Supporting Information for

Bimetallic Ni/Co Single-Atom Catalysts Guided by Energy Descriptor for Efficient CO₂ Electroreduction to Syngas

Yuye Qiu^a, Tao Zheng^a, Rui Liu^b, Jingjing Liu^a, Xiangdong Xue^c, Wengang Liu^{a,*}, Jian Liu^{*,a,c}

^a College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

^b Qingdao Central Hospital, University of Health and Rehabilitation Sciences, Qingdao 266042, China
 ^c Key Laboratory of Photoelectric Conversion and Utilization of Solar Energy, Qingdao New Energy Shandong Laboratory, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China.

Experimental Details

Chemicals and Materials

All chemical reagents and materials were used as received without further purification. All reagents involved in this were commercially available and used without further purification. Cobaltous acetate tetrahydrate ($C_4H_6CoO_4\cdot 4H_2O$, 99.5%), Nickel(II) acetate tetrahydrate ($NiC_4H_6O_4\cdot 4H_2O$, 98%), Sulfuric acid (H_2SO_4 , 95% ~ 98%) were purchased from Sinopharm Chemical Reagent Co.,Ltd. Magnesium oxide (MgO, 50 nm, 99.9%), Nafion 117 perfluorinated resin solution (5 wt%) were purchased from Shanghai Macklin Biochemical Co., Ltd. 1,10-Phenanthroline ($C_{12}H_8N_2$, 97%) was bought from Beijing InnoChem Science & Technology Co., Ltd.

Characterizations

The as-obtained products were characterized by X-ray diffraction (XRD) patterns on Rigaku Miniflex 600 X-ray diffractometer with Cu K α (λ = 1.5406 Å) radiation. XRD patterns were scanned over the angular range of 5-90°(20) with a step size of 0.01°. The metal loadings of samples were determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The transmission electron microscopy (TEM) images were measured by JEM-2100PLUS instrument. The scanning electron microscope images (SEM) were measured by JSM7500F instrument. HAADF-STEM characterization and EELS were conducted on a TALOS F200 instrument. Atomic dispersion was measured by Thermo Fisher Titan Themis G2 60-300 spherical aberration electron microscopy. X-ray photoelectron spectroscopy (XPS) measurements were performed on Thermo Scientific K-Alpha. X-ray absorption fine structure (XAFS) measurements were performed on the k-edge of Co / Ni using synchrotron radiation, and the local chemical structures around Co and Ni were characterized. Nitrogen adsorption and desorption tests were performed with micromeritics ASAP2460. Before the test, the samples were degassed at 120 °C for 10 h. The specific surface area of all samples was obtained by the brunner-emmet-teller (BET) method. The desorption temperature of CO₂ was obtained by ASAP AutoChem II 2920 TPD.

Electrochemical Measurements

The electrochemical test was carried out on the Shanghai Chenhua Electrochemical Workstation (CHI660E). The H-type electrolytic cell was composed of a counter electrode (CE, Pt sheet), a working electrode (WE, hydrophobic carbon cloth) and a reference electrode (RE, Ag/AgCl). The electrolyte was 0.5 M KHCO₃ aqueous solution. When preparing the electrode, 10 mg samples were dispersed in ethanol (950 μ L) and 5 wt % Nafion (50 μ L) solution, and ultrasonically dispersed. 100 μ L of the above suspension droplets were added to the hydrophobic carbon cloth (working area 1.0 cm⁻², loading 1 mg·cm⁻¹

²), and 0.5 M KHCO₃ solution saturated with CO₂ was added to the dry double-chamber pool at room temperature. Each compartment is filled with 50 mL of electrolyte. A proton exchange membrane (Nafion 117) was used to separate the catholyte and anolyte. The reference electrode and the working electrode are placed in the cathode chamber, and the counter electrode is placed in the anode chamber.

In order to measure the amount of electrochemical CO_2 reduction, cyclic voltammetry (CV) was used for 20 cycles to obtain a stable CV curve. After testing the current density by scanning linear voltammetry curve, the performance at constant potential was tested. In the electrochemical reaction process, the gas phase product at the outlet of the gas chamber directly enters the gas chromatograph (GC9790Plus) for on-line analysis. H₂ was analyzed by thermal conductivity detector (TCD), and CO was analyzed by flame ionization detector (FID). Gas chromatography was started every 30 min. High purity argon was used as carrier gas.

