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# **Supporting Information**

# Atomically Dispersed Single Ni Site Catalysts for High-Efficiency CO<sub>2</sub> Electroreduction at Industrial-Level Current Densities

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# **1. Experimental Section**

## 1.1. Chemicals.

All chemicals used were of analytical grade and used as received without further purification. Zinc nitrate hexahydrate ( $Zn(NO_3)_2$ ·6H<sub>2</sub>O, 99.0%), nickel nitrate nonahydrate ( $Ni(NO_3)_2$ ·6H<sub>2</sub>O, >98.0%), 2-methylimidazole (99.0%), methanol (>99.8%) and ethanol (99.5%) were purchased from Alfa Aesar.

# 1.2. Catalyst Synthesis.

## 1.2.1 Synthesis of ZIF-8 of various sizes

 $Zn(NO_3)_2$  hexahydrate and 2-methylimidazole (2-mim) were separately dissolved with methanol. The methanolic solution of  $Zn(NO_3)_2$  is sonicated for 10 minutes to ensure complete solvation. Afterward, the methanolic solution of 2-mim is slowly added to the  $Zn(NO_3)_2$  solution without stirring. Within seconds, the mixture turns milky, indicating the formation of ZIF-8 particles. The mixture is left to incubate in a 60 °C oven for 24 hours to complete the self-assembly process. After the colloidal solution containing the precipitated ZIF-8 crystals is taken out of the oven, it is left to naturally cool to room temperature before being centrifuged and washed three times with ethanol. The collected solid is then dried in a vacuum oven at 50 °C for 3 hours. Agglomeration and hardening of the powder can be observed with increased drying time for smaller-sized ZIF-8 particles, which led to carbons with the low surface area after carbonization. It is also notable that the Zn salts used for ZIF-8 preparation are highly sensitive to moisture which might lead to variations to the final product. For the optimal ZIF-8 preparation, it is recommended that Zn salts that are properly dehydrated be used. In general, however, a larger ratio of methanol to  $Zn(NO_3)_2$ and 2-mim lead to smaller particle sizes, as has been discussed in our previous publication.

#### 1.2.2 Synthesis of nitrogen-rich carbon hosts with hierarchical porosity of various sizes (NC)

100.0 mg of the ZIF-8 powder is placed inside an alumina boat and is subjected to pyrolysis in an Argon atmosphere at either 900, 1000, or 1100 °C for an hour using a ramping rate of 10 °C min<sup>-1</sup>. These samples are denoted as 'NC'.

# 1.2.3 Synthesis of Ni-doped carbon catalysts (Ni-N-C)

The double-solvent method was developed to introduce Ni into the carbon host. In a typical procedure, 50 mg of NC carbonized at 1000 °C is dispersed in 10 mL n-hexane via sonication for 1 minute. Afterward, 50  $\mu$ L of 50 mg mL<sup>-1</sup> Ni(NO<sub>3</sub>)<sub>2</sub> aqueous solution is added to the n-hexane solution. The prefix Ni is added to the beginning of the sample name to indicate Ni-doping. As a control, 10, 50, and 70  $\mu$ L of 50 mg mL<sup>-1</sup> Ni(NO<sub>3</sub>)<sub>2</sub> solution is added to the 120 nm NC. The mixture is then sonicated for an hour and stirred for 3 hours before being centrifuged and dried at 50 °C for an hour. The Ni-doped NC is then subjected to heat treatment at 900 °C for an hour (10 °C min<sup>-1</sup> ramp rate) to form the final Ni-N-C structure. As a second control, a 120 nm NC doped with 30  $\mu$ L of 50 mg mL<sup>-1</sup> Ni(NO<sub>3</sub>)<sub>2</sub> is also prepared using heat treatment at 400, 700, and 1200 °C.

