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Supporting Information

Boron dopant simultaneously achieving nanostructure control and electronic structure tuning of graphitic carbon nitride with enhanced photocatalytic activity

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Experimental

Preparation of boron doped carbon nitride (BCN)

BCN was fabricated by a two-step thermal treatment process. Specifically, 10 g of urea and different amount of H_3BO_3 (1, 5, and 10 mg) were dissolved in 10 mL of Milli-Q water under magnetic stirring at 80 °C. When the water was evaporated, the mixture was kept in an oven at 150 °C for 3 h. During this process, the solid mixture was melted into a liquid state. Subsequently, the liquid material was transferred into a porcelain boat with a cover, followed by heating at 500 °C in a tube furnace for 3 h with the continue flow of N_2, and the obtained BCN was ground to fine powder. The obtained samples with different H_3BO_3 contents in the precursor were denoted as BCNx (x refers to the amount of H_3BO_3 in the precursor). To investigate the effect of preheating temperature, 10 g of urea and 5 mg of boric acid were added into a beaker and heated at 100, 150, 180 °C for 3 h, while the subsequent calcination process was kept the same. The obtained samples were denoted as BCN-y (y refers to the preheating temperature). To investigate the impact of the preheating time on the samples, 10 g of urea and 5 mg of boric acid were added into a beaker and heated at 150 °C for 1, 2, 3, and 4 h, while the subsequent calcination process was unchanged. The obtained samples were denoted as BCN-t (t refers the preheating time).

Preparation of pure g-C_3N_4

To compare the influence of boric acid on the morphology, crystal structure, electronic structure and photocatalytic properties of g-C_3N_4, pure g-C_3N_4 without boric acid was also prepared. In the absence of boric acid, pristine g-C_3N_4 was prepared by directly placing 10 g of urea in an oven at 150 °C for 3 h, followed by annealing in a tube furnace at 500 °C for 3 h in with the continue flow of N_2, and the product was denoted as CN.

Preparation of B-doped g-C_3N_4 without preheating treatment (BCN5-U)

To demonstrate the effect of preheating treatment, 10 g of urea and 5 mg of H_3BO_3 were firstly dissolved in 10 mL of Milli-Q water. After being magnetic stirred at 80 °C until the water was evaporated, the precursor was directly annealed at 500 °C in a tube furnace for 3 h with the continue follow of N_2 without the preheating process. The product was denoted as BCN5-U.

Characterization

Morphologies of the samples were characterized by field emission scanning electron microscopy (FESEM, Zeiss Gemini 300) and transmission electron microscopy (TEM, FEI TalosF200x). Phase structures of the samples were confirmed by powder X-ray diffraction (XRD, D8 Advance, Bruker) with Kα (λ=0.15406 nm) radiation. Micromeritics Tristar 3000 was applied to collect the N_2 adsorption/desorption isotherm curves of the samples to calculate their specific surface areas. An X-ray photoelectron spectroscope (XPS) equipped with an Al Kα (hν=1253.6 eV) radiation source was applied to analyze the elemental compositions and surface chemical states. Fourier transform infrared (FTIR) spectra of the samples were collected on a Thermo Scientific Nicolet iS5 spectrometer. Solid-state nuclear magnetic resonance spectrometry (Bruker BioSpin GmbH, 10000Hz) was used to measure ^{13}C NMR spectra of the samples. Photoluminescence (PL) spectra at room temperature were recorded using a fluorescence spectrophotometer (FLS-1000, Edinburgh Instruments) using an excitation light of 370 nm. A spectrophotometer (UV-2600i, Shimadzu) was carried out to measure the UV-vis absorption spectra of all samples.

