Electronic supplementary information

Boosting CO$_2$ electroreduction over Co nanoparticles supported on N, B-co-doped graphitic carbon

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Experimental Section

Experimental materials

Boric acid (99.5%) was provided by InnoChem Technology. 2-Methylimidazole (MIM, 99%) was provided by J&K Technology. Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, >98%) and cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, 99 %) were supplied by Sinopharm Chemical Reagent. The ionic liquid, 1-butyl-3-methylimidazole hexafluorophosphate ([Bmim]PF$_6$, > 99%) was provided by the Green Chemistry and Catalysis Center, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Nafion N-117 proton exchange membrane (thickness 0.180 mm, exchange capacity $\geq 0.90$ meq g$^{-1}$) and Toray carbon paper (CP, TGP-H-60, 19 × 19 cm$^2$) were obtained from Alfa Reagent. Polytetrafluoroethylene concentrated dispersion (PTFE, 60 wt % dispersion) was provided by Aladdin Reagent. Deionized water, methanol (analytical grade), ethanol (analytical grade), CO$_2$ (> 99.999%) were purchased from Beijing Analytical Instrument Factory.

Synthesis of precursors Co/Zn ZIFs

Co(NO$_3$)$_2$·6H$_2$O (0.273 g) and Zn(NO$_3$)$_2$·6H$_2$O (0.558 g) were first dissolved in 20 mL of methanol (solution A), and then 2-methylimidazole (0.616 g) was dissolved in 20 mL of methanol (solution B). The solution B was added dropwise to the solution A and the mixture was stirred at room temperature for 12 h. The suspension was separated by centrifugation at 6000 rpm for 5 min and washed three times with methanol to obtain the precipitate. Finally, the precipitate was dried overnight at 70 °C under vacuum to obtain Co/Zn ZIFs.

Synthesis of target catalytic materials

Co/Zn ZIFs and boric acid were ground and mixed well at the mass ratio of 5:1, 2:1 and 1:1, and the above precursors were kept at 800 °C for 1 h under Ar atmosphere (heating rate: 5 °C min$^{-1}$), then at 900 °C for 1 h, and then at 1000 °C for 1 h. After cooling to room temperature, Co-NB-1, Co-NB-2 and Co-NB-3 were obtained by artificial polishing for 20 min.

Synthesis of contrasting catalytic material
In order to reveal whether the boron element in Co-NB has any effect on the catalytic performance, a loaded cobalt catalyst (Co-N) was synthesized as a comparison material, and Co-N was prepared by the method described above for the synthesis of Co-NB, except that no boric acid was added.

**Materials characterizations**

X-ray diffraction (XRD) of the materials was measured on a Rigaku D/max-2500 diffractometer with an X-ray incident wavelength of 0.154 nm, a gas pedal voltage of 40 kV, and an acceleration current of 200 mA. Scanning electron microscope (SEM, HITACHI S-4800), Transmission Electron Microscope (TEM, JEOL-1011), and high-resolution transmission electron microscope (HRTEM, JEOL-2100F) were used to characterize the morphology of the materials. X-ray photoelectron spectroscopy (XPS) was performed by an X-ray photoelectron spectrometer Thermo Scientific ESCA Lab 250Xi using a 200 W Al Kα target with a basic pressure of about $3 \times 10^{-10}$ mbar in the analysis chamber. The elemental content of cobalt was determined with an inductively coupled plasma emission spectrometer (VISTA-MPX). The elemental content of carbon, nitrogen and boron was determined with an elemental analyzer (Flash EA1112). The specific surface area and pore properties of the materials were determined by Micromeritics ASAP 2020 sorptometer with Brunauer-Emmett-Teller (BET) method. X-ray absorption spectroscopy (XAS) was performed at the 1W1B experimental station of Beijing Synchrotron Radiation Center (BSRF), and the data were processed using Athena and Artemis software.

**Electrode preparation**

A mixture of cobalt-based catalyst (1.0 mg), 6 wt% PTFE dispersion and 100 µL acetone was sonicated for 10 min to form a homogeneous ink. 100 µL of the ink was quantitatively pipetted with a pipette gun and dropped onto a $0.5 \times 1$ cm$^2$ surface of carbon paper and blown dry with N$_2$ to obtain a working electrode.

