

Supporting Information

Carbon-Doped Boron Nitride Nanosheet as an Efficient Metal-Free Catalyst for the Selective Oxidation of H₂S

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1. Experimental Methods

1.1 Experimental

Boric acid (H_3BO_3 , $\geq 99.5\%$) and Urea ($\text{CH}_4\text{N}_2\text{O}$, $\geq 99.5\%$) were purchased from Sinopharm Chemical Reagent (Shanghai, China). Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, $\geq 99\%$) and activated carbon (AC) were obtained from Aladdin Co., Ltd. Ethanol (99.7%) was supplied by Shanghai Macklin Biochemical Co., Ltd. A reaction gas containing H_2S (5000 ppm) and O_2 (2500 ppm) was supplied from Dalian Special Gases (Dalian, China). Deionized water was supplied from local sources. All the chemicals and solvents were used without further purification.

1.2 Synthesis

Preparation of *h*-BN. Typically, 4.0 g boric acid and 4.0 g urea were dissolved in 150 mL of deionized water, followed by heating at 100 °C under stirring till complete evaporation of solvents. The obtained white solid was ground into powder and then heated to 900 °C (5 °C/min) for 6 h. After that, the resulting solid was soaked in 5 M HCl solution (300 mL) for 30 min to remove impurities. Then the mixture was washed deionized water until the pH of supernatant above 7.0. At last, the *h*-BN was obtained by drying at 80 °C for 12 h.

Preparation of BCN-X. First, a total of 10.0 g boric acid, urea and glucose (the mass ratios are 4:4:2, 2:2:6 and 1:1:8, respectively) were dissolved in 150 mL of deionized water, followed by heating at 100 °C under stirring till complete evaporation of solvents. The obtained white solid was ground into powder and then heated to 900 °C (5 °C/min) for 6 h. After that, the resulting solid was soaked in 5 M HCl solution (300

mL) for 30 min to remove impurities. Then the mixture was washed deionized water until the pH of supernatant above 7.0. The resulting products are herein denoted as BCN-2, BCN-6 and BCN-8, respectively.

1.3 Characterizations

The X-ray powder diffractometer (XRD) measurements were performed on a PANalytical diffractometer adopting Cu K α radiation ($\lambda= 1.5418\text{\AA}$) at 40 kV and 40 mA. FT-IR spectra were collected on a Nicolet 6700 FT-IR spectrometer. Raman spectrum was analyzed on an inVia Reflex instrument at 532 nm laser excitation manufactured by Renishaw, UK. EPR spectra were obtained over a Bruker model E-500 spectrometer. The UV-vis DRS profiles were recorded over a Lambda 950 instrument. The XPS characterizations were carried out to analyze elements states and the chemical composition of samples on an ESCACAB 250xi X-ray photoelectron spectrometer manufactured by Thermo Fisher Scientific of the US. The electron binding energy was corrected with carbon (C1s = 284.8 eV) as an internal standard. Elemental analysis results were recorded by a Vario EL Cube instrument. Scanning emission microscopy (SEM) (S-4800, Hitachi, Japan) and energy-dispersive X-ray spectroscopy (EDX) technology were used to study the surface morphology and elemental composition of samples. Transmission electron microscopic (TEM) analysis was conducted on a transmission microscope at 200 kV (FEI Tecnai G2 F20, America). The specific surface area and pore structure of the catalyst was analyzed by Micrometrics ASAP 2020 specific surface and pore analyzer.

The CO₂/O₂ temperature-programmed desorption (CO₂/O₂-TPD) experiments were performed on an AutoChem 2920 instrument manufactured by Micromeritics, US.

During the experiment, firstly, 0.1 g of catalyst (40–60 mesh) was purged with high purity helium gas at 250 °C for 1 h to remove the impurity gas adsorbed on the surface of the sample. Cooling to room temperature, the catalyst was purged with 5% CO₂/He (30 mL·min⁻¹) for 1 h. Next, it is purged with high-purity helium for 30 min to remove the physically adsorbed CO₂. Finally, the catalyst heated to the desired temperature at a rate of 10 °C·min⁻¹, and the gas composition signal is recorded and analyzed by TCD and mass spectrometry. As for O₂-TPD, *ca.* 0.1 g of catalyst was similarly pre-heated before cooling to room temperature. Then the 5% O₂/He was fed in reactor at a rate of 30 mL·min⁻¹ for 1 h. Next, O₂ desorption spectra were collected from 50 to 900 °C at a heating rate of 10 °C·min⁻¹.

