A generalized amino-modification strategy to boost \( \text{CO}_2 \) electroreduction current density of single-atom catalysts to industrial application level

Zhipeng Chen\(^1\), Xinxin Zhang\(^1\), Wei Liu\(^2\), Mingyang Jiao\(^1\), Kaiwen Mou\(^1\), Zhiheng Wang\(^1\), Xin Ma\(^1\), Feng Cheng\(^1\), Xiangping Zhang\(^3\) and Licheng Liu\(^1\)\(^*\)

\(^1\)CAS Key Laboratory of Bio-based Materials
Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, 266101, China, *Email: liulc@qibebt.ac.cn

\(^2\)Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China

\(^3\)Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

Abstract

Although Faraday efficiency (FE) for CO production of single-atom catalysts immobilized on nitrogen-doped carbon supports (M-N/C) for \( \text{CO}_2 \) electrocatalytic reduction reaction (CO\(_2\)-RR) is generally over 90%, M-N/C catalysts demonstrate a poor reaction current density, much worse than the current density of industrial level. Herein, we first report a generalized strategy of amino-functionalized carbon supports to regulate electronic structure of M-N/C catalysts (M=Ni, Fe, Zn) to significantly increase current density of CO production. The aminated Ni single-atom catalyst achieves a remarkable CO partial current density of 447.6 mA cm\(^{-2}\) (a total current density over 500 mA cm\(^{-2}\)) with a nearly 90% CO FE at a moderate overpotential of 0.89 V, and especially CO FE can be maintained over 85% in a wide operating potential range from \(-0.5\) V to \(-1.0\) V. DFT calculations and experimental researches demonstrate that the superior activity is attributed to enhanced adsorption energies of CO\(_2^*\) and COOH\(^*\) intermediates caused by the change of electronic structure of aminated catalysts. This work provides an ingenious method for significantly increasing current density at industrial-relevant level of single-atom catalysts for CO\(_2\)-RR.
Introduction

Using renewable electricity to drive CO₂ electrocatalytic reduction to high value-added chemical fuels can not only solve the problem of excessive CO₂ emission, but also can achieve direct conversion of intermittent electric energy to chemical energy, which is of great significance to control carbon balance and optimize energy consumption structure.¹,² Due to the stable binding of C=O bond in CO₂ molecules, CO₂ electrocatalytic reduction reaction (CO₂RR) requires a high energy barrier, and moreover, the competitive hydrogen evolution reaction (HER) is more favored than CO₂RR in kinetics.³-⁵ Therefore, a large number of catalysts have been developed in the study of CO₂RR in recent years, including metals and oxides,⁶-¹⁰ nonmetal,¹¹-¹⁵ single-atom,³,¹⁶-²⁶ and ultra-thin two-dimensional metal,²⁷-²⁹ and molecule catalysts.³⁰

Among these catalysts, transition metal single-atom catalysts immobilized on nitrogen-doped carbon supports (M-N/C) exhibit good application prospects in CO₂RR due to its high atom utilization efficiency and simple synthesis method.³¹-³³ Current research on M-N/C catalysts mainly focuses on regulating coordination environment and increasing loading of single atoms.²⁴, ²⁵, ³⁴-³⁶ Although the Faraday efficiency (selectivity) of CO₂ electroreduction to CO is generally over 90%, M-N/C catalyst demonstrates a poor reaction current density to meet the requirements of industrial applications. For example, CO partial current density of most Fe-N/C catalysts is less than 15 mA cm⁻²,²³,³⁷ and Zn-N/C is less than 20 mA cm⁻².²¹,³⁸ Ni-N/C is less than 25 mA cm⁻²,²⁰,²⁴,²⁶,³⁹ Co-N/C is less than 35 mA cm⁻² at a catalytic potential of -0.8 V (vs. RHE).²⁵,³⁵,⁴⁰ The reason for a low current density is the limited adsorption capacity of catalysts for reaction intermediates, resulting in the concentration of reactants adsorbed on catalysts surface cannot meet the required concentration for reactions at more negative catalytic potentials, thus CO₂RR reaches mass transfer limit. Therefore, enhancing mass transfer of reactions is the most effective way to increase current density, such as modifying catalysts surface,⁴¹,⁴² introducing defects,⁴³ regulating catalysts electronic structure,¹⁹,⁴⁴ or optimizing the reactors (using a gas-fed flow cell or membrane-electrode assembly cell (MEA) to replace conventional H-type cell).⁸,¹⁷,¹⁸,⁴⁵-⁴⁸