#### **1.3 Electrochemical Measurements.**

Before dispersion, all the powdered catalysts were carefully ground with a mortar and pestle and dried in a 60 °C vacuum oven to remove moisture completely. 3.0 mg of each catalyst were weighed and mixed with 370 µL ethanol, 200 µL highly-purified Milli-Q® water, and 30 µL of 5 wt% Nafion® solutions. Subsequently, the mixture was sonicated for at least three continuous hours while ensuring the water bath's temperature did not exceed 25 °C. The Ni-doped catalysts were then drop-casted onto 0.5  $\times$  0.5 cm<sup>2</sup> carbon paper respectively and dried under an infrared lamp to obtain a working electrode with catalyst mass loading of 0.8 mg cm<sup>-2</sup>. Electrochemical tests were carried out in a three-electrode H-cell with a working electrode, a saturated Ag/AgCl reference electrode, and a platinum foil as the counter electrode. The total volume of each compartment is 50.0 mL, with each compartment filled with 40.0 mL 0.1 M KHCO<sub>3</sub> and the two separated by a piece of Nafion-115 membrane. Potentiostatic measurements were carried out using a CHI Instruments Electrochemical Station (Model 630C). The 0.1 M KHCO<sub>3</sub> electrolyte solution is saturated by flowing 30 mL min<sup>-1</sup> of 99.999 CO<sub>2</sub> (Airgas) using a mass-flow controller (Teledyne Hastings Instruments) for an hour. A continuous stream of CO2 at a similar flow rate is introduced to the cells throughout the test, and the catholyte is stirred at approximately 800 rpm. Cyclic voltammetry is repeatedly performed before other tests until stable anodic and cathodic currents are observed. Linear sweep voltammetry (scan rate 40 mV s<sup>-1</sup>) and chronoamperometric measurements were executed using iR compensation for accounting for the solution resistance between the working and counter electrode. All potentials reported are with regard to the reversible hydrogen electrode (RHE), calculated using the following equation:  $E_{vs RHE} = E_{vs Ag/AgCl} + 0.059$ × pH + 0.199V. Electrochemically-accessible surface area (ECSA) of different samples was determined using Ar-saturated 0.1 M KHCO<sub>3</sub> solution, without stirring, at a potential range between 0.3 to 0.5 V. vs. RHE to avoid any Faradaic processes.

The flow cell electrolyzer testing was performed in a custom-made flow cell. A slight modification was done for the catalyst ink preparation. 10.0 mg of Ni-N-C catalyst was mixed with 10.0 mL isopropanol and 40  $\mu$ L of 5 wt% Nafion® solutions. Subsequently, the mixture was sonicated for at least three continuous hours while ensuring the water bath's temperature did not exceed 25 °C. 2.00 mg cm<sup>-2</sup> of catalyst was then carefully spray-coated onto a 0.5  $\times$  0.5 cm<sup>2</sup> carbon paper electrode (Sigracet 38 BC) to be used as the gas diffusion electrode for the cathode under a UV lamp to ensure complete evaporation. In the opposite anodic chamber, a piece of Ni foam is used as the OER catalyst. Sandwiched between these two compartments is a piece of an anion-exchange membrane (Fumasep FAA-3-50). 1.0 M KOH was used as both the catholyte and anolyte and was continuously circulated through the cathode and anode at approximately 10 mL min<sup>-1</sup> using a dual pump-head peristaltic pump. A continuous flow of 55.0 mL min<sup>-1</sup> CO<sub>2</sub> is fed to the cathode throughout the test. The testing was conducted using a constant-current mode, and the cell voltages (average after 20 mins of run) were recorded with iR correction using a Squidstat potentiostat.

#### **1.4. Product Analysis.**

For the faradaic efficiency determination, 1 mL of the aliquot gas from the headspace of the cathode (after 10 minutes of chronoamperometry at select potentials) is injected into an online gas chromatography system (Agilent 7890B) equipped with two HP-Plot Q Capillary Columns and an HP-Plot Molesieve (Agilent) column, the thermal conductivity detector (TCD) for H<sub>2</sub> detection and a methanizer-assisted flame ionization detector (FID) for CO and CH<sub>4</sub> detection. No liquid products are detectable based upon analysis of the used electrolyte solution using nuclear magnetic resonance spectrum (Varian Inova-500 Statler), even at high overpotentials.

