Supporting Information for

Introduction of Carbon-Boron Atomic Groups as an Efficient Strategy to Boost Formic Acid Production toward CO₂ Electrochemical Reduction

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EXPERIMENTAL SECTION

Theoretical Calculation

DFT calculations were carried out using the Vienna *ab initio* Simulation Package (VASP). The Perdew-Burke-Ernzerhof type generalized gradient approximation was used for exchange correlation. All the calculations were carried out using a $(4 \times 4 \times 1)$ supercell, in which a vacuum layer with the thickness of more than 15 Å was introduced to avoid the interaction between two *h*-BN or graphene monolayers. During the structure optimization, the $5 \times 5 \times 1$ k-points mesh was used to sample the entire Brillouin zone. The energy cutoff for plane waves was set as 550 eV, with the residual force less than 0.01 eV Å⁻¹. All energies discussed in this work are free energies. For slabs, they were calculated as:

$$G = E + ZPVE + \sum_{\nu} \frac{h\nu}{e^{h\nu/kT} - 1} - T \times S_{\nu ib}$$

where *G* was the free energy, *E* was the DFT-optimized total energy, *ZPVE* was the zero point energy, *h* was the Planck's constant, *v* was the vibrational frequency, *k* was the Boltzmann's constant, *T* was the temperature, and S_{vib} was the vibrational entropy. In the case of CO₂ activation, an electron was injected into *h*-BN and graphene according to the method proposed by Du and co-workers^{S1}.

Synthesis of BCN-x Flakes

Typically, boron oxide (2 g), urea (4 g) and a certain amount of glucose were grinded fully with an agate mortar. The mixed precursor was put into a horizontal tube furnace. After purging away oxygen in the tube, the sample was heated at 1,100 °C for 5 h. The obtained products were washed with 0.1 M HCl in hot water. The resulting final sample was denoted as BCN-x, where x (10, 30, 40, and 70) is the percentage weight content of glucose to boron oxide. When no glucose was added, the synthesized sample was named *h*-BN. The atomic percentages of C atoms in *h*-BN, BCN-10, BCN-30, BCN-40, and BCN-70 flakes were determined to be 0.5%, 5.1%, 10.2%, 11.7%, and 24.2% by XPS data, respectively.

Electrochemical Measurements

Typically, 1 mg of BCN-x flakes, 4 mg of active carbon, and 30 µL Nafion solution (5 wt%) were dispersed in 1 mL ethanol solution by sonicating for 1 h to form a homogeneous ink. The mixture was then uniformly spread on carbon papers of 1×2 cm² in area. Controlled potential electrolysis of CO2 was performed in an H-cell (separated by Nafion 115) containing 60 mL of 0.1 M KHCO₃ electrolyte at room temperature and under atmospheric pressure. Ag/AgCl (in 3 M KCl solution) and graphite rod were used as the reference and counter electrodes, respectively. After CO₂ was purged into the KHCO₃ solution for at least 30 min to remove residual air in the reservoir, controlled potential electrolysis was performed at each potential for 1 h. The oxygen generated at the anode was vented out of the reservoir. The gas products of CO₂ electrocatalytic reduction were monitored by an online micro gas chromatography (GC) (GC2014, Shimadzu, Japan) equipped with a TCD detector every 8 minutes. The KHCO₃ solution after electrolysis was collected and analyzed on a 400 MHz NMR spectrometer to quantify liquid products. Standard curve was made by using sodium formate (HCOONa·2H₂O, Sinopharm Chemical Reagent Co. Ltd.) and the internal standard (1-Propanesulfonic acid 3-trimethylsilyl sodium salt, DSS, Sigma-Aldrich). The potentials were controlled by an electrochemical station (CHI660E). The current densities and Faradaic efficiencies for the products were obtained as follows.

The molar quantity of HCOOH (N_{HCOOH}) was measured by internal standard method of ¹H NMR. Typically, 0.5 mL of the KHCO₃ solution after electrolysis was mixed with the addition of 0.1 mL of D₂O and 0.1 mL of 6 mM DSS solution as an internal standard. The ¹H NMR spectrum was measured with water suppression by a pre-saturation method. The area ratio of the HCOOH peak to the DSS peak was compared to the standard curve to quantify the concentration of HCOOH. The standard curve of HCOOH was presented in Fig. S12. The N_{HCOOH} was calculated by multiplying the concentration of HCOOH with the volume of electrolyte in cathode. Due to the low current density for HCOOH, we performed 10 cycles of the standard electrolysis to accumulate the HCOOH product in electrolyte.

