred in a beaker for 30 min, and heated in a hydrothermal kettle at $180^\circ C$ for 10 h. After the reaction, the product was cooled down to room temperature in a natural environment. The borated melamine was washed several times with deionized water and then dried in a vacuum oven at $60^\circ C$ overnight. Finally, the obtained precursor was calcined under Ar atmosphere at a ramping rate of $2^\circ C\ min^{-1}$ at $550^\circ C$ for 4 h. The product was ground into a yellow powder named BCN.

1.4. Synthesis of KBCN

50 mg of BCN, 4 g of NaCl and 1 g of KCl were mixed and uniformly ground in a mortar for 10 min. the precursor was calcined under Ar atmosphere at a heating rate of $2^\circ C\ min^{-1}$ at $550^\circ C$ for 4 h. The product was washed with deionized water for several times to obtain a yellow powder, named KBCN.

2. Characterization

Use S-4800 field emission scanning electron microscope from Hitachi, Japan was used for testing (SEM) and a TECNAI G2 F20 transmission electron microscope from FEI, USA was used for testing (TEM). An X'Pert3 powder diffractometer manufactured by Panalytical, Netherlands, was used for testing with the following parameters: scanning range $5-80^\circ$, operating voltage 40 kV, and operating current 40 mA, and X-ray diffraction (XRD) patterns of the samples were obtained.

A fully digitalized nuclear magnetic resonance spectrometer AVANCE III 500 from Bruker, Switzerland was used for testing (NMR). N₂ adsorption-desorption isotherms, specific surface area and pore size distribution of the samples were recorded using a nitrogen adsorption-desorption instrument (BSD-660M-A683M). X-ray photoelectron spectra (XPS) were recorded using an Escalab-250Xi X-ray photoelectron spectrometer from Thermo Scientific. Electron paramagnetic resonance (EPR) was tested using a Bruker A300. Light absorption capacity and band edge absorption positions were tested using a Lambda950 UV-Vis NIR spectrophotometer from Perkin-Elmer, U.S.A. FT-IR was tested by a Nicolet 6700 FT-IR spectrometer from Thermo Fisher Scientific, U.S.A. The spectra were measured using a Bruker A300 time-resolved photoelectron spectrometer. Photogenerated carrier lifetime (TRPL) was tested using FLS1000 time-resolved fluorescence decay spectrometer.

3. Photocatalytic hydrogen evolution test

The photocatalytic reaction was carried out in a 63 mL airtight quartz vessel by dispersing the photocatalyst powder (10 mg) in an aqueous solution of TEOA (30 mL, 15 vol.%), and adding 100 μ L of H₂PtCl₆·6H₂O for loading of 1 wt% Pt. The suspension was dispersed by ultrasonication for 5 min, and then purged with Ar for 5 min to remove the contained O₂. The quartz vessel was subjected to photocatalytic reaction in a multichannel photocatalytic reactor with simultaneous magnetic stirring (300 r/min). The gas products were analyzed using gas chromatography (Shimadzu, Japan; GC-2014C) with argon as the carrier gas for the chromatography. The apparent quantum efficiencies of the samples were tested under a 300 W xenon lamp as a light source with band-pass filters at 400, 420, 475 and 550 nm and were calculated by the following equations:

$$AQE = \frac{2 \times \text{the number of evolved H}_2 \text{ molecule}}{\text{the incident photos number}}$$

4. Photoelectrochemical testing:

The transient photocurrent (TPC) response and electrochemical impedance spectroscopy (EIS) tests of the samples were recorded using a three-electrode system electrochemical workstation (Modulab XM). Saturated Ag/AgCl was used as the reference electrode and Pt electrode as the counter electrode. The working electrode was prepared by dispersing 3 mg of catalyst in a mixed solution containing 30 μ L of Nafion and 270 μ L of ethanol, coating the suspension on a conductive glass, drying it in an oven for 2 h to evaporate the solvent, and strictly controlling the catalyst

coverage area to be 1x1 cm². the electrolyte solution was 0.2 M Na₂SO₄. the photocurrent response was tested with 40 s switching on/off intervals under intermittent visible light irradiation. light interval to test the photocurrent response. Electrochemical impedance spectra (EIS) were recorded in the frequency range of 10 mHz-100 kHz at 0.6 V with an initial bias of Ag/AgCl and an AC amplitude of 5 mV.

