Supporting Information

Photocatalytic green synthesis of benzazoles from alcohol oxidation/toluene sp^3 C-H activation over metal-free BCN: effect of crystallinity and N-B pairs exposure

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1. Materials

All the reagents were commercially available and used without further purification. Boron acid was purchased from Alfa Aesar. Urea, glucose, N,N-dimethylformamide (DMF), dichloroethane (DCE), tetrahydrofuran (THF) methanol, acetonitrile, benzene were supplied by Sinopharm Chemical Reagent Co. Ltd., China. All the reagents were used as received.

2. Characterization Methods

Powder X-ray diffraction (XRD) patterns were carried out with a LynxEye array detector/Bruker D8 Advance (10-80º). Fourier transform infrared (FT-IR) spectra were obtained on the IRPrestige-21 instrument (500-3500 cm-1). The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed on a Hitachi S-4800 and JEOL JEM-2100F, respectively. Micromeritics ASAP 2020M automatic surface analyzer was used for BET analysis of the samples. X-ray photoelectron spectroscopy (XPS) was measured on UIVAC-PHI 5000 VersaProbe using monochromatized Al Kα X-ray source, in which all of the binding energies were calibrated with reference to the C 1s peak (284.8 eV). Photoluminescence (PL) spectra were tested with the Hitachi F-7000. UV–vis diffuse reflectance spectra (UV–vis DRS) were tested with a Hitachi UH4150 UV–vis DRS

to investigate the optical properties of the samples (200-800 nm). The photoelectrochemical measurements were carried out on an electrochemical workstation (CHI730E, Shanghai Chenhua Limited, China). Electrochemical System was conducted in a conventional three electrode cell, using a Pt sheet as the counter electrode, Ag/AgCl as the reference electrode and 0.5 M Na_2SO_4 aqueous solution as the electrolyte. The working electrode was prepared on fluorine-tin oxide (FTO) glass. The 5 mg sample was totally dispersed in DMF (1 mL) by sonication to gain slurry. Afterward, the resultant slurry was spread onto the FTO glass. Then, the working electrode was dried in the air for 12 h and further dried at 393 K for 2 h to improve adhesion. The frequency used for the EIS analysis is 100 mHz-100 KHz, and Mott–Schottky (M–S) plots were measured at a frequency of 1000 Hz. Electron paramagnetic resonance (EPR) measurement was carried out with Bruker model A300 spectrometer.

3. Catalyst preparation

BCN [1]: With boric acid, urea and glucose as raw materials, BCN with adjustable band gap were synthesized by changing the amount of glucose. 10 g borate, urea, and glucose with different weights (weight ratios: 4:4:2, 3:3:4 and 2:2:6) was well mixed in 70 ml distilled water. The water was evaporated to get white precursor. Then, the precursor was placed in a horizontal tube furnace and heated at 1000 ^oC for 5 h under a nitrogen atmosphere with a 5 ^oC/min heating rate. After natural cooling, grind to powder, 5% hydrochloric acid wash to remove excessive boric acid or boron oxide as well as 60 ^oC vacuum drying, the BCN was obtained. The obtained catalysts were named BCN-A for weight ratio 4:4:2, BCN-B for weight ratio 3:3:4 and BCN-C for weight ratio 2:2:6, respectively.

P-BCN: Porous BCN were prepared by KCl-assisted molten salt method. 3 g boric acid, 3 g urea, 4 g glucose, 2 g potassium chloride were dissolved in 70 ml distilled water. The water was evaporated to get white precursor. Then, the precursor was placed in a horizontal tube furnace and heated at 1000 ^oC for 5 h under a nitrogen atmosphere with a 5 ^oC/min heating rate. After natural cooling, grind to powder, 5% hydrochloric acid wash to remove KCl, excessive boric acid or boron oxide, as well as 60 ^oC vacuum drying, the P-BCN was obtained.

4. Photocatalytic reaction

The reaction was performed in a sealed reaction tube under blue light irradiation. 10 mg catalyst was weighted into the tube, and then 0.1 mmol *o*-aminobenzenethiol, 0.3 mmol benzyl alcohol and 2 ml DMF were added into the sealed tube. After the reaction, the mixture was centrifuged and filtered, the products were analysed with LC and LC-MS.