Photocatalytic hydrogen evolution

Photocatalytic H_2 production performances of the samples were assessed in a photocatalytic activity evaluation system (Beijing China Education Au-Light Co., Ltd., CEL-PAEM-D8). A Xenon arc lamp (350 nm$<\lambda<$780 nm) was served as the light source for the photocatalytic test. Specifically, 50 mg of the photocatalyst was dispersed into 60 mL of an aqueous solution comprising 20 mL of methanol and 40 mL of deionized water. Before the photocatalytic test, the system was firstly extracted for 20 min to remove the air inside, followed by light illumination for 10 min to deposit the platinum (Pt) cocatalyst onto the photocatalyst surface in the presence of a H_2PtCl_6 aqueous solution. The loading amount of Pt cocatalyst was controlled to be 1 wt%. The reactor under light illumination was magnetically stirred during the entire experiment. Gas chromatography (Beijing China Education Au-Light Co., Ltd., GC-7920) was used to measure the amount of hydrogen every hour for a total of five measurements controlled by the software.

The apparent quantum efficiency (AQE) for hydrogen production was tested under the illumination of a monochromatic light at 420 nm. The AQE value was calculated based on the following equation: AQE (%) $=N_e/N_p \bullet 100\% = 2MN_Ahc/SPt\lambda \bullet 100\%$,[1] where N_e is the number of reacted electrons, while N_p refers to the amount of incident photons. N_e and N_p can be calculated by the amount of hydrogen generated (M, mol), the Avogadro constant ($N_A=6.02\times10^{23}$), the Planck constant ($h=6.63\times10^{-34}$ J·s), the speed of light (c), the exposed area for light illumination ($S=19.6$ cm^2), the power density of the incident light (P), the irradiation time (t), and the wavelength of the monochromatic light ($\lambda=420$ nm).

Photoelectrochemical measurements

All photoelectrochemical (PEC) performances were evaluated in a three-electrode cell using Ag/AgCl (saturate KCl) as the reference electrode and Pt as the counter electrode. An electrochemical workstation (CHI700e, CH Instruments, Inc) was used to set the testing modes. 1 mg of the sample and 20 μL of the Nafion solution were added into 1 mL of ethanol, followed by ultrasonication for 20 min to make a uniform slurry. The slurry was deposited on a fluorine doped SnO_2 (FTO) glass substrate by a drop casting process. After air dried, the obtained working electrodes were thermal treated at 300 °C for 2 h in a Muffle furnace. The electrolyte was prepared by adding 0.1 mol of Na_2SO_4 (Sigma-Aldrich, 99.5%) and 0.02 mol of Na_2SO_3 (Sigma-Aldrich, 98%) into 100 mL of Milli-Q water. Electrochemical impedance spectroscopy (EIS) plots were collected with an AC voltage amplitude of 10 mV at the open circuit potentials of the electrodes in the dark (frequency range: 0.01 Hz~100 kHz). Photocurrent responses were obtained at the open circuit potential under light illumination for 400 s with an interval of 50 s every 50 s. During all experiments, light was illuminated through an AM 1.5 G filter with an intensity of ca. 100 mW cm^{-2} calibrated by a thermopile optical detector (Beijing China Education Au-Light Co., Ltd.).