Given that two electrons were involved in the transformation of a CO_2 molecular to a HCOOH molecular, the total charge involved in the HCOOH formation (Q_{HCOOH}) in one cycle of the standard electrolysis was calculated by the equation:

 $Q_{\rm HCOOH} = 2N_{\rm HCOOH} \times F / 10$

where F corresponded to the Faradaic constant.

Accordingly, the partial current density of the HCOOH (j_{HCOOH}) was obtained.

 $j_{\rm HCOOH} = Q_{\rm HCOOH} / St$

where S referred to the area of electrode, t referred to the time of electrolysis.

The partial current density of the CO (j_{CO}) and H₂ (j_{H2}) were determined by internal standard method of gas chromatograph with N₂ as the interior label.

$$j_{\text{CO}} = S_{\text{CO}} / S_{\text{N2}} \times 1 / \alpha_{\text{CO}} \times Flow \ rate \times 2F / S$$
$$j_{\text{H2}} = S_{\text{H2}} / S_{\text{N2}} \times 1 / \alpha_{\text{H2}} \times Flow \ rate \times 2F / S$$

where S_{CO} , S_{H2} , and S_{N2} were the peak area of CO, H₂, and N₂, respectively. S was the area of electrode, F was the Faradaic constant. α_{CO} and α_{H2} were the conversion factor of CO and H₂ molar amount with respect to that of N₂, which was calibrated by the gas chromatograph with standard CO or H₂ gas.

Consequently, we can calculate the Faradaic efficiencies through the equations:

$$FE_{\text{HCOOH}} = j_{\text{HCOOH}} / j$$
$$FE_{\text{CO}} = j_{\text{CO}} / j$$
$$FE_{\text{H2}} = j_{\text{H2}} / j$$

where j was the geometric current density in the electrolysis.

The energy efficiency for the conversion of CO_2 into HCOOH was calculated by the following equation:

$$\boldsymbol{\Phi}_{\text{HCOOH}} = \frac{\text{FE (\%)} \times \Delta \boldsymbol{E}_{\text{HCOOH}}^{0}}{\Delta \boldsymbol{E}_{\text{HCOOH}}}$$

where Φ_{HCOOH} was the energy efficiency for the conversion of CO₂ into HCOOH, $\Delta E0$ HCOOH was the difference between the standard half reaction potentials for water oxidation (1.23 V vs RHE) and the reduction of CO₂ into HCOOH (-0.2 V vs RHE), and ΔE_{HCOOH} was the difference between the standard water oxidation potential and the working potential at the cathode, respectively.

Linear sweep voltammetry (LSV) curves, double-layer capacitance (C_{dl}) measurements, and electrochemical impedance spectra of BCN-x catalysts were all performed in H-cell. The scan rate of LSV was 10 mV s⁻¹. C_{dl} was determined by measuring the capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammogram (CV). The CV ranged from 0.6 V to 0.7 V vs RHE. The C_{dl} was estimated by plotting the Δj (j_a - j_c) at 0.65 V vs RHE against the scan rates, in which the j_a and j_c were the anodic and cathodic current density, respectively. The slope is twice that of the double-layer capacitance C_{dl} . The electrochemical impedance spectra of BCN-x catalysts were recorded at -0.2 V vs RHE.

