Edge-hosted Fe single-atomic sites fabricated by a Bi-assisted pyrolysis strategy for electroreduction of CO₂

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Experimental Section

Materials

1,3,5-benzenetricarboxylic acid (H₃BTC), iron nitrate (Fe(NO₃)₃·9H₂O), bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), 2-methylimidazole (C₄H₆N₂), zinc nitrate (Zn(NO₃)₂·6H₂O), dicyandiamide (DCDA) were purchased from Aladdin Co., Ltd. Methanol anhydrous (CH₃OH), ethanol (CH₃CH₂OH), N,N-dimethylformamide (DMF) were provided by Guangdong Guanghua Sci-Tech Co., Ltd. All chemicals were directly used without further purification.

Catalyst preparation

Synthesis of FeBi-MOF and Bi-MOF

The FeBi-MOF was synthesized through a solvothermal method as follows: H₃BTC (750 mg), Fe(NO₃)₃·9H₂O (3 mg) and Bi(NO₃)₃·5H₂O (150 mg) were added in a mixed solvent system containing DMF (45 mL) and methanol (15 mL) at room temperature. After further sonication for 1 min, the resultant solution was transferred into a 100 ml Teflon lined stainless steel reactor and subjected to thermal treatment at 120 °C for 24 h to obtain FeBi-MOF. The FeBi-MOF precipitate was isolated by centrifugation, sequentially rinsed with methanol, then dried at 80 °C for 6 h. The Bi-MOF was prepared following an identical procedure excluding the addition of Fe(NO₃)₃·9H₂O.

Synthesis of Fe-ZIF-8

A methanol solution (100 mL) containing $Fe(NO_3)_3 \cdot 9H_2O$ (0.12 g) and $Zn(NO_3)_2 \cdot 6H_2O$ (2.23 g) was combined with a separate 100 mL methanol solution containing 5.21 g of 2-methylimidazole under vigorous stirring. Subsequently, the above mixed solution was subjected to continuous stirring for 24 h at room temperature to obtained Fe-ZIF-8 precipitate. After centrifugation, the final product was dried in an oven at 60 °C for 6 h.

Synthesis of NiBi-MOF and CoBi-MOF

The synthesis of NiBi-MOF and CoBi-MOF followed the same procedure as that of FeBi-MOF, with $Fe(NO_3)_3 \cdot 9H_2O$ substituted by $Ni(NO_3)_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$, respectively.

Preparation of e-Fe-NC

The obtained FeBi-MOF and 300 mg dicyandiamide were separately added in two porcelain boats and pyrolyzed in a tubular furnace under flowing Ar atmosphere. The temperature was ramped at 3 °C min⁻¹ to 1000 °C and maintained for 3 h. After cooling naturally to ambient temperature to yield the e-Fe-NC.

Preparation of e-NC

The preparation process is the same as that of e-Fe-NC, except that FeBi-MOF was replaced by Bi-MOF.

Preparation of Fe-NC

FeZn-ZIF (100 mg) was pyrolyzed in a tubular furnace under flowing Ar atmosphere. The temperature was ramped at 3 °C min⁻¹ to 1000 °C and maintained for 3 h. After cooling to room temperature, the product Fe-NC was obtained.

Preparation of e-Ni-NC and e-Co-NC

The preparation of e-Ni-NC and e-Co-NC followed the same procedure as that of e-Fe-NC, with FeBi-MOF substituted by NiBi-MOF or CoBi-MOF respectively.

Preparation of e-Fe-NC-950 and e-Fe-NC-1050

The preparation of e-Fe-NC-950 and e-Fe-NC-1050 followed the same procedure as that of e-Fe-NC, with pyrolysis conducted at 950 and 1050 °C respectively.

Catalyst characterization

Powder X-ray diffraction (XRD) patterns of the samples were collected with a Rigaku diffractometer (D/MAX/IIIA, 3 kW) employing Cu K α radiation (40 kV, 30 mA, $\lambda = 0.1543$ nm). Raman spectra were recorded on a LabRAM Aramis Raman spectrometer (HORIBA Jobin Yvon). N₂ adsorption/desorption isotherms were obtained on an ASAP 2460 instrument at 77 K. The surface morphology and size of the materials were investigated by a high-resolution scanning electron microscopy (SEM, HITACHI, SU8100). The structure and element mapping were determined by a high-

resolution transmission electron microscope (TEM, JEOL, JEM-2100F). The atomic structure of the catalyst was characterized using a Titan Cubed Themis G2300 (FEI, Netherlands) transmission electron microscope operated equipped with double spherical aberration correctors at 300 kV. X-ray photoelectron spectroscopy (XPS) was performed by using a Thermo Scientific Escalab 250Xi system with a base pressure of 2×10^{-9} Torr. Synchrotron-based X-ray absorption fine structure (XAFS) spectra at the Fe K-edge were collected at BL14W1 station in Shanghai Synchrotron Radiation Facility (SSRF). The metal contents of the samples were determined by inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima 8300, PE). The Fourier transform infrared spectroscopy (FT-IR) of the samples was measured on a Nicolet IS10.