**Electrocatalytic CO$_2$ reduction**

The electrocatalytic reduction of CO$_2$ was tested in an H-type electrochemical cell in a three-electrode system. The counter electrode was Pt net and the reference electrode was Ag/Ag$^+$. The working and reference electrodes were placed in the cathode chamber
and the counter electrode was placed in the anode chamber. In the experiments, the cathode and anode compartments were separated through a Nafion 117 proton exchange membrane. H$_2$SO$_4$ aqueous solution (0.5 M) was used as anodic electrolyte. H$^+$ can be transferred from anode compartment to cathode compartment through Nafion 117 proton exchange membrane, which is the proton source. Before the test, CO$_2$ was passed through the electrolyte for at least 30 min to form a saturated solution of CO$_2$. Linear scanning voltammetry (LSV) curves were measured in the CO$_2$-saturated electrolyte, acetonitrile solution containing 0.5M 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF$_6$), with a potential range of 0 V to -2.4 V and a scan rate of 20 mV/s.

**Product analysis**

The gaseous products were collected in gas bags and analyzed by gas chromatography (GC, HP 4890D) for the composition of the gaseous products and the liquid products were detected by nuclear magnetic resonance (¹H-NMR, BrukerAvance III 400 HD).

**Calculation of the Faraday efficiency of products.**

Since the products are mainly CO and H$_2$, only the Faraday efficiencies of the gaseous products needed to be calculated. The volume % of CO and H$_2$ could be obtained from the GC peak areas and calibration curve of the TCD detector. Since the CO$_2$ flow rate was constant, the moles of CO and H$_2$ per second could be calculated. The theoretical moles of CO and H$_2$ per second could be obtained from the current density. Therefore, the Faraday efficiency was:

$$FE = \frac{\text{moles of product per second}}{\text{theoretical moles of equivalent per second}}$$

**Calculation of TOF.**

The TOF for CO was calculated as follows, and the method is the same as the literature$^{81}$:

$$TOF = \frac{l_{CO}/nF}{m_{cat} \times \omega \times \alpha/M_{co} \times 3600}$$

TOF: turnover frequency, h$^{-1}$.

$I_{CO}$: partial current for certain product, A.

$n$: the number of electrons transferred for product formation, which is 2 for CO
F: Faradaic constant, 96485 C mol\(^{-1}\).

\(m_{\text{cat}}\): catalyst mass in the electrode, g.

\(\alpha\): the ratio of active atoms in Co NPs (estimated as the ratio of surface area to volume)

\(\omega\): Co loading in the catalyst.

\(M_{\text{Co}}\): atomic mass of Co, 58.93 g·mol\(^{-1}\).

TOF of Co-NB-2 at -2.4 V:

\[
I_{\text{CO}} = 18.4 \text{ mA}, \quad m_{\text{cat}} = 1.0 \text{ mg}, \quad \omega = 11.86\%, \quad r = 12.5 \text{ nm}; \quad \alpha \approx \frac{4\pi r^2}{4\pi r^3/3} = 0.24;
\]

\[
\text{TOF} = \frac{I_{\text{CO}}/nF}{m_{\text{cat}} \times \omega \times \alpha/M_{\text{Co}}} \times 3600 = 40.93 \text{ h}^{-1}
\]

**Quasi-operando X-ray photoelectron spectroscopy**

To study the valence state of cobalt during the reaction, quasi-operando XPS measurements of the four catalysts were carried out in a glove box after 30 min of the reaction. The reacted electrode materials were immersed in acetone solution and then immediately placed in the glove box. The electrode materials were blown dry with an earwash ball, cut to 2 × 2 mm and glued onto the holder. The holder was evacuated to prevent oxidation of the material. The subsequent procedure was the same as conventional XPS.

**Tafel analysis**

The partial current density of CO was measured at different potentials and the equilibrium potential was known by extrapolation. The overpotential was obtained from the difference between the equilibrium potential and the applied potential. Repeated electrolysis experiments were performed at each potential to obtain data on the overpotential and partial current density of CO in the H-type electrolytic cell. Finally, the Tafel plots were plotted.