Supplementary Figures

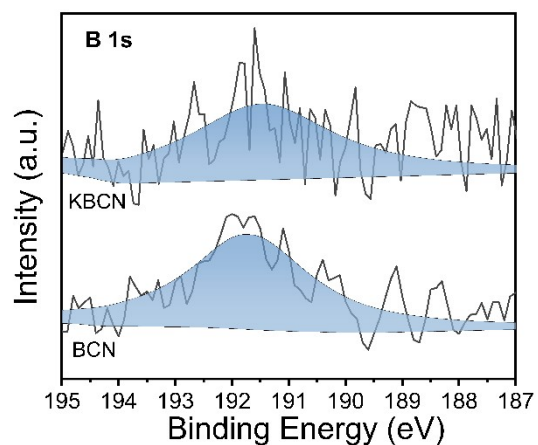


Fig. S1. XPS spectra of B 1s of BCN and KBCN.

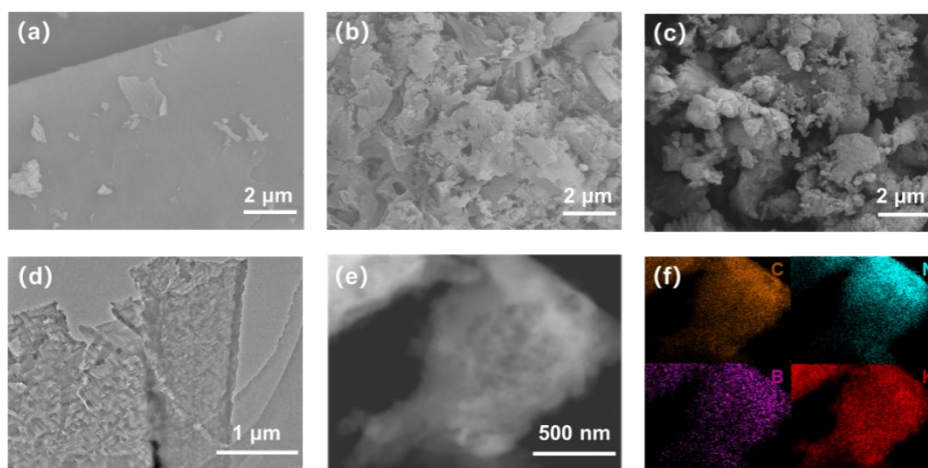


Fig. S2. SEM of (a) CN, (b) BCN, (c) KBCN. (d) TEM of KBCN. (e) HRTEM images of KBCN. (f) TEM elemental mapping images of KBCN.

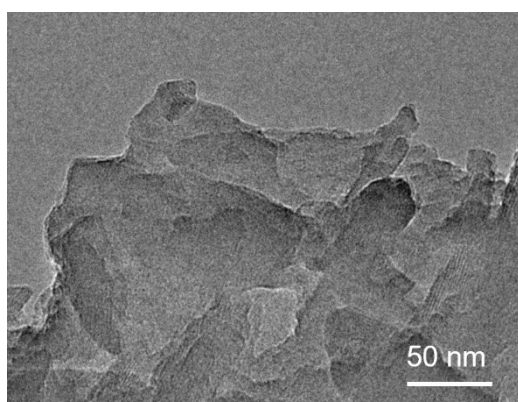


Fig. S3. HRTEM of KBCN sample.

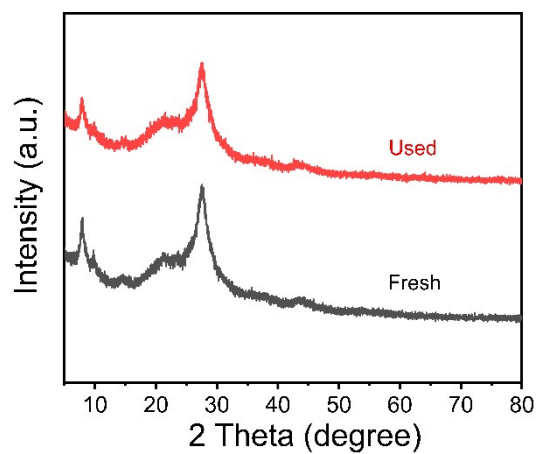


Fig. S4. XRD of fresh and used of KBCN.

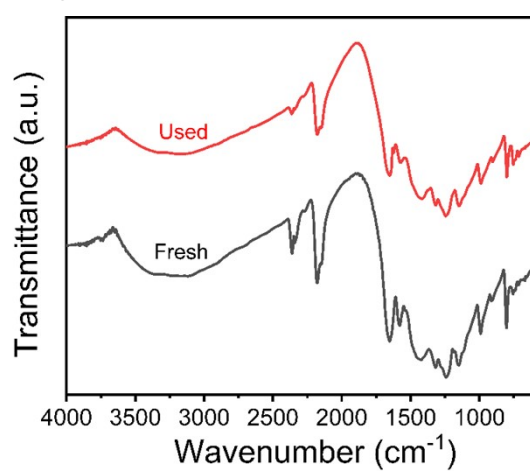


Fig. S5. FT-IR spectra of fresh and used of KBCN.

