

Supplementary Information

Cyano&potassium-rich g-C₃N₄ hollow tubes for efficient visible-light-driven hydrogen evolution

*Jian Yang^a, Yujun Liang^{a, *}, Kai Li^b, Gui Yang^a, Kun Wang^a, Rui Xu^b, Xianjun Xie^{b, *}*

^a Engineering Research Center of Nano-Geomaterials of Ministry of Education, Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, China

^b State Key Laboratory of Biogeology and Environmental Geology & School of Environmental Studies, China University of Geosciences, Wuhan 430074, China

***Corresponding author:** Tel.: +86 27 67884814; fax: +86 27 67883733.

E-mail address: yujunliang@sohu.com (Yujun Liang)

xjxie@cug.edu.cn (Xianjun Xie)

Experimental section

Preparation of photocatalysts

All reagents used in this work were of analytical reagent grade and without further purification. In a typical process, 1 g melamine was fully ground together with 5 g of eutectic mixture of LiCl and KCl (in molar ratio of 59:41, with the eutectic point of 352 °C (Fig. S7))¹ in an agate mortar more than 15 min to obtain a homo-disperse mixture. After that, the grinded mixture was placed in an alumina crucible which covered and wrapped with aluminium-foil paper, and then annealed in a muffle furnace at 450 °C for 4 h with a heating rate of 5 °C/min. After cooling down naturally to room temperature in the furnace, the obtained samples were washed with hot deionized water and ethanol for several times, and then dried at 80 °C overnight. Finally, the as-prepared sample was denoted as T-CN.

For the sake of comparison, the bulk g-C₃N₄ was also prepared by a conventional thermal polymerization route. Briefly, 1 g melamine was placed in the crucible with a ceramic lid and heated at 520 °C for 4 h with a heating rate of 5 °C/min. The resultant product was simply designated as B-CN.

Characterization

Powder X-ray diffraction (XRD) data of the as-prepared samples were collected on an X-ray diffractometer (D8-FOCUS, Bruker, Germany) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra in the wavenumber range of 4000-500 cm⁻¹ were recorded on a Nicolet 6700 spectrometer with KBr pellet (Thermo scientific, USA). The morphology and microstructure observation were

examined by field emission scanning electron microscope (FE-SEM, SU8010, Hitachi, Japan) and transmission electron microscope (TEM, Tecnai G2 T20, FEI, America). Meanwhile, the energy-dispersive X-ray spectroscopy (EDS) spectra and elemental mapping images were collected in an EDAX Genesis, which was attached to the FE-SEM. The N₂ adsorption/desorption isotherms at 77 K were conducted on an automatic surface area analyzer (MicroActive for ASAP 2460, America), and the specific surface areas of as-prepared samples were measured using the Brunauer-Emmett-Teller (BET) method. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo Scientific Escalab 250X spectrometer equipped with an Al K α X-ray source. UV-vis diffuse reflectance spectra (DRS) were tested on an UV-2550PC spectrophotometer (Shimadzu Corporation, Japan), using BaSO₄ as the reflectance standard. The photoluminescence (PL) spectra of photocatalysts were measured by a fluorescence spectrometer (Fluoromax-4P, Horiba Jobin Yvon, New Jersey, USA), which was equipped with a 150 W xenon lamp as the excitation source.

Photocatalytic H₂ evolution

The photocatalytic H₂ production experiments were conducted in a sealable quartz reactor with top visible light irradiation. A 300 W Xe lamp with a cut-off filter ($\lambda > 420$ nm) was used as the visible light source, and the fixed light-to-liquid distance was 10 cm. In detail, 100 mg of the as-prepared sample was dispersed in 100 mL aqueous solution containing 10 vol% triethanolamine (TEOA) as the sacrificial agent for the holes, and 3 wt% Pt as the cocatalyst was loaded on the surface of catalyst by the conventional in situ photodeposited method using H₂PtCl₆·6H₂O. The mixture

solution was continuously stirred by a magnetic stirrer. Before visible light irradiation, the reactant system was purged by N₂ for 30 min to remove air. The amount of H₂ evolution was analyzed by a gas chromatograph (GC7900, Techcomp) equipped with a thermal conductivity detector.