1.4 Catalytic Experiments

The H₂S selective oxidation was performed in a tubular fixed-bed continuous-flow reactor equipped with gas chromatography (GC). 0.2 g of catalyst (40–60 mesh) was loaded in a catalyst reactor. The reaction was carried out under reaction conditions of atmospheric pressure, 100–250 °C, V(H₂S/O₂/N₂) = 0.5/0.25/99.25, WHSV = 6000 mL·g⁻¹·h⁻¹. The emission gas (H₂S and SO₂) from the reactor was analyzed by Fu Li-9720 GC equipped with a thermal conductivity detector (TCD). H₂S conversion, sulfur selectivity, and sulfur yield were defined as follows:

$$\text{H}_2\text{S Conversion} = \frac{[\text{H}_2\text{S}]_{\text{in}} - [\text{H}_2\text{S}]_{\text{out}}}{[\text{H}_2\text{S}]_{\text{in}}} \times 100\% \quad (1)$$

$$\text{Sulfur Selectivity} = \frac{[\text{H}_2\text{S}]_{\text{in}} - [\text{H}_2\text{S}]_{\text{out}} - [\text{SO}_2]_{\text{out}}}{[\text{H}_2\text{S}]_{\text{in}} - [\text{H}_2\text{S}]_{\text{out}}} \times 100\% \quad (2)$$

$$\text{Sulfur yield} = [\text{H}_2\text{S Conversion}] \times [\text{Sulfur Selectivity}] \quad (3)$$

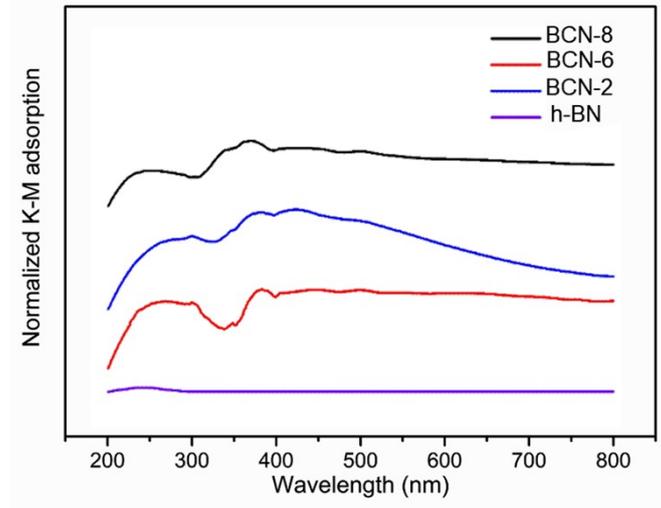


Figure S1. UV-vis DRS spectra of h-BN and BCN- x .

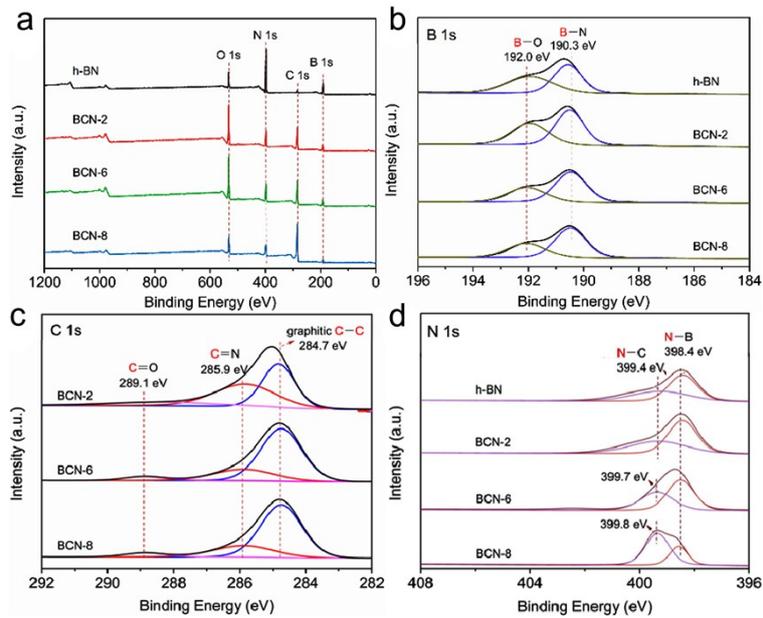


Figure S2. XPS spectra of h-BN and BCN- x : (a) Survey, (b) B 1s, (c) C 1s and (d) N