**Electrochemical surface areas (ECSAs) study**

The electrochemical surface area was proportional to the \(C_{\text{dl}}\) value. Cyclic voltammetry was performed in MeCN containing 0.5 M [Bmim]PF\(_6\) solution using a three-electrode system at 25 °C. Cyclic voltammograms were measured at six different scan rates of
20, 30, 50, 80, 100, and 120 mV s\(^{-1}\) at -1.60 to -1.70 V vs Ag/Ag\(^+\) for the catalysts, and the double layer capacitance (C\(_{dl}\)) of the catalysts were obtained. C\(_{dl}\) was estimated by plotting \(\Delta j (j_a - j_c)\) at -1.65 V vs Ag/Ag\(^+\) versus the scan rate, where \(j_a\) and \(j_c\) were the anode and cathode current densities, respectively. The linear slope was equivalent to twice the C\(_{dl}\).

**Electrochemical impedance spectroscopy (EIS) study**

EIS measurements were performed in 0.5 M [Bmim]PF\(_6\)-MeCN at open circuit potential (OCP) with an amplitude of 5 mV of \(10^{-1}\) to \(10^6\) Hz.
Supplementary Figures

Fig. S1 A) SEM image and B) XRD pattern of ZIF-8.

Fig. S2 SEM images of A) Co-N, B) Co-NB-1 and C) Co-NB-3.

Fig. S3 A) TEM image and particle size distribution and B) HR-TEM image of Co-N.
Fig. S4 A) TEM image and particle size distribution, B) HR-TEM image and C) Elemental mappings images of Co-NB-1.

Fig. S5 A) TEM image and particle size distribution, B) HR-TEM image and C) Elemental mappings images of Co-NB-3.
Fig. S6 N₂ adsorption/desorption isotherms of A) Co-N, B) Co-NB-1, C) Co-NB-2, D) Co-NB-3.
Fig. S7 XPS spectra of Co 2p orbits for A) Co-N, B) Co-NB-1, C) Co-NB-3.

Fig. S8 XPS spectra of N1s orbits for A) Co-N, B) Co-NB-1 and C) Co-NB-3.
Fig. S9 XPS spectra of B1s orbits for A) Co-N, B) Co-NB-1, C) Co-NB-2, D) Co-NB-3.
Fig. S10 A) First derivative curves of different samples. B) Co EXAFS spectra of different samples in k space.
Fig. S11 Gas chromatography of gas products after CO\textsubscript{2} electrolysis on Co-NB-2 at an applied potential of -2.4 V vs Ag/Ag\(^+\).

In the presence of only H\textsubscript{2} and CO as products, FE\textsubscript{CO} can be calculated according to the following equation:

\[
FE_{CO} = \frac{12.23 A_{CO}}{12.23 A_{CO} + A_{H2}}
\]

The retention time of 0.810 min corresponds to H\textsubscript{2} with a peak area (A\textsubscript{H2}) of 13.103 and the retention time of 2.564 min corresponds to CO with a peak area (A\textsubscript{CO}) of 41.015. FE\textsubscript{CO} of Co-NB-2 at -2.4 V:

\[
FE_{CO} = \frac{12.23 \times 41.015}{12.23 \times 41.015 + 13.103} \times 100\% = 97.5\%
\]
Based on the $^1$H NMR spectrum of [Bmim]PF$_6$/MeCN catholyte after 24 h electrolysis over Co-NB-2 at an applied potential of -2.4 V vs. Ag/Ag$^+$ (Fig. S12), we can find that there is no notable change in the spectra, indicating that [Bmim]PF$_6$ was stable during the electrolysis.
**Fig. S13** Current densities for CO production under different potentials and the equilibrium potential obtained by extrapolation method.

**Fig. S14** The partial current density of CO for Co-N, Co-NB-1, Co-NB-2 and Co-NB-3.
Fig. S15 A) TEM image and particle size distribution, B) HR-TEM image and C) Elemental mappings images of Co-NB-2 after electrolysis.

Fig. S16 XPS spectra of Co 2p orbits of Co-NB-2 before and after electrolysis.
Fig. S17 SEM images of A) Co-NB-1 and B) Co-NB-3 after electrolysis.

Fig. S18 EDS images of A) Co-NB-1 and B) Co-NB-3 after electrolysis.