Mott-Schottky measurement

The Mott-Schottky plots were collected on a standard three-electrode electrochemical analyzer (CHI760E, Shanghai). The as-prepared sample coated onto the FTO electrode was served as the working electrode, an Ag/AgCl (saturated KCl) as the reference electrode, and a Pt foil as the counter electrode. The Na₂SO₄ (0.1 M) solution and 300 W Xe lamp were employed as electrolyte and light source, respectively. The working electrodes were prepared according to previously reported method²: 5 mg of photocatalyst powder and 10 μL of Nafion solution (5 wt%) were dispersed into 100 μL isopropanol and 300 μL water, and then ultrasonic treatment for 1 h to prepare a homogeneous catalyst colloid. Finally, the resultant catalyst slurry was coated onto the precleaned FTO glass surface with an active area of ca. 1.00 cm × 1.00 cm and then dried in air.

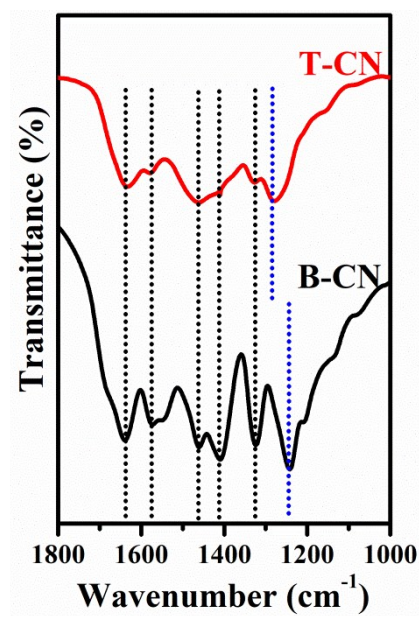


Fig. S1 The enlarged version of FT-IR spectra of B-CN and T-CN.

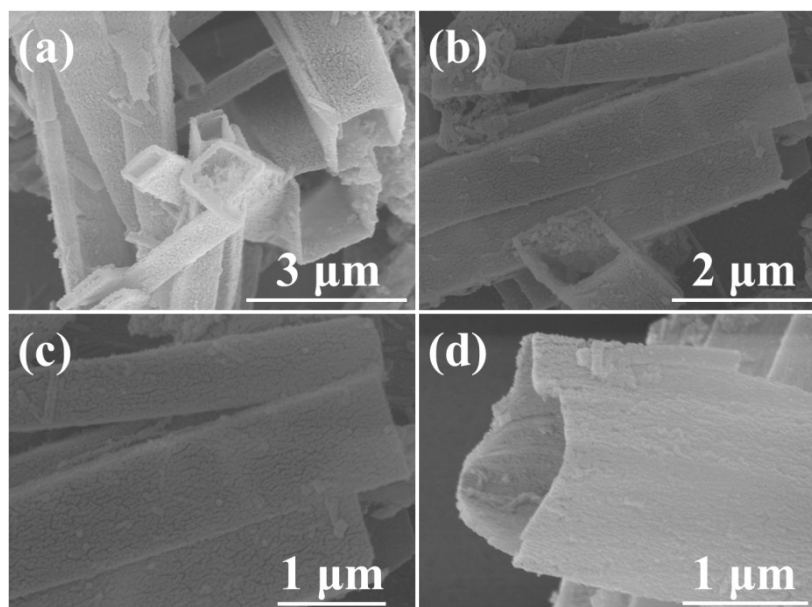


Fig. S2 Typical SEM images of T-CN.

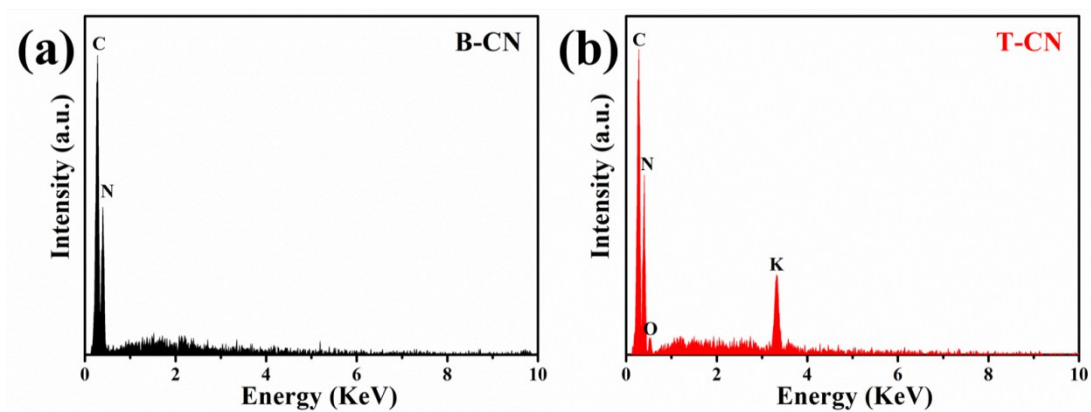


Fig. S3 EDS spectra of (a) B-CN and (b) T-CN.

