

B-doped Copper oxide nanobundles for electroreduction of carbon dioxide to ethylene

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1. Experimental Section

Materials. Copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) ($\geq 99.0\%$) and sodium hydroxide ($\geq 99\%$) were supplied by Sinopharm Chemical Reagent Co., Ltd. Ethanol (A. R. Grade), isopropanol (A. R. Grade) and acetone (A. R. Grade) were obtained from Beijing Chemical Works. Deionized water, N_2 (99.999%) and CO_2 (99.999%) were provided by Beijing Analysis Instrument Factory. Polyethylene glycol (PEG, average MW=20000) and potassium bicarbonate (KHCO_3 , $\geq 99.5\%$) were provided by Beijing J&K Chemicals Reagent Co., Ltd. Boric acid (99.5%) was bought from Innochem Reagent Co., Ltd. Nafion D-521 dispersion (5% w/w in water and 1-propanol, ≥ 0.92 meq g^{-1} exchange capacity), Nafion N-117 membrane (0.180 mm thick, ≥ 0.90 meq g^{-1} exchange capacity) and Toray carbon paper (CP, TGP-H-60, 19×19 cm) were purchased from Alfa Aesar China Co., Ltd.

Synthesis of CuO with B. A series of CuO with different B contents were synthesized by varying the dosage of boric acid used, while the other experimental conditions were the same. 1 mmol $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 3 mL of boric acid aqueous solution (1 $\text{mg} \cdot \text{mL}^{-1}$) and 1.0 g of PEG were added into 200 mL of deionized water and stirred for 30 min, followed by the addition of 1.2 mL sodium hydroxide aqueous solution (6 $\text{mol} \cdot \text{L}^{-1}$) drop by drop. After reaction for 2 h, the solid was separated by centrifugation, washed three times with acetone and ethanol and dried in a vacuum oven at 60 °C for 24 h. A series of CuO with different B contents were synthesized by the same procedure with the addition of 0.5 mL, 1.0 mL, 3.0 mL, 6.0 mL of boric acid aqueous solution.

Synthesis of CuO without B: The preparation of boron-free CuO sample was basically the same with the above, but without boric acid addition.

Material characterizations. X-ray diffraction (XRD) was determined by a Rigaku D/max-2500 diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 200 mA. The morphologies of samples were observed on scanning electron microscope (SEM, HITACHI S-4800), transmission electron microscope (TEM, JEOL JEM-1011) and high resolution transmission electron microscope (JEOL JEM-2100F) from which the mapping images of Cu, O and B in the sample pictures were also captured. Fourier transform infrared (FT-IR) spectroscopy spectra were performed by a Bruker Tensor 27 spectrometer. The KBr pellet method was applied to prepare the solid samples. The element contents of Cu and B were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, VISTA-MPX, Varian). X-ray photoelectron spectroscopy (XPS) was carried out with a multipurpose X-ray photoemission spectroscope (Thermo Scientific ESCALAB 250Xi). X-ray absorption fine structure (XAFS) measurement for Cu K-edge was carried out at room temperature at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF). For XAFS analysis, the extraction of the $\chi(k)$ function was performed using the Athena program. The averaged k^3 -Weighted $\chi(k)$ function was Fourier transformed in the $\Delta k = 1.549\text{-}11.228 \text{ \AA}^{-1}$ interval with a Rbkg value of 1.0 and the uncorrected phase shift. The X-ray absorption near-edge structure (XANES) spectrum was calibrated by setting the Cu K-edge energy to $\approx 9005 \text{ eV}$ in the reference channel (Cu foil).

