Supplementary Materials

Atomically dispersed Ni sites for selective electroreduction of CO₂

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Figure S1. Wide-survey XPS spectra of Ni/NC_850, Ni/NC_900, Ni/NC_950, and Ni/NC_1100 and Ni 2p XPS

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Experimental

Materials and reagents. Nickel acetate tetrahydrate $(Ni(CH_3COO)_2 \cdot 4H_2O)$, nickel hexammine iodide $(Ni(NH_3)_6I_2)$, isopropyl alcohol (IPA), and potassium bicarbonate (KHCO₃) were obtained from Aladdin. Nafion solution was purchased from Aldrich. Carbon black (Vulcan XC-72) was purchased from Carbot Corp. Toray Carbon Paper (TGP-H-60) was obtained from Alfa Aesar. All reagents were of analytical grade and used without further purification treatment. Argon (99.999%) and carbon dioxide (99.9999%) were purchased from Beijing Haipu Gas Co. Ltd.

Synthesis of Ni/NC. Typically, 10 mg of Ni(NH₃)₆I₂ and 138.15 mg of carbon black were dispersed in 10 mL of IPA. Then the mixture was ultrasonicated for 60 min at room temperature. The precipitates were dried at 60 °C overnight. Subsequently, the sample was placed in a quartz tube furnace and heated at 850, 900, and 950 °C for 2 h in Ar to yield Ni/NC. Ni/NC catalysts with varying nickel weight contents were obtained by controlling the corresponding amount of carbon black.

Synthesis of Ni/C. In a typical procedure, 5 mg of Ni(CH₃COO)₂·4H₂O and 115.86 mg of carbon black were dispersed in 10 mL of IPA and the mixture was subject to ultrasound for 60 min at room temperature. The precipitates were dried at 60 °C overnight. Subsequently, the sample was placed in a quartz tube furnace and heated at 950 °C for 2 h in Ar to yield Ni/C.

Synthesis of NC. Typically, a mixture of carbon black (138.15 mg) and a nitrogen-containing precursor, such as polyaniline (2.03 mg), polyacrylonitrile (2.03 mg), and urea (4.35 mg) was dispersed in IPA under bath ultrasonication for 60 min at room temperature. After drying in an oven overnight, the obtained sample was annealed under N₂ with a flow rate of 20 sccm at 950 °C for 2 h. The obtained NC by pyrolysis of polyaniline, polyacrylonitrile, and urea in the presence of carbon black was named as N (PAN)C_950, N (PANI)C_950, and N(urea)C_950, respectively.

Characterization. XPS experiments were carried out using Thermo Scientific ESCALAB 250Xi instrument. The instrument was equipped with an electron flood and scanning ion gun. All spectra were calibrated to the C 1s binding energy at 284.8 eV. X-ray powder diffraction (XRD) was performed with a D/MAX-RC diffractometer operated at 30 kV and 100 mA with Cu K α radiation. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was conducted using a JEOL ARM200 microscope with 200 kV accelerating voltage. STEM samples were prepared by depositing a droplet of suspension onto a Cu grid coated with a Lacey Carbon film. The liquid products were quantified by nuclear magnetic resonance (NMR) (Bruker AVANCE AV III 400) spectroscopy using dimethyl sulfoxide as an internal standard. During chronoamperometry, effluent gas from the cell went through the sampling loop of gas chromatograph (GC, Agilent 7890B) and was analyzed in 30 min intervals to determine the concentration of gas products. The GC was equipped with a molecular sieve TDX-01 and Al₂O₃ capillary column with flowing Ar (Ultra high purity) as a carrier gas. The separated gas products were analyzed by a thermal conductivity detector (for H₂ and CO) and a flame ionization detector (for hydrocarbons).

Electrochemical test. Electrochemical CO₂ reduction was carried out on an electrochemical working station (CHI 660E, Shanghai CH Instruments Co., China). The cyclic voltammetry (CV) and linear sweep voltammetry (LSV) scans were conducted in a single compartment cell with a three electrode configuration consisted of glassy carbon as working electrode, platinum gauze as counter electrode, and Ag/AgCl (in saturated KCl solution) as reference electrode. The working electrodes were fabricated by dropping sample suspensions onto the pre-polished glassy carbon electrodes. Briefly, 10 mg of a catalyst powder was dispersed into 1 mL of ethanol with 10 μ L of 0.5 wt% Nafion solution. The mixture was ultrasonicated for 45 min to form a uniform suspension. Then 10 μ L of the dispersed catalyst ink was dropped onto the glassy carbon electrode (3 mm in diameter). Prior to experiment, the electrolyte was bubbled with Ar or CO₂ for 30 min. LSVs were recorded in Ar- or CO₂-saturated 0.1 M KHCO₃ solution in the potential range from -0.2 to -1.2 V (*vs.* RHE) at a desired sweep rate. All potentials in this study were referenced to the RHE and converted to the RHE reference scale using *E* (*vs.* RHE) = *E* (*vs.* Ag/AgCl) + 0.0197 + 0.0591 × pH (Eq. S1)