5. Structure and optical characterization of BCN

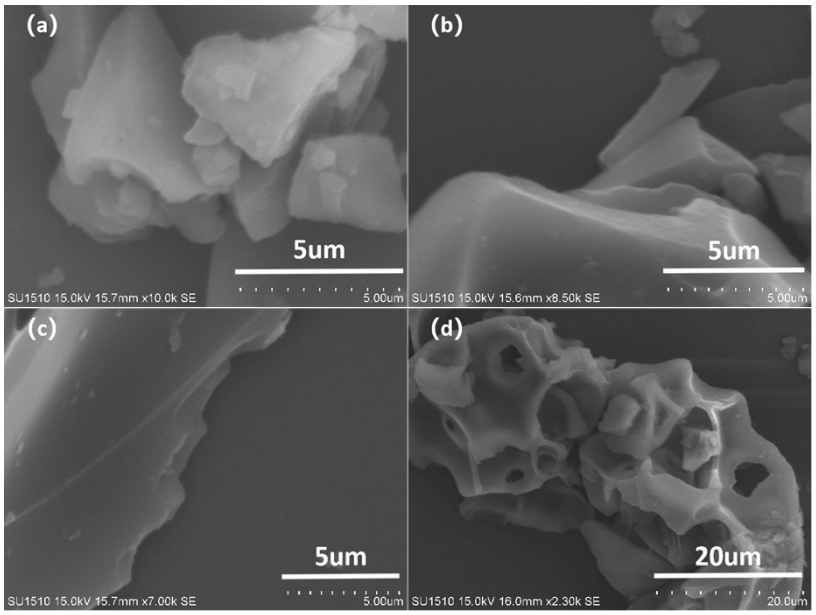


Figure S1. SEM images of BCN-A (a), BCN-B (b), BCN-C (c) and P-BCN (d).

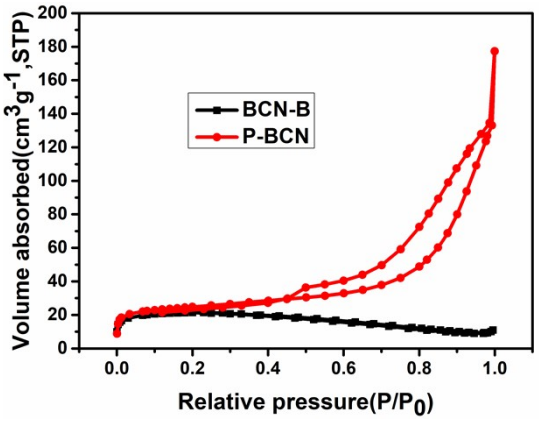


Figure S2. N_2-sorption isotherms collected at 77 K.

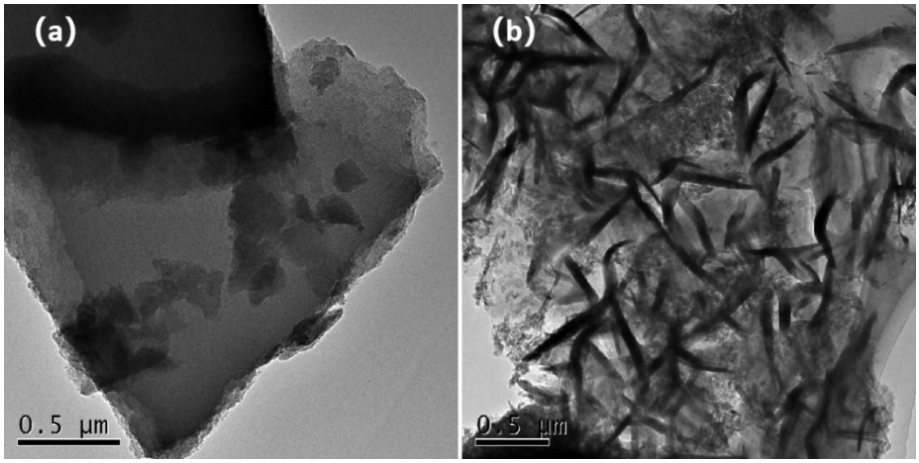


Figure S3. TEM images of BCN-B (a) and P-BCN (b).