Electroreduction of CO_2 . To obtain a uniformly distributed and firmly attached working electrode, 2.0 mg of catalyst and 30 μL of 5% Nafion 117 solution were added to 400 μL of isopropanol, and sonicated for 60 min to obtain a uniformly dispersed ink like dispersion solution. Then, with the help of a hair dryer, the dispersion was evenly dripped onto the surface of the CP electrode (1 mg cm^{-2}). Electrochemical CO_2 reduction experiment was carried out in an H-type double fluid electrochemical cell with a three-electrode system in CO_2 -saturated 0.1 M KHCO_3 electrolyte at electrochemical workstation (CHI660E) in which Ag/AgCl (filled with 3.5M KCl) electrode and gauze platinum (1 $\text{cm} \times 1\text{cm}$) worked as reference and counter electrodes, respectively. The working and reference electrodes were placed in the cathode chamber, while the counter electrode was placed in the anode chamber, which were connected with a piece of Nafion 117 ionic exchange membrane. Linear sweep voltammetry (LSV) test with a scan rate of 10 mV s^{-1} and electrochemical impedance spectra (EIS) with frequencies of 10^{-1} - 10^5 HZ were performed in a single fluid cell with 0.1 M KHCO_3 electrolyte. The pH values of the saturated CO_2 0.1 M KHCO_3 electrolyte solution is 7.2. The potentials were measured against the standard calomel electrode (SCE) and converted to versus reversible hydrogen electrode (vs. RHE) by using the fellow formula:

$$E (\text{vs. RHE}) = E (\text{vs. SCE}) + 0.2046 \text{ V} + 0.0592 \text{ pH}$$

All the potentials were recorded vs. RHE. For the faradaic efficiency analysis, gas products were detected by gas chromatograph (GC, Agilent7890D), which was equipped with FID and TCD detectors using argon as internal standard. The liquid product was analyzed by ^1H nuclear magnetic resonance ($^1\text{H NMR}$) spectroscopy (Bruker Avance III 400 HD). All experiments were performed at room temperature and atmospheric pressure.

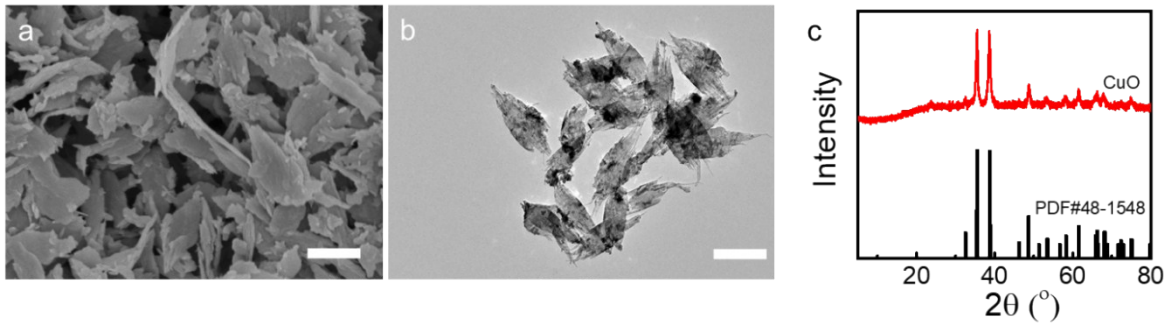


Fig. S1. SEM (a), TEM (b) images and XRD pattern (c) of CuO. Scale bar: 500 nm.

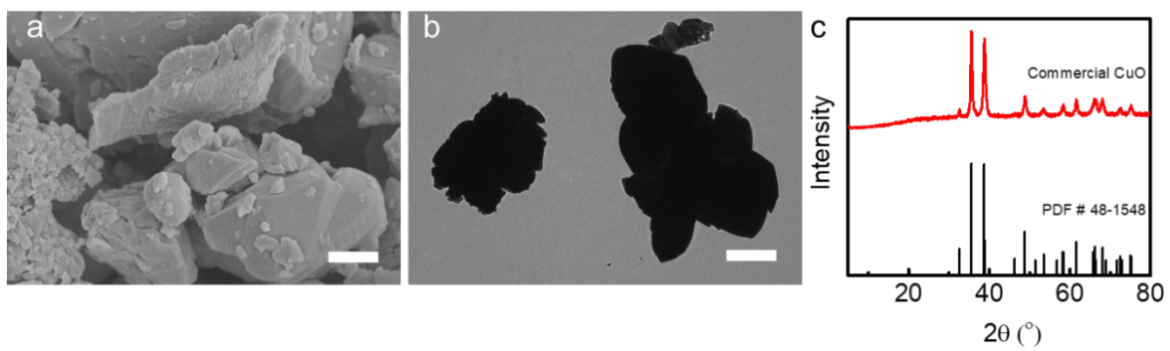


Fig. S2. SEM (a), TEM (b) images and XRD pattern (c) of commercial CuO. Scale bar: 500 nm.