The Faraday efficiency (FE) of the gas phase product ($C_{product}$) is calculated using the concentration detected by gas chromatography as follows: ¹

$$FE = \frac{C_{\text{product}} \times 10^{-6} \times FCO_2 \times n \times 96485}{60 \times V_m \times I} \times 100\%$$

 $C_{product}$ (ppm) is the concentration of gaseous products, FCO₂ is the flow rate of CO₂ (24 mL·min⁻¹), n is the number of transferred electrons, Vm (L·mol⁻¹) is the molar volume of gas, and I (A) is the electrolysis current.

The electrochemically active surface area (ECSA) of the electrode was evaluated by double-layer capacitance (C_{dl}). In 0.5 M KHCO₃ solution, the open circuit voltage of the catalyst was tested, and cyclic voltammetry (CV) was used to determine C_{dl} in a certain potential range at different scanning rates. The slope of the current density versus the scan rate gives the value of C_{dl} .

X-ray absorption spectra Analysis

The X-ray absorption spectra (XAS) including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of the samples at Ni K-edge and Co K-edge were collected at the Shanghai Synchrotron Radiation Facility (SSRF). A double Si (111)-crystal monochromator was used for energy selection. Metal foil was employed to calibrate the energy. The spectra were collected at transmission mode at room temperature. The XAFS raw data were background-subtracted, normalized, and Fourier-transformed by the standard procedures with the Athena program (version 0.9.25). A least-squares curve fitting analysis of the EXAFS $\chi(k)$ data was carried out using the Artemis program (version 0.9.25) with the theoretical scattering amplitudes, phase shifts, and the

photoelectron mean free path for all paths calculated by the ab initio code FEFF8.

Computational methods

In this work, density functional theory (DFT) was employed for computational analysis. The M-N₄ (M = Ni, Co) configuration was modeled within a graphene layer. Core electrons were represented using the projector augmented wave (PAW) potential, while the exchange-correlation effects were treated with the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA). The convergence criterion was set with a maximum force of 0.002 Ha/Å and a maximum atomic displacement of 0.005 Å. Self-consistent field (SCF) calculations were converged to a tolerance of 1.0e⁻⁵. For k-point sampling in reciprocal space, a grid of $3 \times 3 \times 1$ was applied, ^{2, 3} with a smearing parameter of 0.005 Ha. The atomic orbital basis set utilized a double numerical basis set with d-orbital polarization functions (DND), and version 3.5 of the basis set file was employed.

The adsorption energy (E_a) can be calculated as: ^{4, 5}

$$E_a = E_{AB} - E_A - E_B$$

The adsorption energy of E_{AB} total adsorption system, the energy of E_A adsorbate, the energy of E_B adsorption matrix.

Gibbs free energy calculation formula ($\triangle G$):

$$\triangle G = E + ZPE - TS$$

E is the total energy of a substance calculated by DFT, ZPE is the zero-point vibration energy, S is the entropy, T = 298.15 K

The mechanism of CO₂RR reduction to CO:⁶

*+CO₂
$$\rightarrow$$
*CO₂
*CO₂+H⁺+e⁻ \rightarrow *COOH
*COOH + H⁺+e⁻ \rightarrow *CO+H₂O
CO \rightarrow CO+

The mechanism of HER side reaction to generate H₂:⁷

$$* + H^+ + e^- \rightarrow * H$$
$$* H + H^+ + e^- \rightarrow * + H_2$$

In-situ electrochemical IR test

The test was carried out on a FT-IR spectrometer with a MCT detector and cooled by liquid nitrogen during the test. The working electrode adopts a silicon semi-cylindrical prism with a diameter of 20 mm, and is coated with ink after gold plating on its surface. Ag/AgCl is the reference electrode and Pt wire is

the counter electrode. By gradually switching the potential from -0.03 V (vs RHE) to -1.03 V (vs RHE), the signal is recorded in a CO_2 -saturated 0.5 M KHCO₃ solution, and the spectrum collected at the open circuit voltage is used for background subtraction.

Supplementary Fig.S and Tables



Fig. S1. The elementary reaction steps involved in the electrocatalytic CO_2 reduction process under alkaline electrolytes.