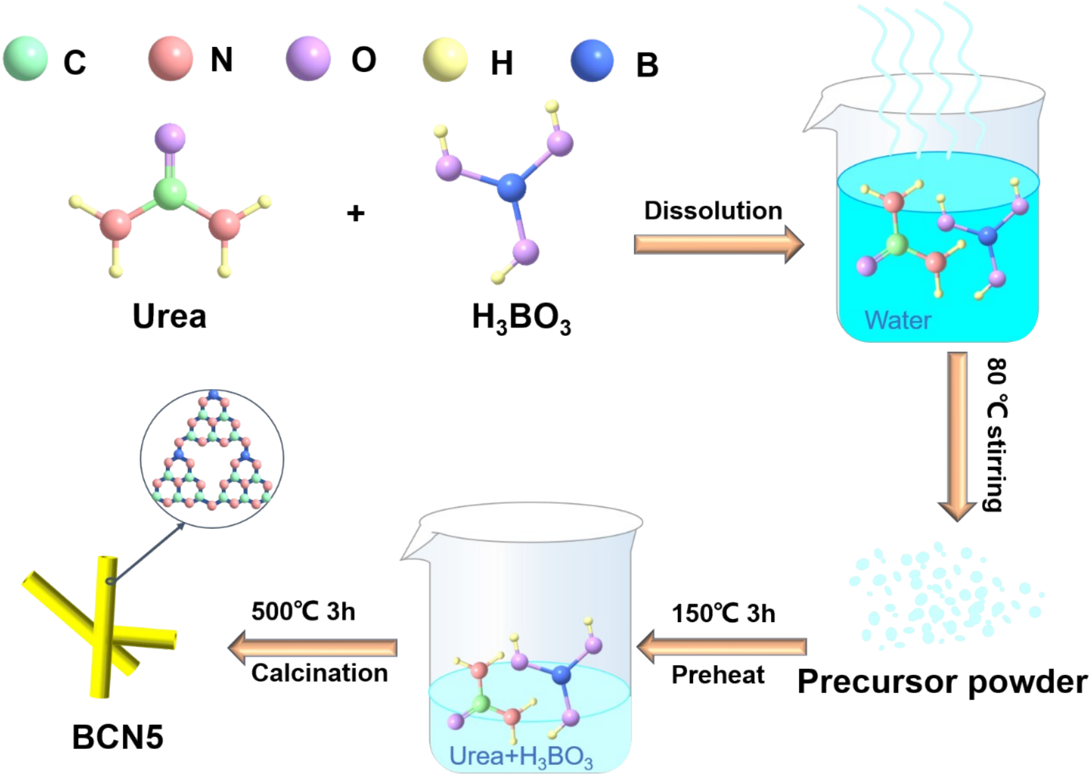

Fig. S1. Scheme of preparation procedure for BCN5.

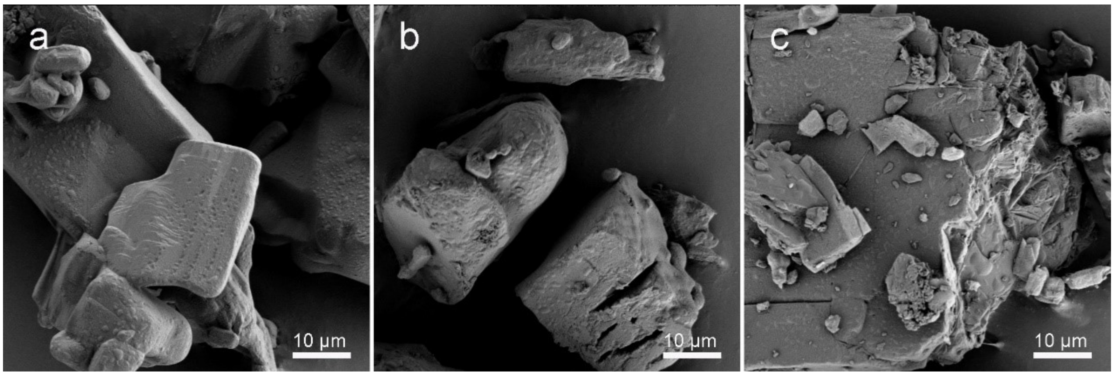

Fig. S2. SEM images of the unannealed precursor samples: (a) P1, (b) P2, and (c) P3.