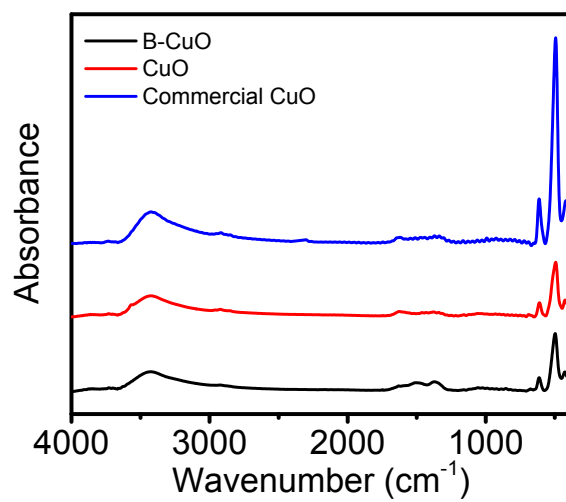


Fig. S3. FT-IR spectra for B-CuO, CuO and commercial CuO.

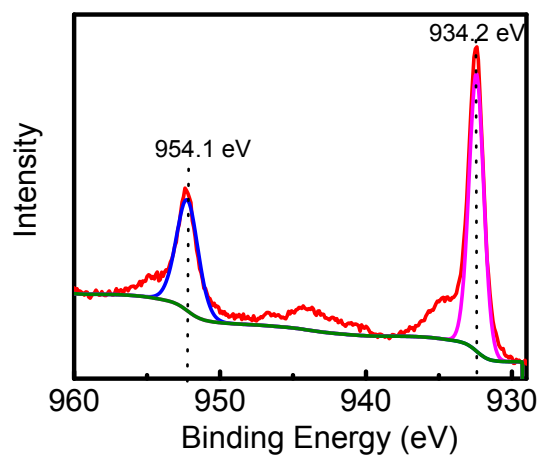


Fig. S4. Cu₂p XPS spectrum of B-CuO.

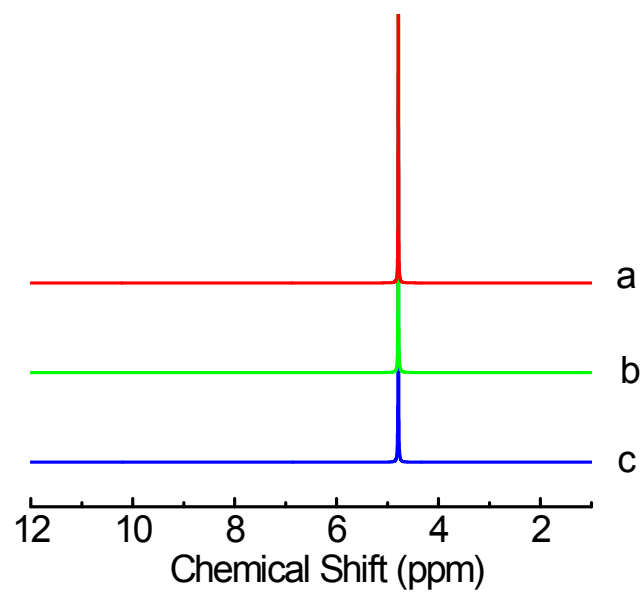


Fig. S5. ¹H NMR spectra of the electrolyte after CO₂ reduction at -1.1 V vs. RHE for B-CuO (a), CuO (b) and commercial CuO (c).

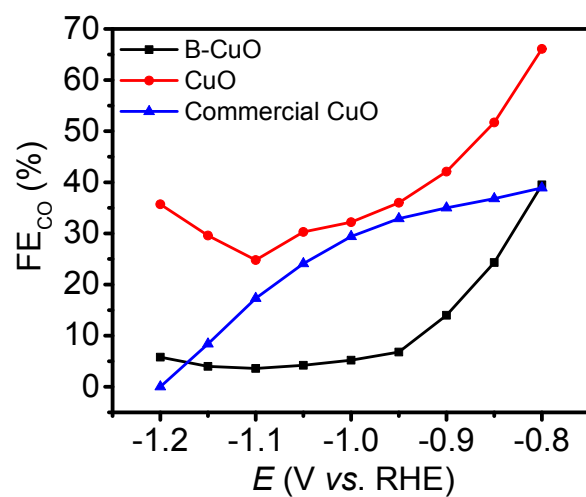


Fig. S6. FE of CO as catalyzed by B-CuO, CuO and commercial CuO.