Fig. S2. DFT models: top and side views of Metal-N₄-C (M=Mn Fe Co Ni Cu Zn) structure. The schematic structures of CO_2 and H_2O adsorption on M-N-C.



Fig. S3. The XRD patterns of Ni-N-C, Co-N-C and Co/Ni-N-C.

The diffraction peak observed in the Co-N-C sample in Fig. S3 corresponds to residual MgO from the synthesis process. The absence of corresponding peaks for Ni-N-C and Co/Ni-N-C samples is due to the more effective removal of MgO during the acid leaching step in these cases. Importantly, this residual MgO peak in Co-N-C does not interfere with the detection of Co species, as no XRD-detectable crystalline Co phases are present.



Fig. S4. N₂ adsorption/desorption isotherms (a) and pore distribution curves (b) of the Ni-N-C.



Fig. S5. N₂ adsorption/desorption isotherms (a) and pore distribution curves (b) of the Co-N-C.



Fig. S6. N_2 adsorption/desorption isotherms (a) and pore distribution curves (b) of the Co_1Ni_1 -N-C.



Fig. S7. SEM and the corresponding EDS elemental mappings of Ni-N-C



Fig. S8. SEM and the corresponding EDS elemental mappings of Co-N-C



Fig. S9. TEM images of Co₁Ni₂-N-C.



Fig. S10. XPS spectra for the Ni-N-C (a) the high-resolution Ni XPS spectrum of Ni-N-C that the binding energy of the Ni $2P_{3/2}$ peak (~855.7 eV), (b) the N 1s spectrum can be deconvoluted into pyridinic-N(~398.9 eV), graphitic-N(~400.8 eV), oxidized-N(~403.3 eV) N species, (c) the O 1s spectrum can be deconvoluted into C=O (~531.4 eV), C-O (~533.0 eV) O species, (d) the C 1s spectrum can be deconvoluted into graphitic-C (~284.8 eV), C-O/N (~286.0 eV), C=O (~288.4 eV) C species.



Fig. S11. XPS spectra for the Co-N-C (a) the high-resolution Co XPS spectrum of Co-N-C that the binding energy of the Co $2P_{3/2}$ peak (~780.7 eV), (b) the N 1s spectrum can be deconvoluted into pyridinic-N(~398.8 eV), graphitic-N(~400.4 eV), oxidized-N(~403.4 eV) N species, (c) the O 1s spectrum can be deconvoluted into C=O (~531.3 eV), C-O (~533.20 eV) O species, (d) the C 1s spectrum can be deconvoluted into graphitic-C (~284.8 eV), C-O/N (~286.1 eV), C=O (~288.4 eV) C species.



Fig. S12. XPS survey characterization of Co_1Ni_2 -N-C. (a) high-resolution Ni XPS spectrum of Co_1Ni_2 that the binding energy of the Ni $2P_{3/2}$ peak (~855.5 eV) (b) high-resolution Co XPS spectrum of Co_1Ni_2 that the binding energy of the Co $2P_{3/2}$ peak (~780.9eV), (c) the O 1s spectrum can be deconvoluted into C=O (~531.6 eV), C-O (~533.2 eV) O species. (d) the C 1s spectrum can be deconvoluted into graphitic-C (~284.8 eV), C-O/N (~286.2 eV), C=O (~288.3 eV) C species.



Fig. S13. Wavelet transformation of EXAFS data for Co references and bimetallic Co₁Ni₂-N-C singleatom sample.



Fig. S14. Wavelet transformation of EXAFS data for Ni references and bimetallic Co₁Ni₂-N-C singleatom sample.



Fig. S15. (a) The EXAFS best fitting curve of Co foil in k spaces, the yellow dot denotes the experimental signal and the dark black line represents the best-fit one. (b) The EXAFS best fitting curve of Ni foil in k spaces, the red dot denotes the experimental signal and the dark black line represents the best-fit one.



Fig. S16. Linear sweep voltammetry in the CO₂-saturated (solid line) and N₂-saturated (dotted line) 0.5 M KHCO₃ aqueous solution at a scan rate of 50 mV \cdot s⁻¹ for Ni-N-C, Co-N-C and Co₁Ni₂-N-C.



Fig. S17. Electrocatalytic performance of Co_3Ni_1 -N-C catalyst. (a) Faraday efficiency, (b) CO/H₂ ratio diagram, (c) partial current density of CO and H₂.