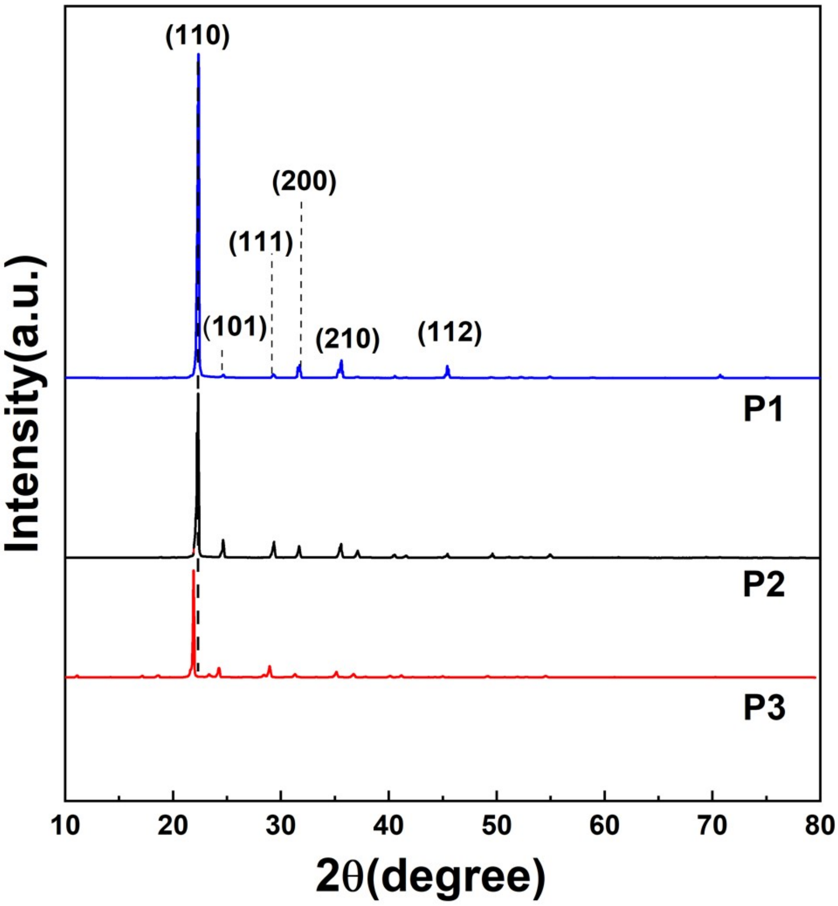

Fig. S3. XRD patterns of P1, P2 and P3.

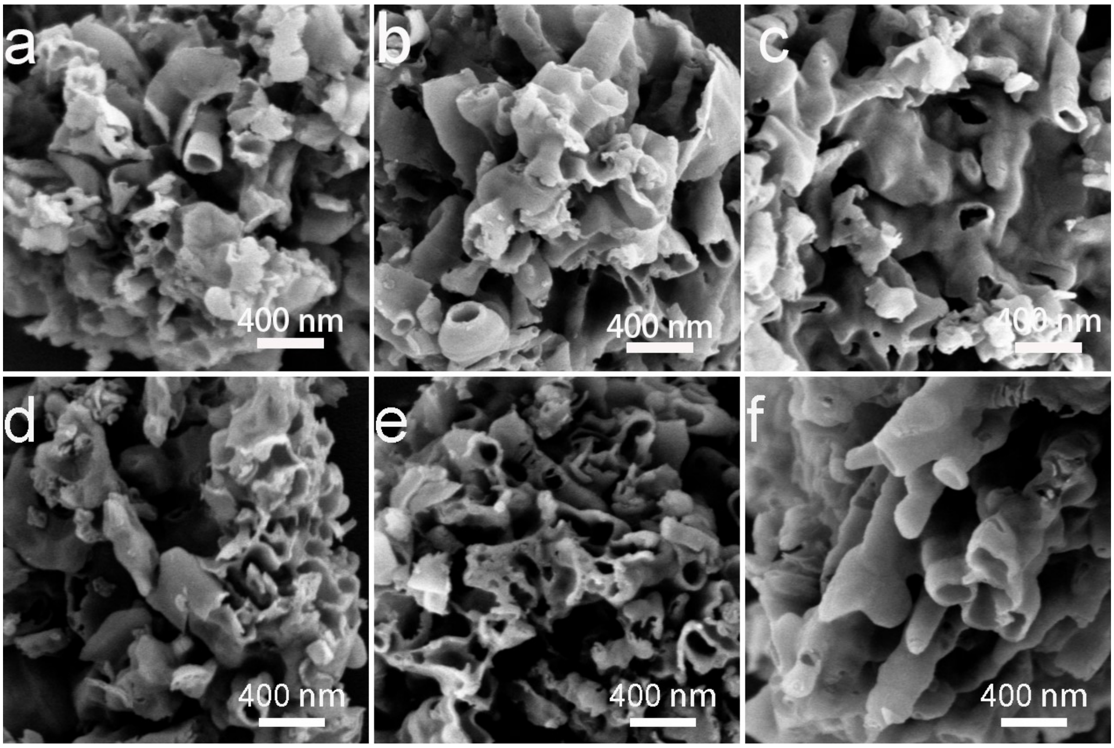

Fig. S4. SEM images of (a) BCN5-100°C, (b) BCN5-180°C, (c) BCN5-U, (d) BCN5-1h, (e) BCN5-2h and (f) BCN5-4h.