## **1.5.** Physical Characterization.

Catalyst morphology and particle sizes were studied using scanning electron microscopy, SEM (Hitachi SU 70 microscope) with a 5 kV working voltage. Different crystal facets of each sample

were identified using a powder X-ray diffraction, XRD (Rigaku Ultima IV diffractometer) with Cu K-a X-rays. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS Ultra DLD XPS system equipped with a hemispherical energy analyzer and a monochromatic Al K- $\alpha$  operated at 15 keV and 150 W with pass energy fixed at 40 eV for high-resolution scans. Samples were prepared as pressed powders for the XPS analysis. Ni K-edge X-ray absorption spectroscopy was measured at beamline 12BM, Advanced Photon Source (APS), Argonne National Laboratory (ANL). Data reduction, analysis, and EXAFS fitting were performed with the Athena, Artemis, and IFEFFIT software packages. The catalyst surface area and porosity distribution were determined using the Brunnauer-Emmett-Teller (BET) and density functional theory (DFT) analyses of the N<sub>2</sub> isothermal sorption measurement recorded at 77K on a Micrometritics TriStar II with samples degassing condition of 6 hours at 150 °C under vacuum. The samples' crystallinities were determined using Raman spectroscopy with a Renishaw Raman system with an excitation laser of 514 nm, a microscope objective of  $100 \times$ , and a constant excitation power of 150 µW. Thermogravimetric analysis (TGA) was performed using TA Instruments DSC SDT Q600 Thermogravimetric Analyzer using a ramping rate of 10 °C per min in an N<sub>2</sub> atmosphere. HAADF-STEM and EELS acquired in the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) were collected on a Nion UltraSTEM equipped with a Gatan Enfina spectrometer. The instrument was operated at 60 kV with a semiconvergence angle of ~31 mrad. Custom Python scripts were used to background subtract and average EELS data from multiple point spectra taken on individual bright atoms.

#### **1.6. DFT Calculations**

Faradaic efficiency (FE) of evolved gases at each applied potential was calculated using the following equation:

$$FE = (z \cdot P \cdot F \cdot V \cdot v_i)/(R \cdot T \cdot J)$$

z = number of electrons transferred per mole of gas, which is 2 for H<sub>2</sub> and CO and 8 for CH<sub>4</sub>

- P = atmospheric pressure  $(1.01 \cdot 10^5 \text{ Pa})$
- F = Faraday's constant (96500 C mol<sup>-1</sup>)

V = the flow rate of the CO<sub>2</sub> supplied to the H-cell throughout electrolysis (30 mL min<sup>-1</sup> or  $5.0 \cdot m^3 s^{-1}$ )

 $v_i$  = the concentration of gas products determined by GC (ppm)

R =the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>)

T = temperature (298.15 K)

J = current density from the potentiometric test at exactly 600 s.

The partial current density of CO,  $J_{CO}$  (or other evolved gases) can subsequently be calculated by multiplying the obtained FE with the total current density.