Fig. S18. Electrocatalytic performance of Co_1Ni_6 -N-C catalyst. (a) Faraday efficiency, (b) CO/H₂ ratio diagram, (c) partial current density of CO and H₂.



Fig. S19. Electrocatalytic performance of (Co_1+Ni_1) -N-C catalyst. (a) Faraday efficiency, (b) CO/H₂ ratio diagram, (c) partial current density of CO and H₂.



Fig. S20. Electrocatalytic performance of (Co_1+Ni_9) -N-C catalyst. (a) Faraday efficiency, (b) CO/H₂ ratio diagram, (c) partial current density of CO and H₂.



Fig. S21. Electrocatalytic performance of (Co_1+Ni_{14}) -N-C catalyst. (a) Faraday efficiency, (b) CO/H₂ ratio diagram, (c) partial current density of CO and H₂.



Fig. S22. CO₂-TPD spectra of Ni-N-C and Co-N-C.



Fig. S23. Double-layer capacitance measurements for determining the electrochemical active surface area for the (a) Ni-N-C, (b) Co-N-C, (c) Co₁Ni₂-N-C with mass loading 1 mg cm⁻². (d) The plots of current density against the scan rate for three samples.



Fig. S24. Tafel slope of Ni-N-C and Co-N-C catalysts.



Fig. S25. Schematic diagram of the in-situ Attenuated Total Reflection Surface-Enhanced Infrared Absorption Spectroscopy (ATR-SEIRAS).

Sample	ICP data				
	Co(wt%)	Ni(wt%)			
Co-N-C	2.13	-			
Co ₃ Ni ₁ -N-C	1.70	2.30			
Co ₁ Ni ₂ -N-C	0.57	2.15			
Co ₁ Ni ₆ -N-C	0.08	2.92			
Ni-N-C	-	4.77			

 Table S1. The Ni and Co contents of the samples obtained from ICP-OES measurements.

 Table S2. Element contents of catalysts.

Sample	XPS data					
	C(at%)	N(at%)	O(at%)	Co(at%)	Ni(at%)	
Ni-N-C	73.88	7.63	17.29		1.2	
Co-N-C	80.13	8.26	10.97	0.65		
Co ₁ Ni ₂ -N-C	81.74	8.27	8.74	0.28	0.96	

Sample	Shell	CN	R (Å)	$\sigma^{\wedge 2} (10^{-2}\text{\AA}^2)$	$\Delta \mathbf{E}_{0}$ (eV)	r-factor
Co foil	Co-Co	12*	2.49	0.6	6.0	0.0007
Co-N-C	Co-N	3.9	1.87	0.8	-12.3	0.004

Table S3. The best-fitted EXAFS results of Co sample^a.

^aCN is the coordination number for the absorber-backscatterer pair, R is the average absorberbackscatterer distance, σ^2 is the Debye-Waller factor, and ΔE_0 is the inner potential correction. * S_0^2 was fixed to 0.70 as determined from Co foil fitting. The data range used for data fitting in k-space (Δk) and R-space (ΔR) are 3.0-10.5 Å⁻¹ and 1.0-1.9 Å, respectively.

Sample	Shell	CN	R (Å)	$\sigma^{\wedge 2} (10^{-2}\text{\AA}^2)$	$\Delta \mathbf{E}_{0} \ (\mathbf{eV})$	r-factor
Ni foil	Ni-Ni	12*	2.48	0.4	5.4	0.0007
Ni-N-C	Ni-N	4.1	1.87	0.8	0.6	0.001

Table S4. The best-fitted EXAFS results of Ni sample^a.

^aCN is the coordination number for the absorber-backscatterer pair, R is the average absorberbackscatterer distance, σ^2 is the Debye-Waller factor, and ΔE_0 is the inner potential correction. S_0^2 was fixed to 0.70 as determined from Ni foil fitting. The data range used for data fitting in k-space (Δk) and R-space (ΔR) are 3.0-11.6 Å⁻¹ and 1.0-1.9 Å, respectively.