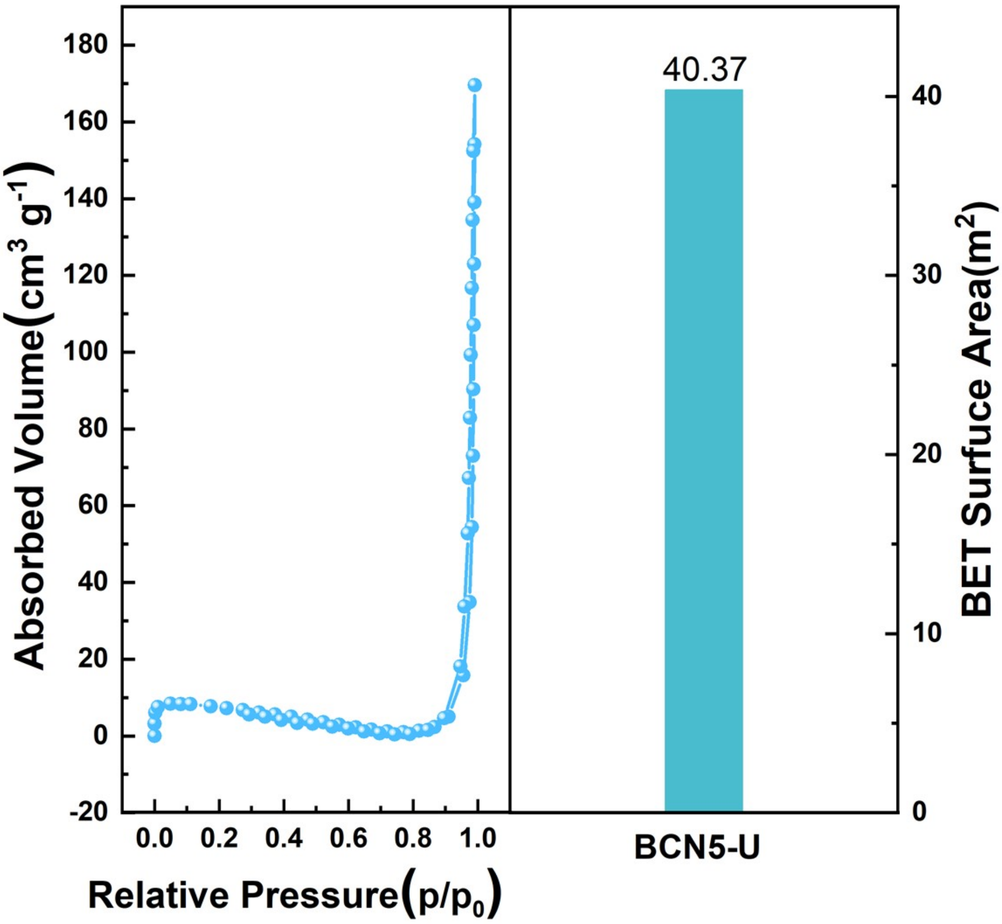

Fig. S5. N_2 adsorption and desorption isotherms and BET surface area of BCN5-U.