## **1.7. Computational Methods**

The Vienna Ab Initio Simulation Package (VASP)<sup>1-4</sup> was used to perform the spin-polarized density functional theory (DFT)<sup>5-7</sup> calculations. The revised Perdew-Burke-Ernzerhof (RPBE)<sup>8</sup> generalized gradient approximation (GGA)<sup>9</sup> and the projector augmented wave (PAW)<sup>10</sup> pseudopotential were used in our DFT calculations. A plane-wave basis set with a kinetic energy cutoff of 400 eV was used to expand the wave functions. Atomic force below 0.01 eV/Å was set as the convergence criterion during the relaxation of atomic structures, and the convergence of system energy was set to be  $1 \times 10^{-6}$  eV. The Brillouin zone was sampled using a  $4 \times 4 \times 1$  Monkhorst-Pack grid<sup>11</sup> for the structure model containing Ni-N<sub>4</sub> or Ni-N<sub>3</sub> sites, and a  $4 \times 3 \times 1$  grid was used for the structure model containing a Ni-N<sub>2+2</sub> site. The unstrained Ni-N<sub>4</sub> and Ni-N<sub>3</sub> sites were simulated in a 9.84×8.52 Å periodic supercell, whereas the unstrained Ni-N<sub>2+2</sub> site was simulated in a 9.84×12.79 Å periodic supercell of a single graphene layer. A vacuum of 14 Å was added perpendicular to the graphene layer to minimize interaction between periodic images. The reversible hydrogen electrode (RHE) was used as the reference in free energy change calculations

for adsorbed intermediates, for which the  $H^++e^-$  energy can be calculated as that of  $1/2H_2$ . The free energy change was calculated as follow:

$$\Delta G = \Delta E_{ads} + \Delta E_{ZPE} - neU + E_{sol} + \Delta H - T\Delta S$$

where  $\Delta E_{ads}$  is the DFT calculated energy change for intermediates adsorption,  $\Delta E_{ZPE}$  is the zeropoint energy correction. The energy shift due to the applied electrode potential was evaluated as – *neU*, where *n* is the number of electrons transferred and the electrode potential U is given with reference to RHE. The solvation energy correction  $E_{sol}$  for \*COOH and \*CO was adopted from previous studies.<sup>12</sup> The enthalpy change  $\Delta H$  was calculated by the integration of vibrational heat capacity and the entropy change  $\Delta S$  was evaluated from the vibrational frequencies of adsorbates. Data for free molecules from NIST database<sup>13</sup> were used for thermodynamic calculations.

# Additional results and discussion



**Figure S1.** XRD reflections of the large, medium, and small pristine ZIF-8 show the peaks typical of a ZIF-8 crystal. Sizes were varied by varying the ratio of Zn nitrate and methanol, as described in the catalyst synthesis section.



**Figure S2.** (a)  $N_2$  adsorption/desorption isotherms of the pristine ZIF-8 (120 nm), and (b) their corresponding pore size distributions, the inset of (b) is an enlarged pore size distribution from 10 to 60 nm.



**Figure S3.** XRD reflections of the N-C and Ni-N-C samples show a typical profile of partially graphitized amorphous carbon with no obvious metallic/oxide Ni peaks across the different types of Ni-N-C prepared.



**Figure S4.** SEM images of pristine ZIF-8 with a particle size of 120 nm. (a) Low-resolution image and (b) high-resolution image.



**Figure S5.** SEM images of (a, b) small- (~40 nm) and (c, d) large-sized (~2000 nm) ZIF-8. These images have shown a largely-homogeneous particle size distribution.



**Figure S6.** (a) XRD patterns and (b) Raman spectra of Ni-N-C at different thermal activation temperatures (T = 25 (Ni<sup>2+</sup>-N-C inactivated sample), 400, 800, 900, 1000, and 1200 °C). (c) The spectra corresponding to the EELS MCR maps for Ni-N-C catalysts treated from 900 and 1200 °C.



**Figure S7.** The N<sub>2</sub> adsorption/desorption isotherms (a) and pore size distributions (b) of Ni-N-C at different thermal activation temperatures (T = 25 (Ni<sup>2+</sup>-N-C inactivated sample), 400, 800, 900, and 1200 °C), respectively. Inset is the enlarged area (10 to 60 nm) from (b).



**Figure S8.** Morphology, structure, and composition of the Ni-N-C activated at 400 °C. (a-c) HAADF-STEM images, and (d) the EDS mapping of Ni from the area shown in (b). These results indicate that some Ni-based clusters (highlighted by the red circle in a and b) are presented at a low thermal activation temperature.