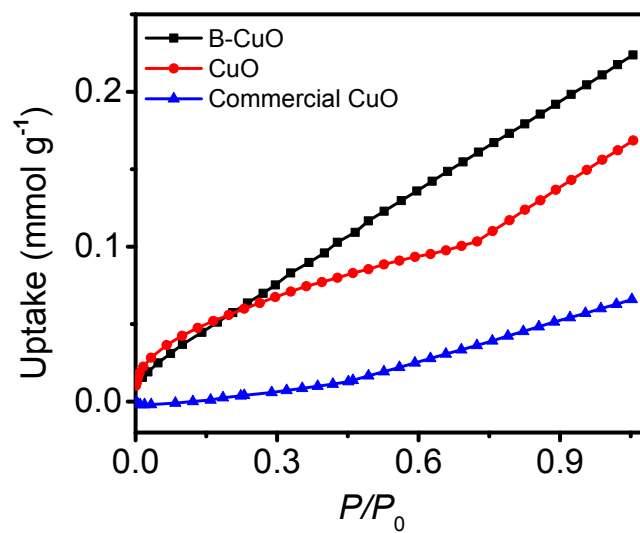


Fig. S7. CO₂ adsorption curves of B-CuO, CuO and commercial CuO.

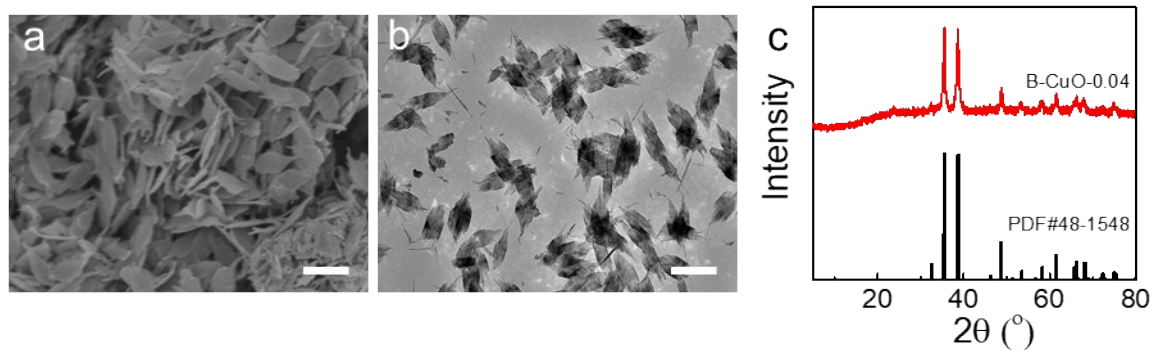


Fig. S8. SEM (a), TEM (b) images and XRD pattern (c) of B-CuO with B content of 0.04 wt%. Scale bar: 500 nm.

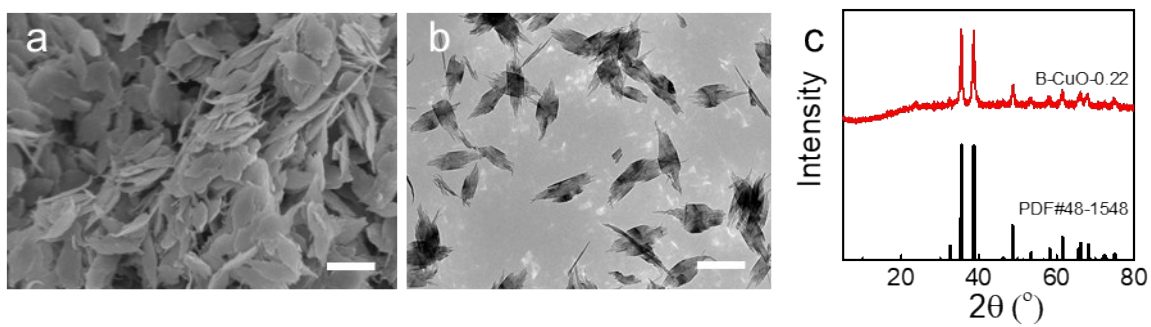


Fig. S9. SEM (a), TEM (b) images and XRD pattern (c) of B-CuO with B content of 0.22 wt%. Scale bar: 500 nm.