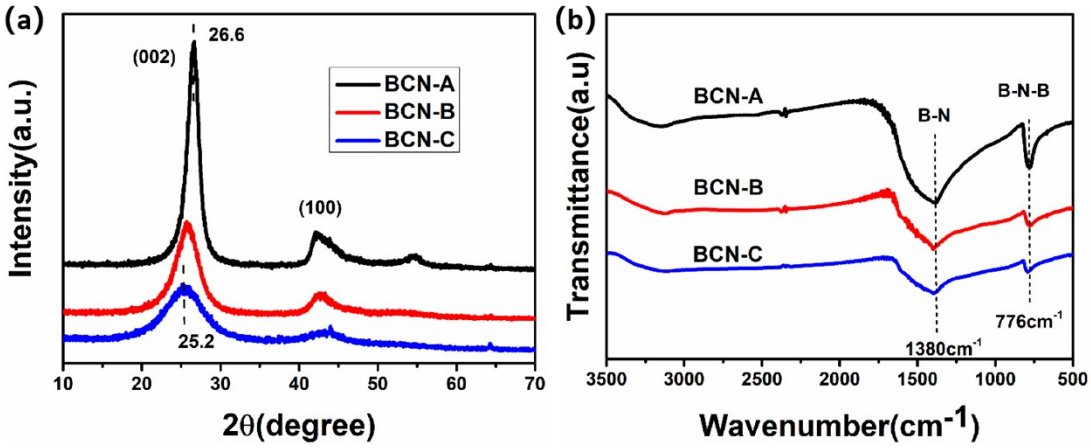


Figure S4. (a) X-ray diffffraction (XRD) patterns of BCN-A, BCN-B and BCN-C. (b) FTIR spectra of BCN-A, BCN-B and BCN-C.

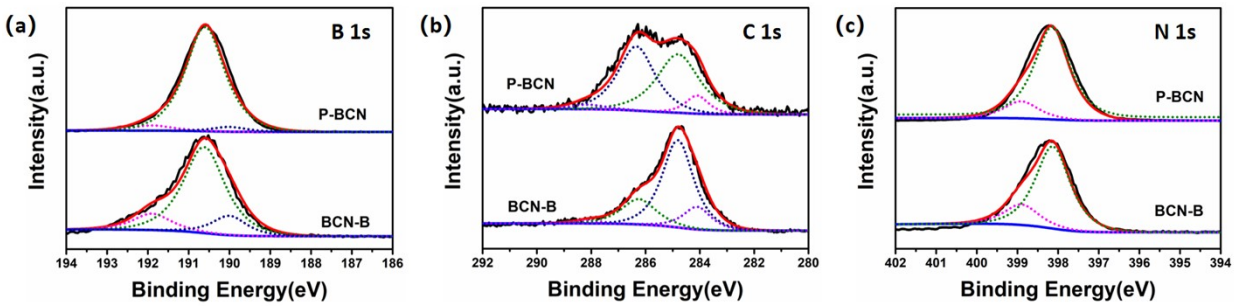


Figure S5. B 1s (a), C 1s (b), and N 1s (c) XPS characterization of BCN-B and P-BCN.

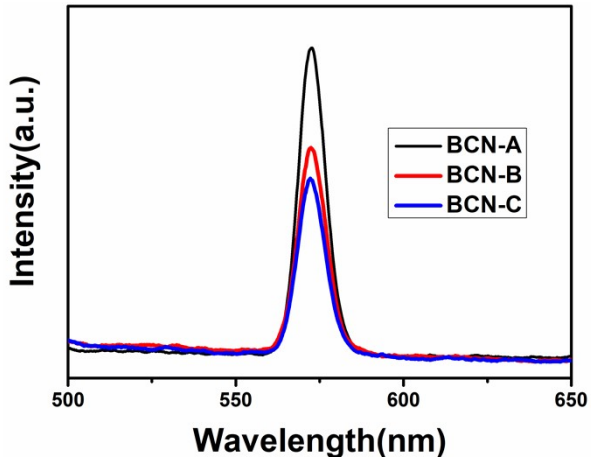


Figure S6. PL spectra of BCN-A, BCN-B and BCN-C with 390 nm excitation.