**Figure S9.** XPS survey spectra of the Ni-N-C catalyst activated at different temperatures. The content of Zn in these samples is at a low level, which is consistent with the EDS results (**Figure 2**). For example, the atomic Zn content in Ni-N-C-900 was measured to be 0.03 at.%, and the atomic ratio between Ni and Zn was 50/50.

**Table S1.** Breakdown of XPS elemental analysis of Ni-N-C at different thermal activation temperatures. All values are given in the absolute atomic percentage relative to all elements present. O is omitted from the table.

Samples	C (at%)			N (at%	<b>(0)</b>	Ni (at%)	Zn (at%)		
	Total	C=C	C-N/C-C	Total	Pyridinic	Graphitic	Ni-N <sub>x</sub>	Total	Total
400 °C	84.5	47.6	20.1	5.7	2.12	1.67	0.97	1.1	0.8
900 °C	88.9	49.9	17.4	5.3	1.98	1.53	0.78	0.5	0.6
1000 °C	90.6	49.7	17.4	4.8	1.78	1.55	0.75	0.5	0.5
1200 °C	93.6	57.8	15.2	2.9	0.85	1.05	0.34	0.3	0.1



**Figure S10.** (a) C 1s and (b) Ni 2p spectra of the samples with 50  $\mu$ L of 50 mg mL<sup>-1</sup> aq. Ni(II) nitrate solution was added thermally activated at 400, 900, 1000, and 1200 °C.



**Figure S11.** (a) C 1s, (b) N 1s, and (c) Ni 2p spectra of the samples with 10, 30, and 70  $\mu$ L of 50 mg mL<sup>-1</sup> aq. Ni(II) nitrate solution was added thermally activated at 900 °C.

**Table S2.** Breakdown of XPS elemental analysis of Ni-N-C with different Ni loadings. All values are given in the absolute atomic percentage relative to all elements present. Zn and O are omitted from the table.

Samples	C (at%	)		N (at%	Ni (at%)			
	Total	C=C	C-N, C-C	Total	Pyridinic	Graphitic	Ni-N <sub>x</sub>	Total
10 µL Ni	87.5	49.9	18.2	6.0	2.47	1.72	0.69	0.2
50 µL Ni	88.9	49.9	17.4	5.3	1.98	1.53	0.78	0.5
70 µL Ni	88.6	50.8	16.5	6.3	2.49	1.78	0.92	0.6



**Figure S12.** C 1s and Ni 2p spectra of the samples with 50  $\mu$ L of 50 mg mL-1 aq. Ni(II) nitrate solution was added thermally activated at 900 °C doped on small (~40 nm), medium (~120 nm), and large (~2000 nm) ZIF-8-derived N-C hosts.

**Table S3.** Breakdown of XPS elemental analysis of Ni-N-C of different N-C hosts sizes. All values are given in the absolute atomic percentage relative to all elements present. Zn and O are omitted from the table.

Samples	C (at%)				N (at%)			
	Total	C=C	C-N, C-C	Total	Pyridinic	Graphitic	Ni-N <sub>x</sub>	Total
Small Ni-N-C	94.8	56.1	14.9	2.2	0.48	0.92	0.20	0.2
Medium Ni-N-C	88.9	49.9	17.4	5.3	1.98	1.53	0.78	0.5
Large Ni-N-C	95.2	59.1	13.5	2.1	0.43	1.04	0.22	0.2



Figure S13. The k-space EXAFS curve at Ni K-edge for different Ni-N-C catalysts.



**Figure S14.** The FT-EXAFS fitting curve on the basis of metallic Ni and NiPc. The R-space EXAFS-fitting curves at Ni K-edge of and the k-space EXAFS curve at Ni K-edge of (a, b) metallic Ni and (c, d) NiPc.