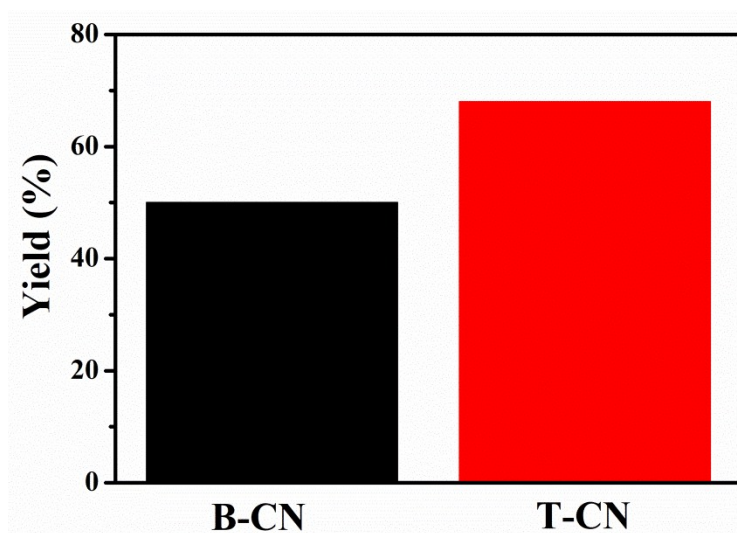


Fig. S4 Comparison of typical yields of as-prepared photocatalysts via the different processes.

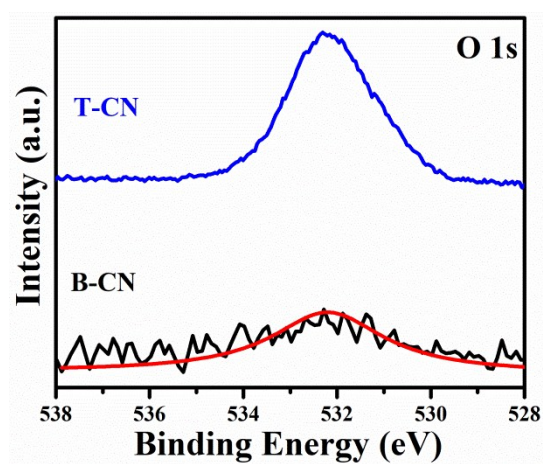


Fig. S5 High-resolution XPS spectra of O 1s region for B-CN and T-CN, respectively.