The electrolysis experiments were conducted at 25 °C in an H-type cell separated by Nafion-117 membrane with carbon paper as working electrode, platinum gauze as counter

electrode, and Ag/AgCl (in saturated KCl) as reference electrode. Toray Carbon fiber paper with a size of 1 cm \times 1 cm was used as working electrode. The catalyst ink was prepared by dispersing 1.0 mg of catalysts into a mixture solution of 0.2 mL of IPA and 1 µL of Nafion (Aldrich, 5 wt %) under ultrasonication for 30 min. H₂SO₄ aqueous solution (0.1 M) and KHCO₃ aqueous solution (0.1 M) were utilized as anodic and cathodic electrolytes, respectively. Then controlled electrolysis was performed at each potential for 60 min.

Quantitative analysis of gaseous and liquid products. The gas-phase product analysis for the electrochemical experiments was carried out using an Agilent 7890B GC system. Two thermal conductivity detectors and one flame ionization detector were used to analyze and differentiate injected samples. To characterize the gas product, 20 mL of produced gas in the dead volume of a gas bag ($\sim 2 \text{ L}$) was injected into the GC at identical experimental conditions e.g., pressure, temperature, and time using sample lock syringe. CO and H₂ mole fractions of injected samples were calculated using GC calibration curve. After electrolysis process, the electrolyte was collected to quantitatively analyze the amounts of liquid products by nuclear magnetic resonance (NMR, Bruker Avance III 400 HD spectrometer).

Faradaic efficiency. The faradaic efficiency for CO production (FE_{CO}) is calculated using the following equation: $EF_{CO} = \frac{J_{co}}{J_{total}} = \frac{v_{co} \times N \times F}{J_{total}}$ (Eq. S2) where J_{CO} is the partial current density for CO production, J_{total} is the total current density, N is the number of electron transferred for product formation (N = 2 for CO formation), v_{CO} is the production rate of CO (measured by GC), and F is Faraday constant (96485 C mol⁻¹).

Turnover frequency (TOF, h⁻¹). The TOF for CO formation was calculated as follows:

$$TOF = \frac{I_{product}/NF}{m_{cat} \times \omega/M_{Ni}} \times 3600$$
(Eq. S3)

where I_{product} is the partial current for a certain product, N is the number of electron transferred for product formation, F is Faraday constant, m_{cat} is the catalyst mass in the electrode, ω is the Ni loading in the catalyst, and M_{Ni} is the atomic mass of Ni (58.69 g mol⁻¹).



Figure S1. (a) Wide-survey XPS spectra of Ni/NC_850, Ni/NC_900, Ni/NC_950, and Ni/NC_1100. (b) Ni 2p XPS spectrum of Ni/NC_950.



Figure S2. (a) and (b) STEM images of Ni/NC_950. Single Ni atoms are circled in yellow to guide the eyes.



Figure S3. (a) The LSV results of Ni/NC_850 in Ar- (black line) or CO₂- (green line) saturated 0.1 M KHCO₃ solution with a scan rate of 5 mV s⁻¹. (b) The LSV results of Ni/NC_900 in Ar-(black line) or CO₂- (blue line) saturated 0.1 M KHCO₃ solution with a scan rate of 5 mV s⁻¹.



Figure S4. ¹H NMR spectroscopy results for the liquid products of Ni/NC after 1 h of CO_2 reduction at -0.8 V (*vs.* RHE). In addition to the water and solvent signals, no other signal was detected, indicating no liquid product formation during ECR.



Figure S5. The CO FE and CO partial current density of the catalysts with different nickel contents at an applied potential of -0.8 V (*vs.* RHE).



Figure S6. CO FE and CO partial current density versus the content of (a) overall N, (b) graphitic N, and (c) pyrrolic N in the prepared Ni/NC catalysts.



Figure S7. (a), (b), (c) Scan-rate dependence of cyclic voltammetric stripping. A series of CV experiments at different scan rates of 10, 20, 40, 60, 80, and 100 mV s⁻¹ were performed in 0.1 M KHCO₃ electrolyte to calculate the C_{dl} of Ni/NC_850, Ni/NC_900, and Ni/NC_950. (d) Current density of CV experiments at 0.15 V (*vs.* RHE) as a function of scan rate. The slope of this line shows double-layer capacitor for each catalyst. This analysis shows that Ni/NC_950 has a higher capacitance and thus a higher roughness factor than both Ni/NC_850 and Ni/NC_900.