Electrochemical measurements

Electrode preparation

A catalytic ink formulation was prepared by ultrasonically homogenizing 1 mg catalyst with 250 μ L ethanol and 10 μ L Nafion D-521 dispersion (2 wt%). The homogeneous suspension was precisely deposited onto the carbon cloth (1×1 cm²) surface using a micropipette. Finally, the electrode was dried under ambient conditions for further use.

Electrocatalytic CO₂ reduction

The CO₂ electrochemical reduction experiments were conducted in a standard Htype electrolytic cell configuration. All electrochemical measurements were performed using a CHI 760E electrochemical workstation. Unless otherwise specified, electrode potentials throughout this study were calibrated relative to the reversible hydrogen electrode (RHE) scale through the established conversion formula: E(vs. RHE) = E(vs.Ag/AgCl) + 0.197 V + 0.059 × pH. The three-electrode system comprises a working electrode (cathode), a counter electrode (carbon rod anode), and a reference electrode (Ag/AgCl with saturated KCl solution), separated by a Nafion-117 proton exchange membrane between cathodic and anodic chambers. A 0.1 M KHCO₃ aqueous solution (30 mL) served as the electrolyte medium. Prior to each electrolysis trial, the catholyte underwent CO_2 purging for 30 minutes through continuous bubbling to achieve solution saturation, ensuring dissolved CO_2 concentration equilibrium. This pretreatment protocol aimed to establish consistent initial conditions for subsequent electrochemical reactions at the electrode-electrolyte interface.

Product analysis

The gaseous product of electrochemical experiments was analyzed by gas chromatography (GC, HP 4890D), which was equipped with FID and TCD detectors using helium as the internal standard. The liquid product was analyzed by ¹H NMR (Bruker Avance III 400 HD spectrometer) in deuterium oxide.

The corresponding faradaic efficiency (FE) was calculated by the following equation:

 $FE\% = znF/It \times 100$

z is electron transfer number (CO was 2), n is moles of products (mol), F is Faraday constant, I is electric current (A), t is reaction time (s).

The turnover frequency (TOF) value of CO_2RR was calculated according to the equation:

 $TOF = j_{CO} / (n \times N \times F)$

 j_{CO} represents the current density of the CO (mA cm⁻²). *n* is electron transfer number, which is 2 for CO. *F* is the Faraday constant (96485 C mol⁻¹), and *N* (mol) is the number of active sites involved in the CO₂RR. *N* can be calculated by the equation:

$$N = m/M \times (ECSA / BET)$$

M represents the relative atomic mass of Fe.

m is the mass of Fe in the catalyst on the electrode surface:

 $m = m_{cat} \times w$

 m_{cat} is mass of the catalyst on the electrode (mg), w (%) is the content of single-atom metal in the catalyst.

ECSA can be calculated by the equation:

$$ECSA = (C_{dl} / C_s) \times A_{geo}$$

 C_{dl} is the double-layer capacitance value. Cyclic voltammogram measurements of the catalysts were conducted from 0.3 to 0.4 V vs. RHE with various scan rates to obtain the double layer capacitance (C_{dl}) of different catalysts. The C_{dl} was estimated by plotting the $\Delta j (j_a - j_c)$ at 0.35 V vs. RHE against the scan rates, in which j_a and j_c were the anodic and cathodic current density, respectively. The linear slope was equivalent to twice of the C_{dl} . C_s is the specific capacitance (typically 0.04 mF cm⁻²) and A_{geo} is the geometric surface area of the electrode (1 cm²).

Zn-CO₂ battery

A polished Zn plate with an area of $2 \times 1 \text{ cm}^2$ was used as the anode. The catalyst ink was prepared by dispersing 2 mg of the e-Fe-NC catalyst in a mixture solution of 350 µL ethanol and 12 µL Nafion D-521 dispersion (2 wt%). Then, the homogeneous suspension was deposited onto the carbon cloth (2×1 cm²). 0.8 M KHCO₃ was used as catholyte, while 0.8 M KOH and 0.02 M Zn (CH₃COO)₂ aqueous solution was used as anolyte. The anodic and cathodic chambers were separated by a bipolar membrane.



Fig. S1 XRD patterns of FeBi-MOF, Bi-MOF, and Fe-ZIF-8.