NiPc	CN	R(Å)	error	E <sub>0</sub> (eV)	error	$\sigma^2(\text{\AA}^2)$	error	<b>R-factor</b>
Ni-N	4.05	1.89	0.01	4.63	1.54	0.0029	0.0014	0.0111
Ni-C	8.10	2.91	0.01	4.63	1.54	0.0043	0.0017	
Ni-N-C	16.21	3.07	0.01	4.63	1.54	0.0251	0.0136	
Ni-N	4.05	3.30	0.01	4.63	1.54	0.0063	0.0047	
Ni-N-N	16.21	3.79	0.02	4.63	1.54	0.0015	0.0091	
Ni-N-C-N	6.08	4.17	0.02	4.63	1.54	0.0009	0.0046	
Ni-N	4.05	4.20	0.02	4.63	1.54	0.0019	0.0148	
Ni-C	4.05	4.25	0.02	4.63	1.54	0.0083	0.0397	
Ni	CN	R(Å)	error	E <sub>0</sub> (eV)	error	$\sigma^2(\text{\AA}^2)$	error	<b>R-factor</b>
Ni-Ni	10.54	2.49	0.01	5.95	1.00	0.0066	0.0010	0.0250
Ni-Ni	5.27	3.52	0.01	5.95	1.00	0.0100	0.0034	
Ni-Ni	21.09	4.31	0.01	5.95	1.00	0.0086	0.0017	
Ni-Ni-Ni	84.36	4.64	0.01	5.95	1.00	0.0144	0.0161	
Ni-Ni-Ni	21.09	4.97	0.01	5.95	1.00	0.0102	0.0019	
Ni-Ni-Ni-Ni	10.54	4.97	0.01	5.95	1.00	0.0081	0.0013	

**Table S4.** Fitting parameters of the Ni K-edge EXAFS for different Ni-N-C catalysts (CN: coordination number, R: distance between absorber and backscatter atoms,  $E_0$ : energy shift,  $\sigma^2$ : Debye-Waller factor (DWF) value, R factor suggests the goodness of fit).



**Figure S15.** The FT-EXAFS fitting curve on the basis of Ni-N-C (400, 900, and 1200 °C). (a), (b), (c) The R-space EXAFS-fitting curves at Ni K-edge. (d), (e), (f) The k-space EXAFS curve at Ni K-edge. The synthesis temperature of the Ni-N-C is listed in the legend.

Ni400	CN	error	<b>R (Å)</b>	error	E <sub>0</sub> (eV)	error	$\sigma^2(\text{\AA}^2)$	error	<b>R-factor</b>
Ni-N	1.62	0.59	1.85	0.02	-2.36	1.83	0.0056	0.0028	0.0180
Ni-C	3.25	1.19	2.89	0.02	-2.36	1.83	0.0096	0.0059	
Ni-N-C	6.50	2.38	3.10	0.02	-2.36	1.83	0.0076	0.0057	
Ni-O	2.44	0.89	1.99	0.02	-2.36	1.83	0.0106	0.056	
Ni900	CN	error	<b>R (Å)</b>	error	E <sub>0</sub> (eV)	error	$\sigma^2(\text{\AA}^2)$	error	<b>R-factor</b>
Ni-N	4.06	0.65	1.87	0.01	1.16	2.03	0.0069	0.0021	0.0165
Ni-C	8.12	1.31	2.87	0.02	1.16	2.03	0.0174	0.0080	
Ni-N-C	16.24	2.61	3.03	0.02	1.16	2.03	0.0086	0.0083	
Ni1200	CN	error	<b>R</b> (Å)	error	E <sub>0</sub> (eV)	error	$\sigma^2(\text{\AA}^2)$	error	<b>R-factor</b>
Ni-N	3.54	0.56	1.87	0.02	-0.72	2.76	0.0074	0.0023	0.0164
Ni-C	7.08	1.12	2.97	0.03	-0.72	2.76	0.0076	0.0022	
Ni-N-C	14.16	2.24	3.11	0.04	-0.72	2.76	0.0008	0.0003	