Catalyst	Synthetic method (precursor)	Electrolyte	J	Maximum CO FE	Stability	TOF (CO)	Ref. (year)
Ni single atoms@N- doped C	Ion exchange followed by annealing at 1000 °C in Ar (2- methylimidazole, $Zn(NO_3)_2 \cdot 6H_2O$, and $Ni(NO_3)_2 \cdot 6H_2O$)	0.5 M KHCO3	-7.37 mA cm ⁻ ² @-1.0 V (<i>vs.</i> RHE)	71.9%@–0. 9 V (vs. RHE)	60 h @-1.0 V (vs. RHE)	5273 h ⁻ ¹ @–1.0 V (vs. RHE)	1 (Ref. 24 in the main text) (2017)
Ni@N- doped graphene	Impregnation and then annealing at 750 °C in NH ₃ (graphene oxide, Ni(NO ₃) ₂ ·6H ₂ O, and NH ₂)	0.5 M KHCO ₃	-11 mA cm ⁻ ² @-0.73 V (<i>vs.</i> RHE)	95.0%@–0. 73 V (vs. RHE)	20 h @-0.58 V (vs. RHE)	210000 h ⁻¹ at a cell voltage of 2.78 V	2 (Ref. 27 in the main text) (2018)
Ni-N ₄ @C	Topo-chemical transformation (dicyandiamide, NH_4Cl , $NiCl_2$, and glucose)	0.1 M KHCO ₃	-28.6 mA cm ⁻ ² @-0.81 V (<i>vs.</i> RHE)	99.0%@–0. 81 V (vs. RHE)	30 h @-0.81 V (vs. RHE)	-	3 (Ref. 7 in the main text) (2017)
Ni ²⁺ @N- doped graphene	Ion adsorption followed by annealing at 300 °C in Ar (dicyandiamide, urea, g -C ₃ N ₄ , glucose, and Ni(NO ₃) ₂ ·6H ₂ O)	0.5 M KHCO₃	-30 mA cm ⁻ ² @-0.88 V (<i>vs.</i> RHE)	92.0%@–0. 68 V (vs. RHE)	20 h @-0.58 V (vs. RHE)	-	4 (Ref. 28 in the main text) (2018)
NiSA-N- CNTs	Multi step pyrolysis (350 °C, 3 h; 650 °C, 3 h in Ar; 700-900 °C) (Ni(acac) ₂ and $C_2H_8N_2$)	0.5 M KHCO ₃	-23.5 mA cm ⁻ ² @-0.7 V (<i>vs.</i> RHE)	91.3%@-0. 7 V (vs. RHE)	12 h @-0.7 V (vs. RHE)	11.7 s ⁻ ¹ @–0.55 V (vs. RHE)	5 (Ref. 19 in the main text) (2018)
Ni-N- modified graphene	Annealing at 900 °C in Ar (pentaethylenehexamine , NiCl ₂ ·6H ₂ O, and graphene oxide)	0.1 M KHCO ₃	-0.2 mA cm ⁻ ² @-0.65 V (vs. RHE)	> 90.0% @-0.7 V ~ -0.9V (vs. RHE)	5 h @-0.65 V (vs. RHE)	4600 h ⁻ ¹ @–0.8 V (vs. RHE)	6 (Ref. 25 in the main text) (2016)
Ni-N-C	Ion adsorption followed by annealing (500 °C, 2 h in Ar), then incipient impregnation, annealing (900 °C, 2 h in Ar), and acid treatment (4,4'- dipyridyl hydrate,	0.1 M KHCO3	-10 mA cm ⁻ ² @-0.7 V (<i>vs.</i> RHE)	85.0%@–0. 78 V (<i>vs.</i> RHE)	-	-	7 (Ref. 26 in the main text) (2017)

Table S1. Comparison of electrochemical CO2 reduction performance of previously reported

Ni electrocatalysts.

CuC	/ _/						
Ni(I) two- anchored carb on N- (C ₃ F doped Ni(C graphene	-stage pyrolysis and ponization process H_6N_6 , $C_3H_7NO_2$, and $CH_3COO)_2 \cdot 4 H_2O$)	0.1 M KHCO ₃	-22 mA cm ⁻ ² @-0.65 V (<i>vs</i> . RHE)	97.0%@–0. 5 V (<i>vs</i> . RHE)	100 h @-0.65 V (vs. RHE)	14800 h ⁻ ¹ @–0.8 V (vs. RHE)	8 (Ref. 2) in the main text (2018)

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