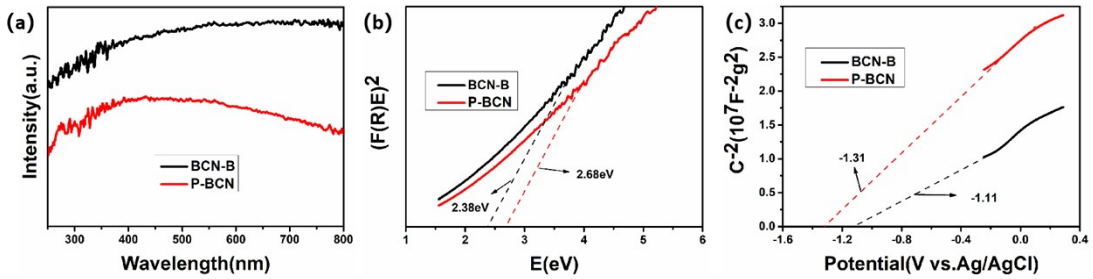


Figure S7. (a) Uv-visible absorption spectra of BCN-B and P-BCN. (b) The Tauc plots of BCN-B and P-BCN *vs* photon energy. (c) The BCN-B and P-BCN conduction band determination with Mott-Schottky method in 0.5 M Na_2SO_4 aqueous solution at 1.0 KHZ in the dark.

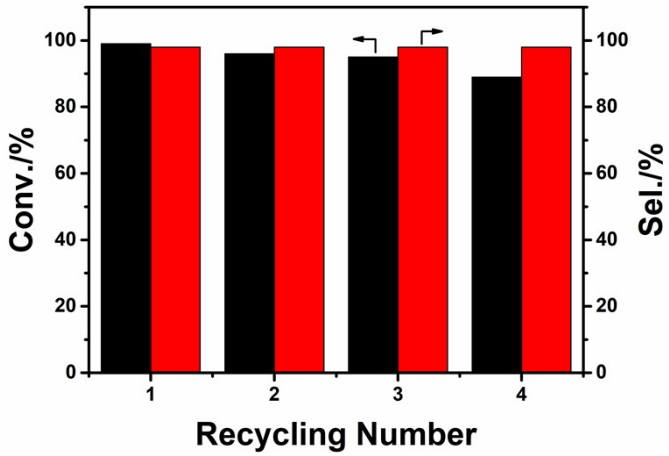


Figure S8. Recycle experiment of *o*-aminothiophenol and benzyl alcohol oxidative condensation to produce 2-phenylbenzothiazole over P-BCN.

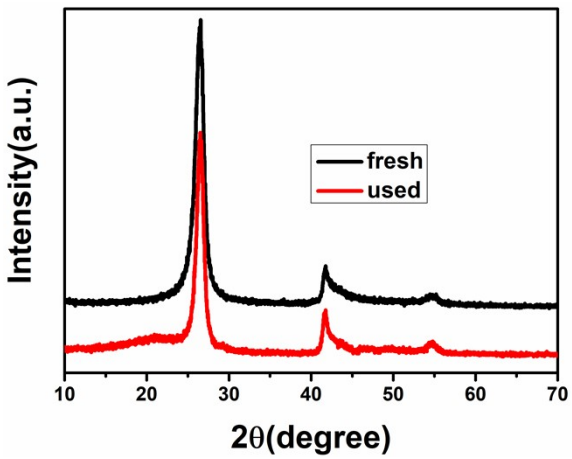


Figure S9. XRD patterns of fresh and used P-BCN.