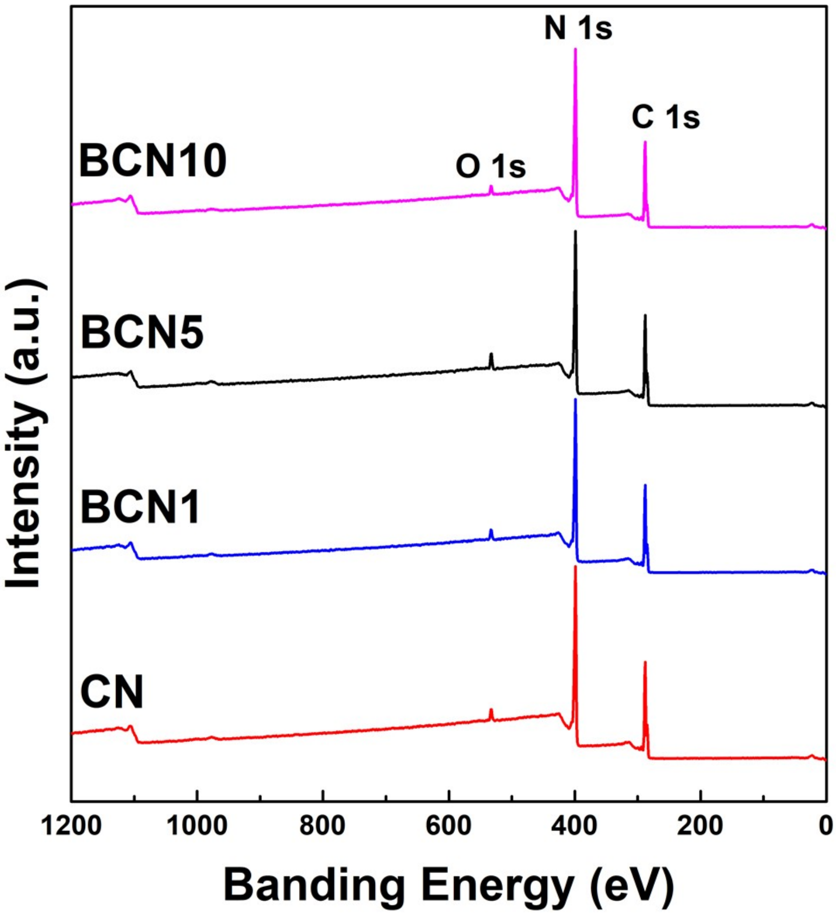

Fig. S6. XPS survey spectra of CN, BCN1, BCN5 and BCN10.

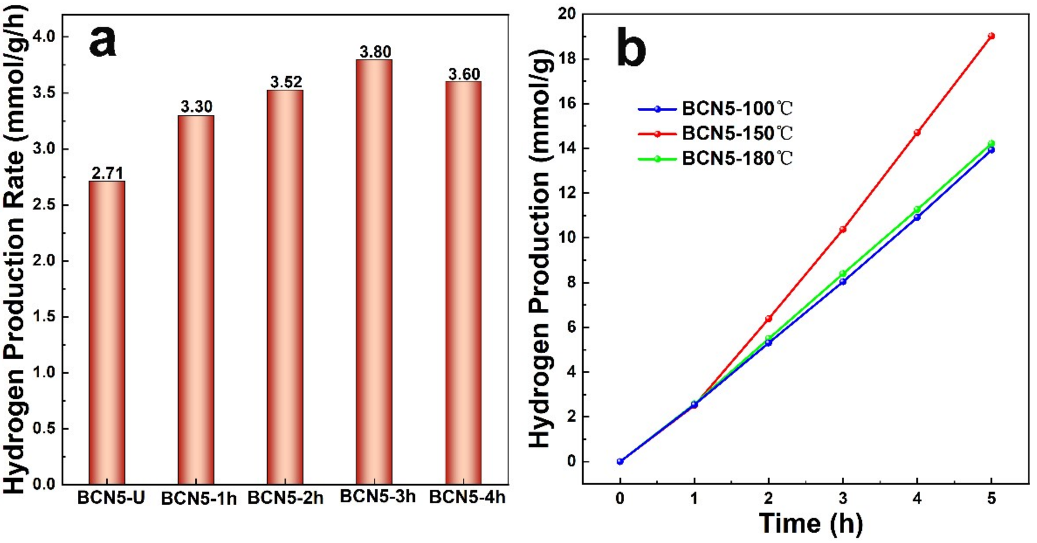

Fig. S7. (a) Photocatalytic hydrogen production rates of BCN5-U, BCN5-1h, BCN5-2h, BCN5-3h and BCN5-4h. (b) Photocatalytic hydrogen evolution plots of BCN5-100°C, BCN5-150°C and BCN5-180°C.