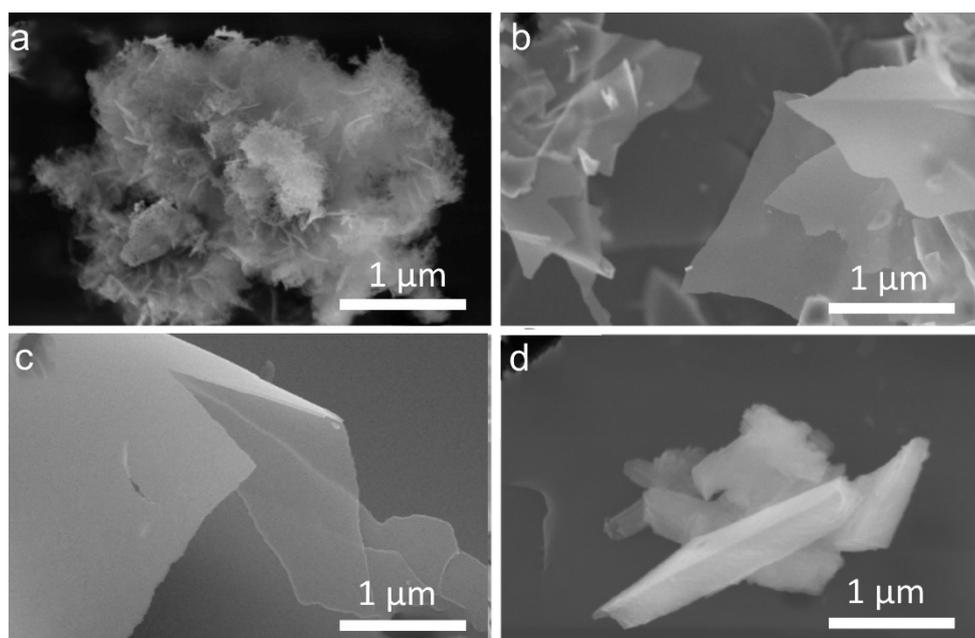
1s.

Table S1. Elemental Analysis and Physical Properties of h-BN and BCN samples

Sample	N (w%)	C (w%)	B (w%)	H (w%)	S _{BET} (m ² /g)
BCN-8	13.6	60.3	9.4	3.8	125.6
BCN-6	15.6	47.1	10.6	2.6	158.7
BCN-2	22.8	16.5	18.1	<0.30	267.5
h-BN	21.6	<0.30	16.4	1.41	293.1

Table S2. XPS characterization: relevant intensity ratio of chemical bond (%)

Bond Type	BCN-8	BCN-6	BCN-2
N-B	0.38	0.56	0.76
N-C	0.62	0.44	0.24

**Figure S3.** SEM images of (a) h-BN (b) BCN-2, (c) BCN-6 and (d) BCN-8.

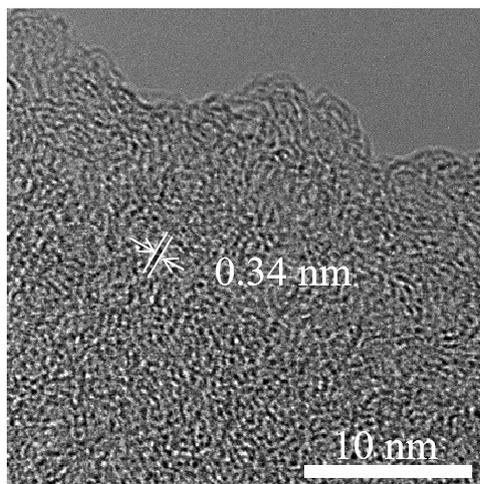


Figure S4. HRTEM image of BCN-6.