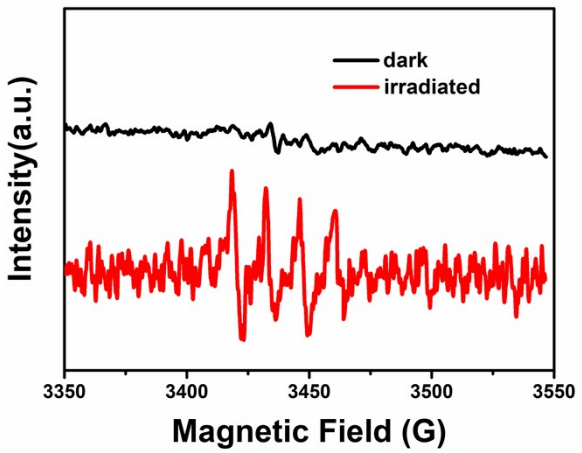


Figure S10. P-BCN EPR measurement with 5,5-dimethyl-1-pyrroline Noxide (DMPO) as the spin trapper, the spectra were taken after the 10 min irradiation.

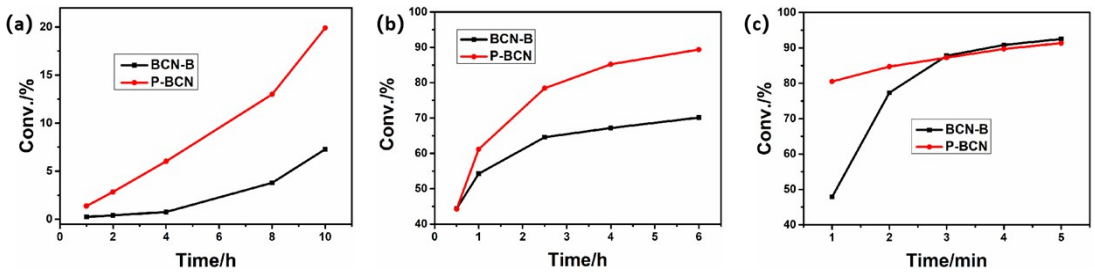
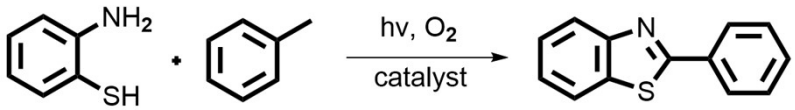


Figure S11. Control experiment over BCN-B and P-BCN: (a) Toluene oxidized to benzaldehyde. (b) Benzyl alcohol oxidized to benzaldehyde. (c) 2-phenylbenzothiazole preparation with benzaldehyde and *o*-aminobenzenethiol.

Table S1. The element content in the BCN materials.

Sample	Boron (wt.%)	Carbon (wt.%)	Nitrogen (wt.%)	Oxygen (wt.%)
BCN-B	35.3%	26.5%	26.1%	12.1%
P-BCN	50.1%	3.2%	42.2%	4.5%

Table S2. Reaction conditions optimization for the 2-phenylbenzothiazole formation with *o*-aminobenzenethiol and toluene. [a]



1a 6a 7a

Entry	Catalyst	Solvent	Time/h	Conv. of 1a/(%)[b]	Sel./%
1	P-BCN	DCE	24	19	97
2	P-BCN	benzene	24	6	98
3	P-BCN	CH_3CN	24	2	97
4	P-BCN	Toluene	24	87	97
5[c]	P-BCN	Toluene	24	2	98

Notes：[a] **1a** = 0.1 mmol, **5a** = 1 mmol, catalyst = 10 mg, solvent = 2 ml, the reaction was carried out under an oxygen atmosphere with the irradiation of 0.75 w/cm^{-2} blue lamp (460 nm). [b] The conversion was detected by liquid chromatography. [c] The reaction was operated under N_2 atmosphere. DCE = dichloroethane.

References

1 S. Z. Wang, F. K. Ma, H. H. Jiang, Y. L. Shao, Y. Z. Wu, and X. P. Hao, *ACS. Appl. Mater. Interfaces.*, 2018, **10**, 19588-19597.