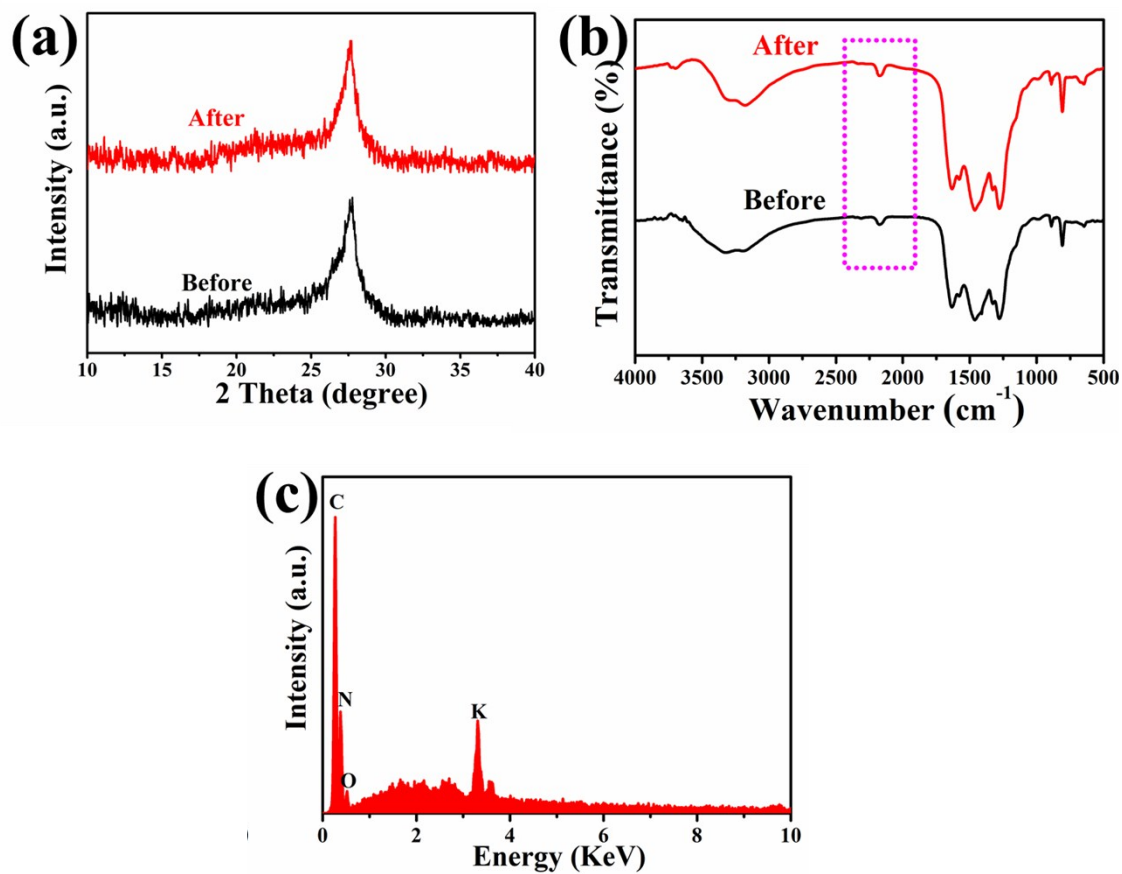


Fig. S6 (a) XRD, (b) FTIR and (c) EDS spectra of T-CN before and after cycling tests for H₂ production under visible light irradiation

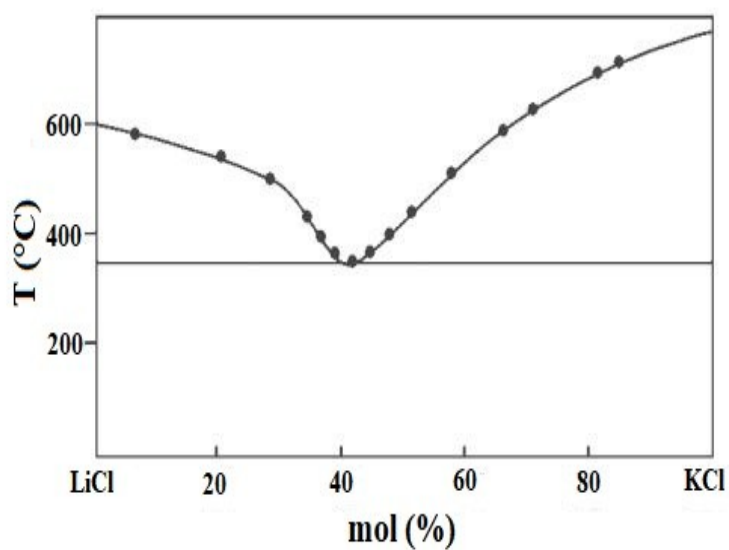


Fig. S7 The binary phase diagram of KCl-LiCl.

Table S1 Elemental compositions of B-CN and T-CN as determined by EDS.

Samples	C (At%)	N (At%)	O (At%)	K (At%)
B-CN	42.54	56.51	0.95	—
T-CN	38.51	52.33	6.61	2.55

The elemental compositions of B-CN and T-CN as measured by EDS are summarized in Table S1. The atomic ratios of C/N for two samples were almost identical (for 0.753 B-CN and 0.736 for T-CN), and the oxygen content of T-CN was higher than that of B-CN, which was consistent with the XPS results.

References

- 1 X.F. Liu, N. Fechler and M. Antonietti, *Chem. Soc. Rev.*, 2013, **42**, 8237-8265.
- 2 G.G. Liu, G.X. Zhao, W. Zhou, Y.Y. Liu, H. Pang, H.B. Zhang, D. Hao, X.G. Meng, P. Li, T. Kako and J.H. Ye, *Adv. Funct. Mater.*, 2016, **26**, 6822-6829.