Fig. S2 The FTIR spectra of Bi-MOF, FeBi-MOF, and H₃BTC.

The Bi-MOF and FeBi-MOF had two peaks at 1614 and 1363 cm⁻¹, attributed to the asymmetric and symmetric vibrations of carboxylate anions in H₃BTC, respectively. Compared with the two peaks (at 1724 and 1405 cm⁻¹) of H₃BTC, those of MOF shifted to shorter wavenumber, confirming the coordination of carboxylate anions of H₃BTC with Bi³⁺ to form Bi–O bond.¹



Fig. S3 XRD patterns of e-NC, Fe-NC, and e-Fe-NC.



Fig. S4 TEM images of e-Fe-NC with different magnifications.



Fig. S5 SEM images of FeBi-MOF pyrolyzed at 500 °C in argon atmosphere with the assistance of DCDA.



Fig. S6 (a, b) SEM images, and (c, d) TEM images of e-NC with different magnifications.



Fig. S7 SEM images of (a, b) e-Co-NC, and (c, d) e-Ni-NC. (e) LSV curves, and (f) product distribution at -0.6 V of e-Co-NC and e-Ni-NC.



Fig. S8 (a) SEM, and (b) TEM images of Fe-NC.



Fig. S9 N_2 adsorption-desorption isotherms of (a) e-NC. Pore size distributions of (b) e-NC, (c) Fe-NC, and (d) e-Fe-NC.



Fig. S10 EXAFS fitting analysis of e-Fe-NC in k space.



Fig. S11 LSV curves in CO₂ and N₂-saturated 0.1 M KHCO₃ utilizing (a) e-NC, (b) Fe-NC, and (c) e-Fe-NC.



Fig. S12 (a) LSV curves, (b) product distribution at -0.6 V of e-Fe-NC obtained at different calcination temperatures.



Fig. S13 ¹H NMR spectra for the electrolyte after electrolysis at -0.6 V vs. RHE.



Fig. S14 Gas chromatographic standard curves for (a) CO and (b) H_2 .



Fig. S15 (a) XRD patterns, (b) SEM, (c) TEM, and (d) aberration-corrected HAADF-STEM images of e-Fe-NC after electrocatalysis.



Fig. S16 Measured CVs of (a) e-NC, (b) Fe-NC, and (c) e-Fe-NC in 0.1 M KHCO_3 electrolyte at different scan rates.

Samples	BET surface area $(m^2 g^{-1})$	Total pore volume $(cm^3 g^{-1})$
e-NC	506.6	0.44
Fe-NC	995.3	0.57
e-Fe-NC	688.4	0.58

 Table S1 The surface areas and pore volumes of different catalysts.

Table S2 Structural parameters of EXAFS fitting of e-Fe-NC.

Catalyst	Path	CN	R(Å)	$\sigma^2(\text{\AA}^2)$	$\Delta E_0(\mathrm{eV})$	R-factor
e-Fe-NC	Fe–N	4.3 ± 0.3	1.98 ± 0.01	0.0084	-2.4 ± 1.7	0.0097

CN: coordination number; *R*: bond distance; σ^2 : Debye-Waller factors; ΔE_0 : the inner potential correction; *R* factor: goodness of fitting.

Catalysts	Electrolytes	Potential (V vs. RHE)	FE _{CO} (%)	<i>j</i> co (mA∙cm ⁻²)	TOF (h ⁻¹)	Ref.
e-Fe-NC	0.1 M KHCO ₃	-0.6	95.2	8.2	5179	This work
Fe-NC-S	0.5 M KHCO ₃	-0.4	93	4	/	2
Fe ₁ NC/S ₁ - 1000	0.5 M KHCO ₃	-0.5	96	6.4	2225	3
Fe-N-G-P	0.1 M KHCO ₃	-0.58	94	4.5	1630	4
Fe-N/CNF	0.1 M KHCO ₃	-0.53	95	4.47	3104	5
Fe SA-NC	0.5 M KHCO ₃	-0.5	95.9	5.07	561.6	6
FeN ₄ Cl/NG	0.5 M KHCO ₃	-0.6	90.5	10.8	1566	7
Fe–N–C-0.5	0.5 M KHCO ₃	-0.64	95	1.9	910	8
FeN ₄ /C	0.5 M KHCO ₃	-0.6	93	1.25	/	9
Co SAs@NCMF	0.5 M KHCO ₃	-1.0	98.4	/	38390	10
Ni-NC(HPU)	0.5 M KHCO ₃	-0.8	91	24.7	/	11

Table S3 Comparison of CO_2RR performances of e-Fe-NC with other electrocatalysts reported in the literature.

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