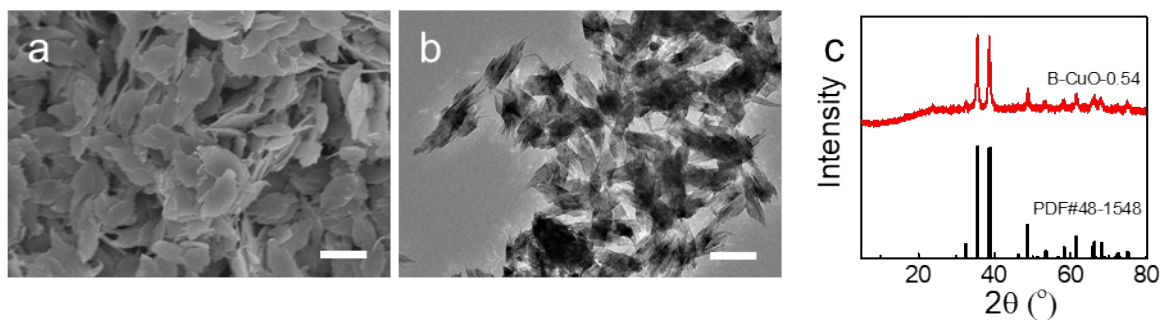


Fig. S10. SEM (a), TEM (b) images and XRD pattern (c) of B-CuO with B content of 0.54 wt%. Scale bar: 500 nm.

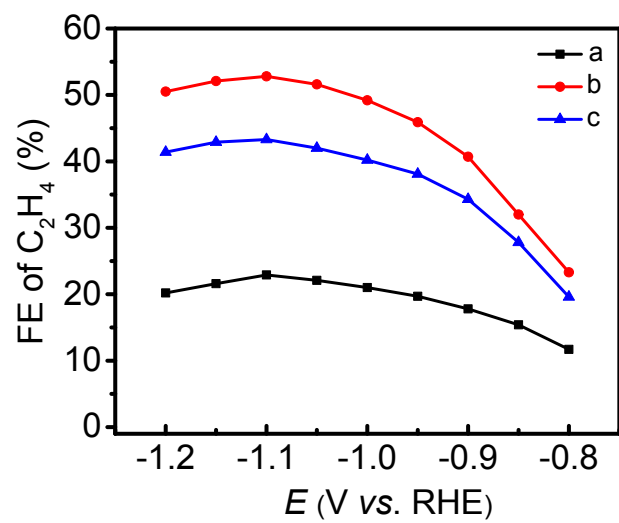


Fig. S11. FE of ethylene as catalyzed by the B-CuO with B contents of 0.04 wt% (a), 0.22 wt% (b) and 0.54 wt% (c).

Table S1. EXAFS fitting results (*R*, Distance; CN, Coordination Number) of commercial CuO (a) and B-CuO with B contents of 0 (b), 0.04 wt% (c), 0.22 wt% (d) 0.49 wt% (e) and 0.54 wt% (f).

| sample | Cu-O bond | | Cu-Cu bond | |
|--------|--------------|-----|--------------|-----|
| | <i>R</i> (Å) | CN | <i>R</i> (Å) | CN |
| a | 1.954 | 4.0 | 2.898 | 4.0 |
| b | 1.960 | 4.4 | 2.967 | 2.8 |
| c | 1.959 | 4.3 | 2.970 | 2.7 |
| d | 1.958 | 4.7 | 2.986 | 2.6 |
| e | 1.959 | 4.3 | 2.995 | 2.5 |
| f | 1.959 | 4.3 | 2.970 | 3.2 |