Instrumentations

Transmission electron microscopy (TEM) images were taken using a Hitachi H-7650 transmission electron microscope at an acceleration voltage of 100 kV. Energy-dispersive X-ray (EDX) spectra were carried out on a scanning electron microscope (SEM, JSM-6700F) operated at 5 kV. Thermal gravimetric analysis (TGA) of the as-synthesized samples were carried out on a Shimadzu TA-50 thermal analyzer at a heating rate of 10 °C min⁻¹ from room temperature to 800 °C in nitrogen and air atmosphere. X-ray diffraction (XRD) patterns were recorded by using a Philips X'Pert Pro Super diffractometer with Cu-K α radiation (λ =1.54178 Å). Raman spectra were detected by a Renishaw RM3000 Micro-Raman system with a 514.5 nm Ar laser. The Fourier transform infrared spectra (FTIR) spectra were measured on a MAGNA-IR 750 at room temperature (Nicolet Instrument Co., USA). X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCALAB MK II X-ray photoelectron spectrometer with an exciting source of Mg K α = 1253.6 eV. The ¹³C and ¹H nuclear magnetic resonance (NMR) spectra were measured by a Bruker AVANCE AV III 400 nuclear magnetic resonance spectroscopy.

References

S1 Q. Sun, Z. Li, D. J. Searles, Y. Chen, G. Lu, A. Du, J. Am. Chem. Soc. 2013, 135, 8246-8253.



Fig. S1. Structure optimization during the formation of COOH*. The COOH* adsorbed on a N atom of *h*-BN would bind with an adjacent B atom after optimization.



Fig. S2. Typical TEM images of different flakes. (a) *h*-BN. (b) BCN-10 flakes. (c) BCN-30 flakes. (d) BCN-40 flakes. (e) BCN-70 flakes.



Fig. S3. SEM-EDX spectrum of BCN-40 flakes. The signal of Si came from the SEM grid.



Fig. S4. TGA curves of *h*-BN and BCN-40 flakes.



Fig. S5. (a) XRD patterns of *h*-BN and BCN-x flakes. (b) Half-peak width of (002) facet in panel a.



Fig. S6. FTIR spectra of *h*-BN and BCN-x flakes.



Fig. S7. XPS survey spectra of *h*-BN and BCN-x flakes.

| | B (At. %) ^a | C (At. %) | N (At. %) |
|--------------|------------------------|-----------|-----------|
| <i>h</i> -BN | 56.0 | 0.5 | 43.5 |
| BCN-10 | 53.8 | 5.1 | 41.1 |
| BCN-30 | 50.2 | 10.2 | 39.6 |
| BCN-40 | 49.7 | 11.7 | 38.6 |
| BCN-70 | 40.5 | 24.2 | 35.3 |

 Table S1 Atomic percentages of different atoms in *h*-BN and BCN-x flakes. The results were determined by XPS.

^a Atomic percentages



Fig. S8. The ratio of integral areas for C-B bonds and C-C bonds (S_{C-B}/S_{C-C}), indicating a different distribution of C atoms in BCN-70 flakes.



Fig. S9. Top view of the hypothesized possible structures of (a) BCN-40 and (b) BCN-70 flakes.



Fig. S10. ¹H NMR spectrum for the liquid solution after electrochemical reduction of CO₂.



Fig. S11. Standard curve for HCOOH in ¹H-NMR.



Fig. S12. Plots of i-t curves at -0.3 V and -0.6 V vs RHE in electrochemical reduction of CO₂.



Fig. S13. Faradaic efficiencies for H_2 production of *h*-BN and BCN-x flakes.

| | Concentration of HCOOH (mmol/L) ^a | Molar quantity of HCOOH (µmol) ^a | $j_{\rm HCOOH}$ (mA cm ⁻²) | FE of HCOOH (%) |
|---------------|---|--|--|--------------------|
| <i>h</i> -BN | 1.0 | 30 | 0.08 | 18.5 |
| BCN-10 | 2.5 | 75 | 0.20 | 65.1 |
| BCN-30 | 3.7 | 111 | 0.30 | 71.7 |
| BCN-40 | 4.5 | 135 | 0.36 | 83.5 |
| BCN-70 | 3.0 | 90 | 0.24 | 42.2 |

Table S2 Summary of the molar quantity of HCOOH, j_{HCOOH} , and FE for HCOOH at -0.3 V vs RHE.

^aThe HCOOH product was accumulated by 10 cycles of the standard electrolysis.



Fig. S14. Faradaic efficiencies for CO production of *h*-BN and BCN-x flakes at -0.5 V and -0.6 V vs RHE.



Fig. S15. Histograms for Faradaic efficiencies of all kinds of product at (a) -0.3 V, (b) -0.4 V, (c) -0.5 V, and (d) -0.6 V.