**Table S5.** Fitting parameters of the Ni K-edge EXAFS for Ni-N-C (400, 900 and 1200 °C).



**Figure S16.** Analysis of the CO<sub>2</sub>RR products by using GC. (a, b) The H<sub>2</sub> and CO calibration curves were constructed by using a custom-made Airgas standard gas consisting of 490.2 ppm H<sub>2</sub>, 494.9 ppm CO and 49.75 ppm CH<sub>4</sub> (CH<sub>4</sub> calibration omitted from the figure). (c) Sample chromatogram from electrolysis at -0.9 V vs. RHE.



Figure S17. LSV comparison between Ni-N-C tested in CO<sub>2</sub> and Ar-saturated electrolyte.



**Figure S18.** (a) Faradaic efficiency towards  $CO_2RR$  and (b) CO partial current density of bestperforming Ni-N-C activated at 900 °C in 0.5 M KHCO<sub>3</sub> with varying catalyst loading.



Figure S19. Faradaic efficiency towards CO<sub>2</sub>RR and CO partial current density of Ni-N-C activated at 900 °C in 0.1 M KHCO<sub>3</sub>.



**Figure S20.** Calculated TOF values for the Ni-N-C catalysts from different thermal activation temperatures.

Catalanta	Loading	Con. of	$J_{CO}$ @ $\eta = 490 \text{ mV}$	Defenences	
Catalysts	(mg cm <sup>-2</sup> )	KHCO <sub>3</sub> (M)	(mA cm <sup>-2</sup> )	References	
Ni-N-C	0.8	0.5	61.1	This work	
Ni-NS-G	0.1	0.5	~30.1 (J)	Yang, H. B., et al. (2018). <u>Nature Energy<sup>14</sup></u>	
NiPc-CNT	0.4	0.5	>40 mA (J)	Zhang, X., et al. (2020). <u>Nature</u> <u>Energy<sup>15</sup></u>	
Ni(I)-CNT	0.5	0.5	~32.0	Zhang, T., et al. (2020). <u>Angewandte Chemie</u> <u>International Edition<sup>16</sup></u>	
Ni-N-CB	0.2	0.5	~10.0 (J)	Zheng, T., et al. (2019). Joule <sup>17</sup>	
NC-CNT (Ni)	0.5	0.1	~7.0	Fan, Q., et al. (2020). Advanced Energy Materials <sup>18</sup>	
Ni/g-CN/CP	n/a	0.5	~18.0	Zhao, C., et al. (2019). Joule <sup>19</sup>	
Ni-CNT	0.1	0.5	~40.0	Liu, S., et al. (2020). <u>Angewandte Chemie</u> <u>International Edition<sup>20</sup></u>	
Ni@NCH	0.5	0.1	~15.0	Daiyan, R., et al. (2020). <u>Nano</u> <u>Energy<sup>21</sup></u>	
Ni-N-C	2.0	1.0	~40.0	Yan, C., et al. (2018). <u>Energy</u> <u>&amp; Environmental Science<sup>22</sup></u>	
Ni-N <sub>2</sub> -C	0.6	0.5	~5.0 (J)	Gong, YN., et al. (2020). <u>Angewandte Chemie</u> <u>International Edition<sup>23</sup></u>	
Ni-N-C	1.0	0.5	~15.0	He, Y., et al. (2020). <u>Nano</u> <u>Energy<sup>24</sup></u>	
Ni-N-C	n/a	0.5	4.0	Li, Z., et al. (2020). <u>Angewandte Chemie</u> <u>International Edition<sup>25</sup></u>	
Ni-PACN (3.4 wt% Ni)	1.0	0.1	~4.0	Koshy, D. M., et al. (2020). <u>Angewandte Chemie</u> <u>International Edition<sup>26</sup></u>	

**Table S6.** Summary of electrochemical  $CO_2$  reduction to CO in an H cell for different Ni-based M-N-C catalysts reported in the literature compared to our work. Note that some publications did not directly disclose the  $J_{CO}$ , and as such, approximations were made to derive their respective CO partial current density.