Entry	Catalyst design & synthesis	CO/H ₂ ratio range	CO/H ₂ ratio modulation	Theory-guided experimentation	Ref.
1	Wet chemical impregnation: Co/Ni single-atom species on N-doped carbon	0.23 - 2.26	Adjusting Co/Ni ratio	Empirical optimization of Co/Ni selection	Angew. Chem., Int. Ed. 2020, 59, 3033.
2	Hydrothermal synthesis: CdS _x Se _{1-x} alloyed nanorods	0.25 - 4.0	Compositional tuning (S/Se ratio in alloy)	Empirical material- specific compositional tuning	Adv. Mater. 2018, 30, 1705872.
3	Calcination of Co/Ni doped ZIF	1.0 - 2.0	regulating the Co/Ni ratio	Empirical exploration of dual- active site configurations	ACS Nano 2023, 17, 22095
4	Calcination of Zn/La/Urea	0.5 - 1.0	Adjusting La/Zn ratio	Empirical optimization of Zn and La ratios	Sci. Adv. 2021, 7, eabl4915
5	ZIF-8/phen/Fe pyrolysis:	1.0 (Fixed)	No tunability; fixed CO/H ₂ ratio	Empirical optimization of Fe- N ₄ active sites	ACS Catal. 2017, 7, 1520
6	Well-defined molecular precursors: Uniform M-N _x sites achieved via SMOC strategy	0.43 - 2.8	Adjustable Co/Ni ratio or physical mixing	Energy descriptor optimization of Co/Ni selection	This work

Table S5. Comparison of Catalyst Design, CO/H₂ Ratio Modulation, and Theoretical Guidance in CO₂ Electroreduction Studies

References

- Lv, K.; Teng, C.; Shi, M.; Yuan, Y.; Zhu, Y.; Wang, J.; Kong, Z.; Lu, X.; Zhu, Y., Hydrophobic and Electronic Properties of the E-MoS₂ Nanosheets Induced by FAS for the CO₂ Electroreduction to Syngas with a Wide Range of CO/H₂ Ratios. *Adv. Funct. Mater.* 2018, **28**, 1802339.
- 2 Tripathi, A.; Thapa, R., Optimizing CO₂RR selectivity on single atom catalysts using graphical construction and identification of energy descriptor. *Carbon* 2023, **208**, 330-337.
- 3 Qi, H.; Li, Y.; Zhou, Z.; Cao, Y.; Liu, F.; Guan, W.; Zhang, L.; Liu, X.; Li, L.; Su, Y.; Junge, K.; Duan, X.; Beller, M.; Wang, A.; Zhang, T., Synthesis of piperidines and pyridine from furfural over a surface single-atom alloy Ru₁Co_{NP} catalyst. *Nat. Commun.* 2023, **14**, 6329.
- 4 Xu, Y. N.; Li, W.; Fu, H. Q.; Zhang, X. Y.; Zhao, J. Y.; Wu, X.; Yuan, H. Y.; Zhu, M.; Dai, S.; Liu, P. F.; Yang, H. G., Tuning the Microenvironment in Monolayer MgAl Layered Double Hydroxide for CO₂-to-Ethylene Electrocatalysis in Neutral Media. *Angew. Chem., Int. Ed.* 2023, **62**, e202217296.
- 5 Qi, H.; Mao, S.; Rabeah, J.; Qu, R.; Yang, N.; Chen, Z.; Bourriquen, F.; Yang, J.; Li, J.; Junge, K.; Beller, M., Water-Promoted Carbon-Carbon Bond Cleavage Employing a Reusable Fe Single-Atom Catalyst. *Angew. Chem., Int. Ed.* 2023, **62**, e202311913.
- Zhang, Q.; Tsai, H. J.; Li, F.; Wei, Z.; He, Q.; Ding, J.; Liu, Y.; Lin, Z. Y.; Yang, X.; Chen, Z.; Hu, F.; Yang, X.; Tang, Q.; Yang, H.
 B.; Hung, S. F.; Zhai, Y., Boosting the Proton-coupled Electron Transfer via Fe-P Atomic Pair for Enhanced Electrochemical CO2 Reduction. *Angew. Chem., Int. Ed.* 2023, 62, e202311550.
- 7 Chen, Y.; Xia, M.; Zhou, C.; Zhang, Y.; Zhou, C.; Xu, F.; Feng, B.; Wang, X.; Yang, L.; Hu, Z.; Wu, Q., Hierarchical Dual Single-Atom Catalysts with Coupled CoN₄ and NiN₄ Moieties for Industrial-Level CO₂ Electroreduction to Syngas. ACS Nano 2023, **17**, 22095-22105.