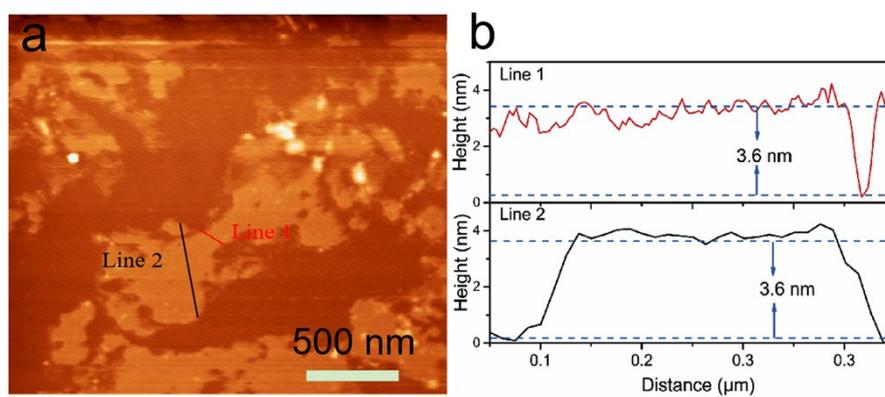


Figure S5. (a) AFM image and (b) height curves along the lines in AFM image of BCN-6.

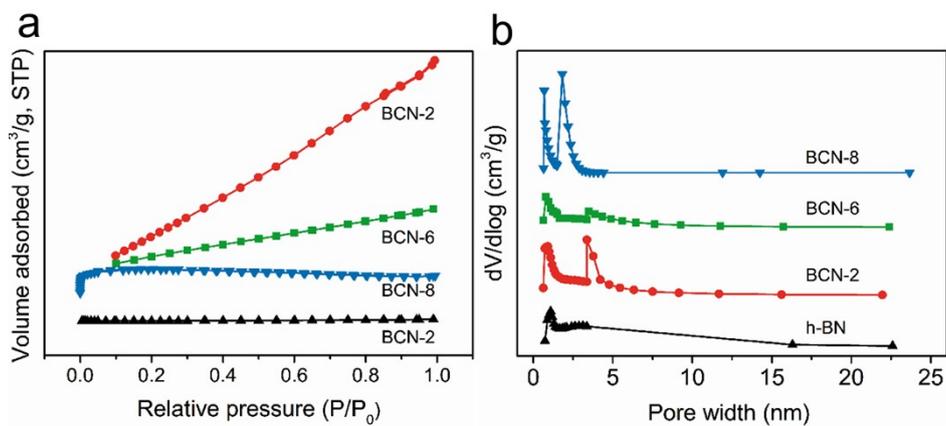


Figure S6. N_2 adsorption-desorption isotherms (a) and pore size distributions (b) of h-BN and BCN- x .

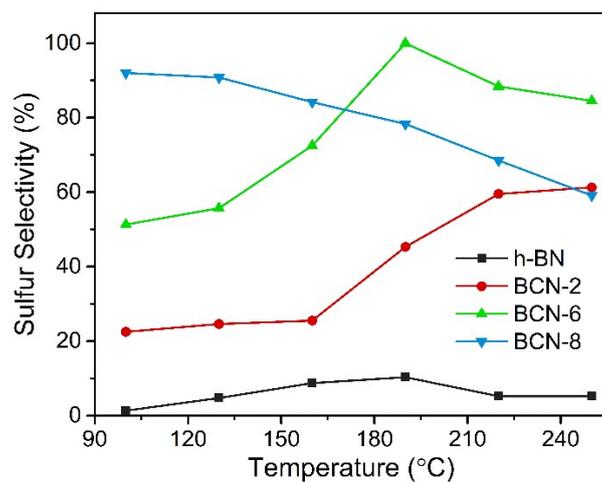


Figure S7. Influence of reaction temperature on sulfur yield for h-BN and BCN-x.

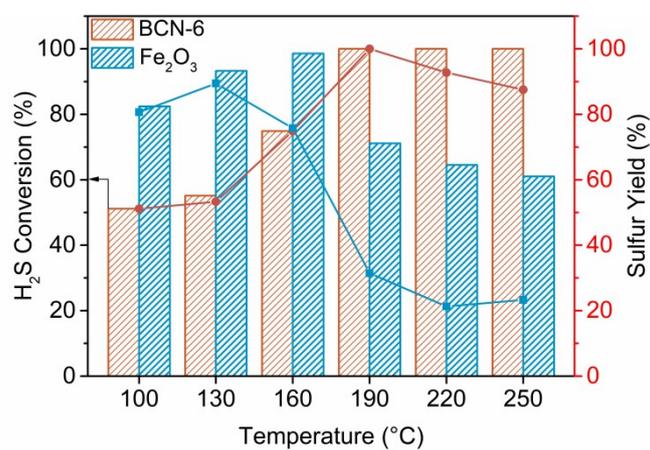


Figure S8. H₂S catalytic oxidation performances for BCN-6 and commercial Fe₂O₃.