Catalyst	Loading (mg cm <sup>-2</sup> )	Catholyte	Cathode potentials (V)	J <sub>CO</sub> (mA cm <sup>-2</sup> )	CO FE (%)	References
Ni-N-C-900	2.0	1.0 M KOH	-1.18	~726	~91%	This work
Ni-N-C-900	2.0	1.0 M KOH	-0.96	~391	~98%	This work
Ni-N-C-900	2.0	1.0 M KOH	-0.70	~195	~97%	This work
Ag NP	4.2	1.0 M KOH	-1.00	~275	~100%	<i>Phys. Chem. Chem.</i> <i>Phys.</i> <sup>27</sup> 2016, 18, 7075
Ag NP	4.2	3.0 M KOH	-1.00	~365	~100%	<i>Phys. Chem. Chem.</i> <i>Phys.</i> <sup>27</sup> 2016 18 7075
Au/MW-CNT	~1.0	1.0 M KOH	-0.55	158	~85%	ACS Energy Lett., <sup>28</sup> 2018, 3, 193
Co Pc-CN/CNT	0.37	1.0 M KOH	-0.67	~31	94%	ACS Energy Lett., <sup>29</sup> 2018 3 2527
NiSA/PCFM	1.0	0.5 M KHCO <sub>3</sub>	-1.20	~337	~83%	<i>Nat. Commun.</i> , <sup>30</sup> 2020, 11, 593
NiPc-OMe MDE	1.0	1.0 M KHCO <sub>3</sub>	-0.69	400	~99%	Nat. Energy, $^{31}$ 2020, 5,
CoPc/Fe-N-C	~1.0	0.5 M KOH	-0.84	~276	>85%	<i>Adv. Mater.</i> , <sup>32</sup> 2019, 31, 1903470

**Table S7.** Summary of electrochemical  $CO_2$  reduction to CO in a flow cell for different catalysts reported in the literature compared to our work.



**Figure S21.** (a) Atomic structures of unstrained and -1.5% compressively strained Ni-N<sub>2+2</sub> sites. In the figure, the gray, blue, cyan, and white balls represent C, N, Ni, and H atoms, respectively. (b) Predicted limiting potential of CO<sub>2</sub>RR on Ni-N<sub>2+2</sub> sites with various strains. (c) Predicted free energy evolution of CO<sub>2</sub>RR on (c) Ni-N<sub>2+2</sub> sites with various strain under the electrode potential of 0 V.



**Figure S22.** Atomic structures of adsorbed intermediate species (i.e., \*COOH, \*CO, and \*H) on  $NiN_4$  sites with and without strain. The gray, blue, cyan, red, and white balls represent C, N, Ni, O, and H atoms, respectively.



**Figure S23.** Atomic structures of adsorbed intermediate species (i.e., \*COOH, \*CO, and \*H) on  $NiN_{2+2}$  sites with and without strain. The gray, blue, cyan, red, and white balls represent C, N, Ni, O, and H atoms, respectively.



**Figure S24.** Predicted limiting potential difference between the CO<sub>2</sub>RR and HER ( $U_{L(CO2RR)}$ - $U_{L(HER)}$ ) on (a) NiN<sub>4</sub> and (b) NiN<sub>2+2</sub> sites with various strains.



**Figure S25.** (a) Predicted free energy evolution of HER on different NiN<sub>x</sub> (x = 3 or 4) sites under the electrode potential of 0 V. (b) Calculated values of  $U_{L(CO2RR)} - U_{L(HER)}$  on different Ni-N<sub>x</sub> (x = 3 or 4) sites.

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