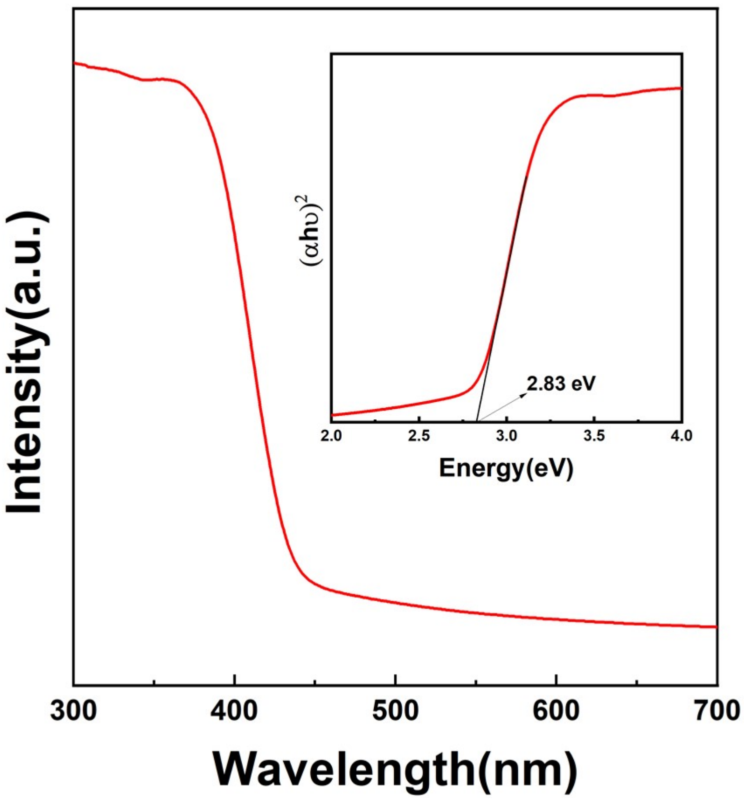

Fig. S8. UV-vis light absorption curves and estimated bandgaps of BCN5-U.

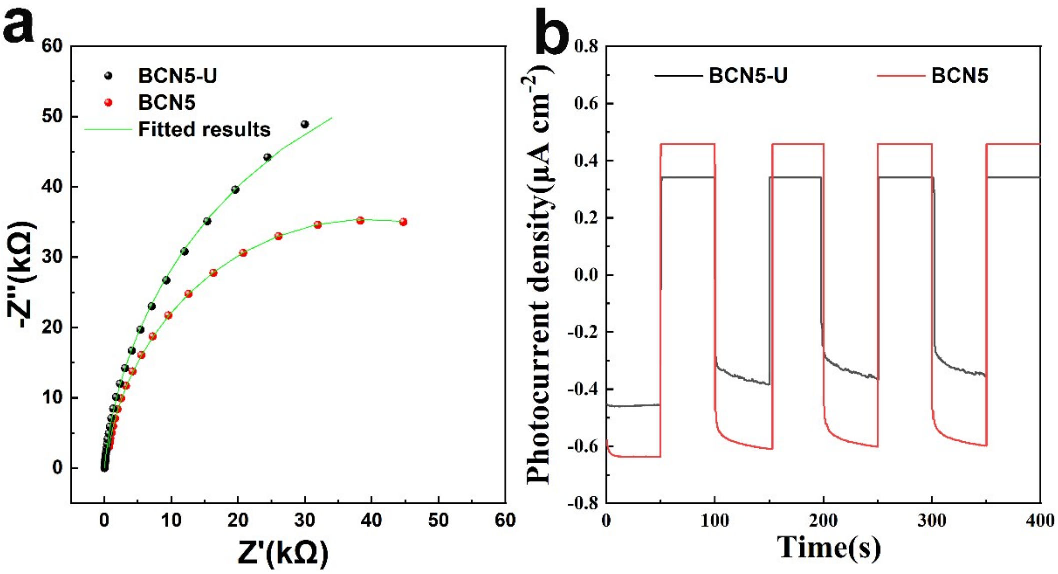

Fig. S9 (a) EIS spectra and (b) transient photocurrent responses of BCN5 and BCN5-U.