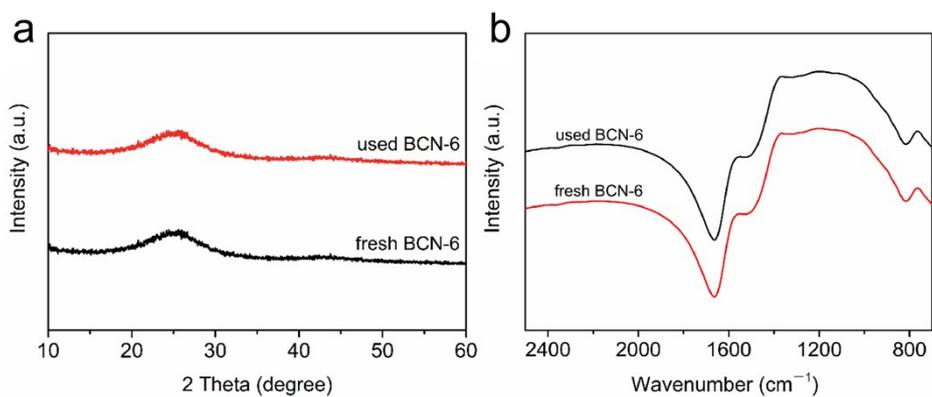


Figure S9. (a) XRD patterns and (b) FT-IR spectra of fresh and used BCN-6 sample.

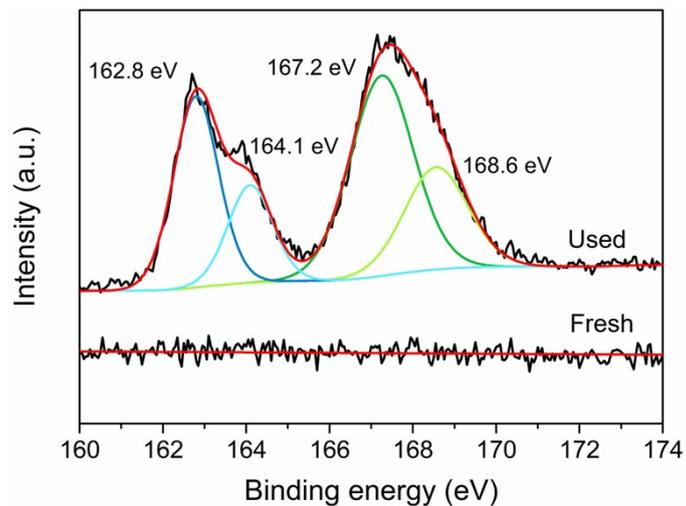


Figure S10. XPS S 2p spectrum of fresh and used BCN-6 sample.

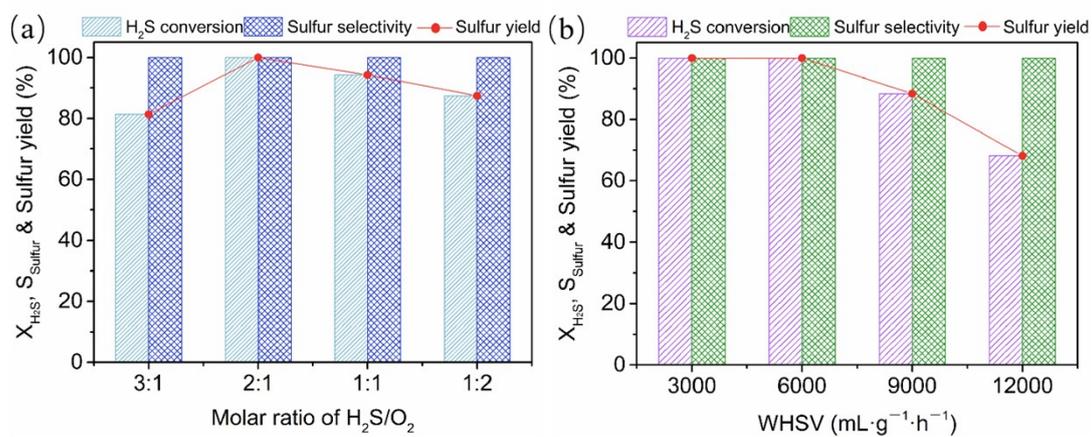


Figure S11. Influence of (a) WHSV and (b) H₂S/O₂ molar ratio of BCN-6 at 190 °C.