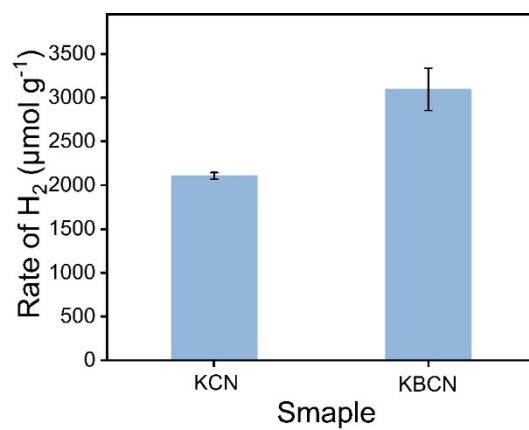


Fig. S6. H₂ evolution performance test of KCN and KBCN.

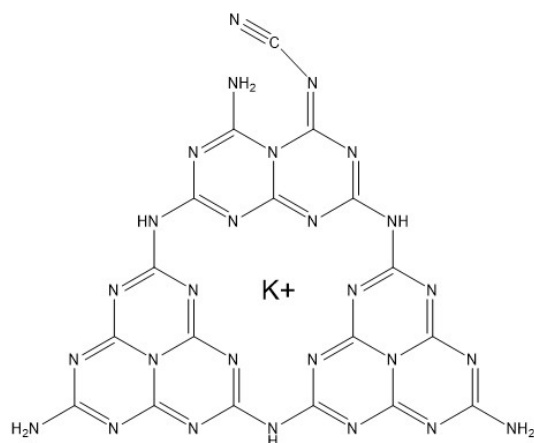


Fig. S7. Possible chemical structure of KBCN.

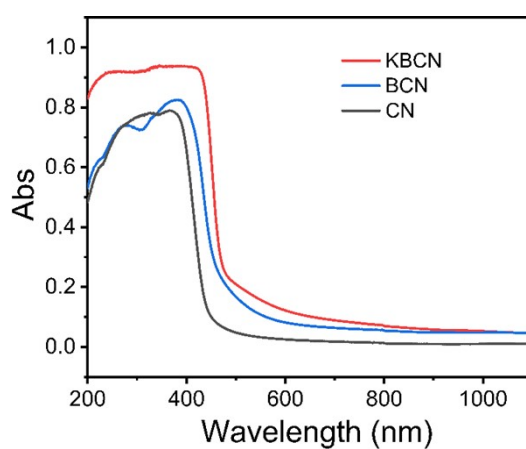


Fig. S8. UV-Vis spectra of CN, BCN and KBCN.

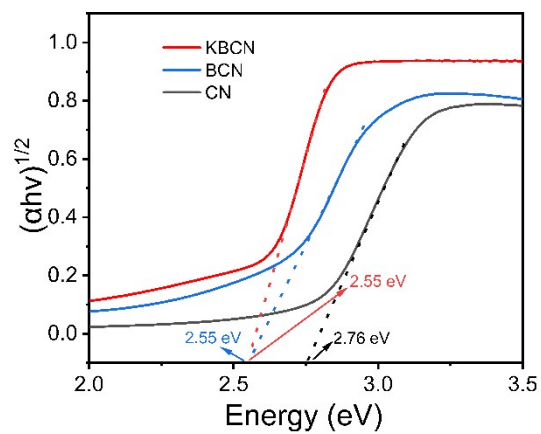


Fig. S9. Bandgaps of CN, BCN and KBCN.

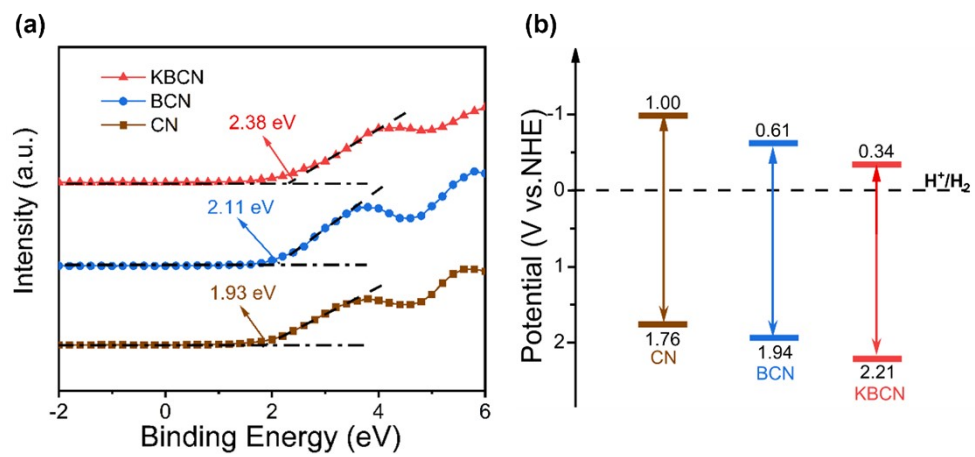


Fig. S10. (a) VB XPS spectra. (b) band structure of CN, BCN and KBCN.