Fig. S19 XPS spectra of Co 2p orbits of Co-NB-1 before and after electrolysis.
Fig. S20 XPS spectra of Co 2p orbits of Co-NB-3 before and after electrolysis.
## Supplementary Tables

### Table S1. Comparison of CO₂ reduction performance on different Co-based catalysts.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Applied potential /V</th>
<th>Electrolyte</th>
<th>Product, FE/%</th>
<th>Current density / mA cm²</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Co-NB-2</td>
<td>-2.4 V vs Ag/Ag⁺</td>
<td>0.5 M [Bmim]PF₆/MeCN</td>
<td>CO, 97.9</td>
<td>18.8</td>
<td>This work</td>
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<tr>
<td>Cu₅₀Co₅₀ NPs</td>
<td>-1.1 V vs RHE</td>
<td>0.1 M KHCO₃</td>
<td>CO, ~2.5</td>
<td>~30</td>
<td>[S2]</td>
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<td>Ag-Co bimetallic catalyst</td>
<td>-2.0 V vs SHE</td>
<td>0.5 M KHCO₃</td>
<td>CO, 7.8</td>
<td>-</td>
<td>[S3]</td>
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<td>Co/Ag(111)</td>
<td>-0.60 V vs. RHE</td>
<td>0.1 M KHCO₃</td>
<td>CO, 87</td>
<td>~2</td>
<td>[S4]</td>
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<td>Co@CoNC-900</td>
<td>-0.80 V vs. RHE</td>
<td>0.1 M KHCO₃</td>
<td>CO, 42</td>
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<td>[S5]</td>
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<td>CoS₂</td>
<td>-0.60 V vs RHE</td>
<td>0.5 M KHCO₃</td>
<td>CO, 86</td>
<td>3.3</td>
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<td>CoPc</td>
<td>-0.70 V vs RHE</td>
<td>1 M KHCO₃</td>
<td>CO, 62</td>
<td>3.2</td>
<td>[S7]</td>
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<td>CoPc-COF</td>
<td>-0.70 V vs RHE</td>
<td>0.5 M KHCO₃</td>
<td>CO, 93</td>
<td>~10</td>
<td>[S8]</td>
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<td>Co-N₂</td>
<td>-0.63 V vs. RHE</td>
<td>0.5 M KHCO₃</td>
<td>CO, 94</td>
<td>18.1</td>
<td>[S9]</td>
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<td>Co-N₄</td>
<td>-0.48 V vs. RHE</td>
<td>0.1 M KHCO₃</td>
<td>CO, 45</td>
<td>~1</td>
<td>[S10]</td>
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<tr>
<td>Co-N₅</td>
<td>-0.79 V vs. RHE</td>
<td>0.2 M NaHCO₃</td>
<td>CO, 99.3</td>
<td>10.2</td>
<td>[S11]</td>
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<td>CoPc@Zn-N-C</td>
<td>-1.24 V vs. RHE</td>
<td>1 M KOH</td>
<td>CH₄, 18.3</td>
<td>44.3</td>
<td>[S12]</td>
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<td>Co₃O₄ layers</td>
<td>-0.87 V vs SCE</td>
<td>0.1 M KHCO₃</td>
<td>HCOO⁻, 85</td>
<td>2.7</td>
<td>[S13]</td>
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<tr>
<td>Ultrathin Co₃O₄</td>
<td>-0.88 V vs SCE</td>
<td>0.1 M KHCO₃</td>
<td>HCOO⁻, 64.3</td>
<td>0.68</td>
<td>[S14]</td>
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<td>partially oxidized Co layers</td>
<td>-0.85 V vs SCE</td>
<td>0.1 M NaSO₄</td>
<td>HCOO⁻, 90.1</td>
<td>~10</td>
<td>[S15]</td>
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<td>partially oxidized Co particles</td>
<td>-0.90 V vs. SCE</td>
<td>0.1 M NaHCO₃</td>
<td>CH₃OH, 71.4</td>
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### Table S2. The ICP results of different catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Co/wt%</th>
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<tr>
<td>Co-N</td>
<td>6.14</td>
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<tr>
<td>Co-NB-1</td>
<td>14.57</td>
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<tr>
<td>Co-NB-2</td>
<td>11.86</td>
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<tr>
<td>Co-NB-3</td>
<td>9.59</td>
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### Table S3. The BET results of different catalysts

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<th>Sample</th>
<th>S_{BET}/ m² g⁻¹</th>
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<tr>
<td>Co-N</td>
<td>584.7</td>
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<tr>
<td>Co-NB-1</td>
<td>410.4</td>
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<tr>
<td>Co-NB-2</td>
<td>137.0</td>
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<td>Co-NB-3</td>
<td>29.2</td>
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References