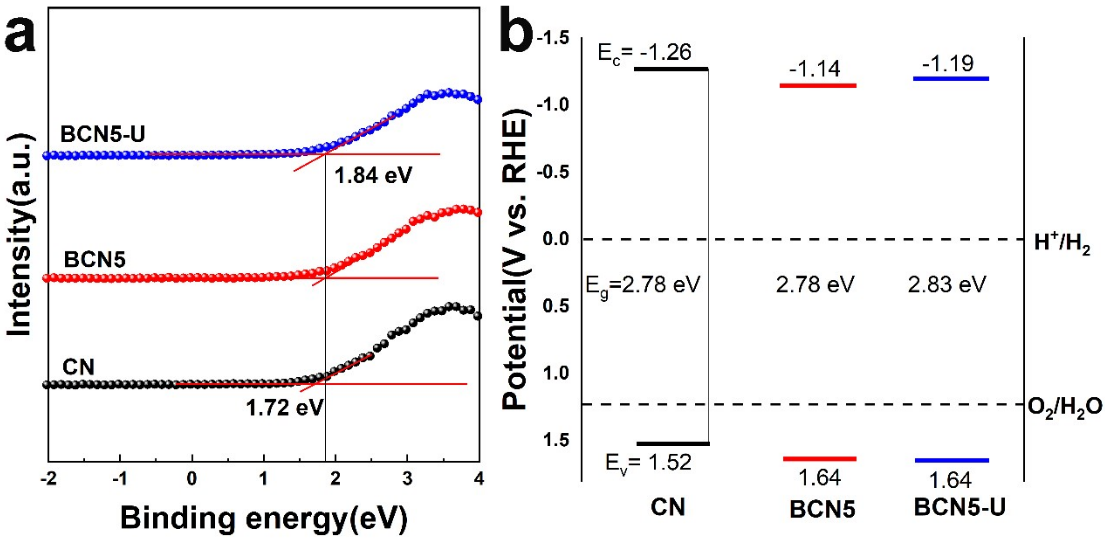

Fig. S10. (a) VB XPS spectra and (b) band structure alignments of CN, BCN5 and BCN5-U.

Table S1. H_2 evolution rate and AQE of g-C_3N_4 nanostructures in recent publications.

Composition	H_2 evolution rate	AQE	Year	Reference
B-doped g-C_3N_4	**3.8 mmol g^{-1} h^{-1}**	**14.46% at 420 nm**	**This work**	
CdS/g-C_3N_4	1.81 mmol g^{-1} h^{-1}	2.79% at 420 nm	2021	2
Ni-doped Ni_3C/g-C_3N_4	1.128 mmol g^{-1} h^{-1}	1.49% at 420 nm	2021	3
$NiL_2(Cl)_2$/g-C_3N_4	1.916 mmol g^{-1} h^{-1}	6.68% at 450 nm	2021	4
CoP/B-doped g-C_3N_4	0.784 mmol g^{-1} h^{-1}	5.32% at 420 nm	2021	5
NiS/$Zn_3In_2S_6$/g-C_3N_4	4.135 mmol g^{-1} h^{-1}	24.3% at 420 nm	2021	6
HOF/Pt-g-C_3N_4	2.264 mmol g^{-1} h^{-1}	5.56% at 420 nm	2021	7
C-doped g-C_3N_4	5.549 mmol g^{-1} h^{-1}	3.8% at 420 nm	2021	8
NiCo-LDH/g-C_3N_4-pDA	1.56 mmol g^{-1} h^{-1}	7.5% at 400 nm	2021	9
MoS_2/P-doped g-C_3N_4	1.741 mmol g^{-1} h^{-1}	5.03% at 420 nm	2021	10
Mesh-like g-C_3N_4	2.746 mmol g^{-1} h^{-1}	13.5% at 400 nm	2021	11

Table S2. R_{ct} of CN, BCN1, BCN5, BCN10 and BCN5-U.

Sample	R_{ct} (Ω)
CN	257250
BCN1	206850
BCN5	79245
BCN10	823380
BCN5-U	124840

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