Table S1 Pore volume and average pore size comparisons results for different catalysts

Samples	Pore volume (cm ³ /g)	Average pore size (nm)
CN	0.03	17.46
BCN	0.06	26.54
KBCN	0.09	10.15

Table S2. Different atomic contents

Samples	C atomic (%)	N atomic (%)	B atomic (%)	K atomic (%)
BCN	43.38	56.10	0.53	0
KBCN	44.30	53.29	0.64	1.77

Table S3 Comparison of carbon nitride-based photocatalysts for photocatalytic H₂ production.

Catalyst	Sacrificial reagents	Light source	H ₂ evolution rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	Reference
KPCN	10 vol.% TEOA	300 W Xenon lamp	1188	[1]
CNF-RSF	10 vol.% TEOA	300 W Xenon lamp	2589	[2]
3%KCN	20 vol.% TEOA	300 W Xenon lamp	1292.52	[3]
HC-C ₃ N ₅	10 vol.% TEOA	300 W Xenon lamp	3010	[4]
CM-K12	10 vol.% TEOA	300 W Xenon lamp	2555.6	[5]
MS-550	10 vol.% TEOA	300 W Xenon lamp	661	[6]
K10-TCN	20 vol.% TEOA	300 W Xenon lamp	941.6	[7]
UFR-NC0.02	20 vol.% TEOA	300 W Xenon lamp	1686	[8]
B-CNNT/CoP	10 vol.% TEOA	300 W Xenon lamp	784	[9]
BCNT-2	20 vol.% TEOA	36 W LED	53.2	[10]
KBCN	15 vol.% TEOA	10 W LED	2923	This work

Table S4 Kinetic parameters of the transient absorption decay of the sample at 375 nm excitation

Samples	Rel (%)	Lifetime, τ (ns)	Average Lifetime, τ (ns)	χ^2
CN	$A_1=42.41$	$\tau_1=2.16$	6.64	1.05
	$A_2=57.59$	$\tau_2=9.95$		
BCN	$A_1=55.18$	$\tau_1=2.04$	4.92	1.09
	$A_2=44.82$	$\tau_2=8.46$		
KBCN	$A_1=68.13$	$\tau_1=1.20$	2.60	1.32
	$A_2=31.87$	$\tau_2=5.59$		

Reference:

- [1] Y. Xu, C. Qiu, X. Fan, Y. Xiao, G. Zhang, K. Yu, H. Ju, X. Ling, Y. Zhu and C. Su, *Appl. Catal. B Environ. Energy*, 2020, **268**, 118457.
- [2] T. Xu, J. Hur, P. Niu, S. Wang, S. Lee, S.-E. Chun and L. Li, *Green Energy Environ.*, 2024, **9**, 890-898.
- [3] P. Song, B. Xu, Q. Yang, D. Wang and P. Yang, *Int. J. Hydrogen Energy*, 2024, **51**, 425-435.
- [4] Y. Shen, X. Du, Y. Shi, L. J. Nguetsa Kuate, Z. Chen, C. Zhu, L. Tan, F. Guo, S. Li and W. Shi, *Advanced Powder Materials*, 2024, **3**, 100202.
- [5] X. Lu, C. Yuan, S. Chen, J. Li, I. Ullah, M. Qi and A. Xu, *Langmuir*, 2024, **40**, 11067-11077.
- [6] J. Yang, Y. Liang, K. Li, G. Yang, K. Wang, R. Xu and X. Xie, *Appl. Catal. B Environ. Energy*, 2020, **262**, 118252.
- [7] X. Jin, H. Wang, X. Lv, Q. Lan, T. Ge, L. Guo, X. Li, H. Sun, C. Ding, Y. Guo, H. Xie and L. Ye, *J. Colloid Interface Sci.*, 2023, **652**, 1545-1553.
- [8] H. Che, G. Che, P. Zhou, C. Liu, H. Dong, C. Li, N. Song and C. Li, *Chem. Eng. J.*, 2020, **382**, 122870.
- [9] Y. Jiao, Y. Li, J. Wang, Z. He and Z. Li, *J. Colloid Interface Sci.*, 2021, **595**, 69-77.
- [10] S. Zhang, C. An, R. Zhang, D. Kong, D. Xu and S. Zhang, *Langmuir*, 2024, **40**, 6453-6462.