Researches in the field of CO₂ adsorption show that amine-modified carbon materials can significantly enhance adsorption capacity of CO₂,⁴⁹-⁵¹ and moreover, combining with amino-modified carbon materials can enhance CO₂RR activity of transition metals.¹³,²,⁵²,⁵³ M-N/C catalysts can be regarded as a kind of carbon material
co-doped with transition metal atoms (M) and nitrogen atoms (N), therefore, it can be reasonably inferred that catalytic activity of CO\textsubscript{2}RR can be effectively increased by modifying the carbon supports in M-N/C catalysts with amino groups such as -NH\textsubscript{2}.

Inspired by these results, we modified M-N/C catalysts (M=Ni, Fe, Zn) by aminating the carbon supports (denoted as M-N/C-NH\textsubscript{2}) to increase current density and achieve a high CO FE simultaneously. Owing to regulation of electronic structure by amination modification, binding energies of COOH\textsuperscript{*} intermediate and charge transfer rate is significantly enhanced, resulting in CO partial current density reaching the industrial level (>440 mA cm\textsuperscript{-2}) with a high CO FE efficiency (>85%).

**Results**

**Synthesis and characterizations of Ni-N\textsubscript{4}/C-NH\textsubscript{2} catalysts.** Ni-N\textsubscript{4}/C-NH\textsubscript{2} was prepared by a two-step method. In brief, Ni-N\textsubscript{4}/C was obtained by pyrolyzing Ni doped ZIF-8 precursor at high temperature firstly, and then Ni-N\textsubscript{4}/C was aminated by impregnation and hydrothermal methods in ammonia water mixture to synthesize final Ni-N\textsubscript{4}/C-NH\textsubscript{2}. Detailed synthesis steps of M-N\textsubscript{4}/C-NH\textsubscript{2} are shown in the section of Methods.

TEM images show that the structure of as-prepared Ni-N\textsubscript{4}/C-NH\textsubscript{2} is similar to that of rhombic dodecahedron with a size of ~250 nm (Figure 1a and 1b). Elemental mappings reveal the homogenous distribution of Ni, C, and N elements in rhombododecahedral structure, and no aggregated nickel particles were observed (Figure 1c and 1d), which also confirmed by XRD analysis (Figure S1). The isolated bright spots in HAADF-STEM images directly demonstrate the atomic dispersion of Ni atoms (Figure 1e and 1f), and actual loading of Ni atoms provided by ICP-OES analysis is 5.32 wt%. The bonds at 3401.2 and 3308.9 cm\textsuperscript{-1} in FT-IR spectrum are corresponding to N-H stretching vibration of -NH\textsubscript{2}, and the bonds at 1580.5 and 1214.1 cm\textsuperscript{-1} are assigned to N-H bending vibration and C-N stretching vibration, respectively (Figure S2), suggesting that amino-modification (-NH\textsubscript{2}) by impregnation and hydrothermal methods in ammonia water mixture is feasible. Furthermore, deconvolution of XPS N\textsubscript{1s} spectrum also confirms the existence of N-H bonds in Ni-N\textsubscript{4}/C-NH\textsubscript{2} (Figure S3). Extended XAFS spectra of Ni-N\textsubscript{4}/C-NH\textsubscript{2} shows a first Ni-N coordination shell at 1.41 Å, which is quite different from Ni foil (Ni-Ni path at 2.09 Å) and NiO (Ni-O path at 1.60 Å) (Figure 1g). Additionally, a similar coordination
Figure 1. TEM images (a, b), low-resolution HAADF-STEM elemental mappings (c, d), high-resolution HAADF-STEM images (e, f) of Ni-N\textsubscript{4}/C-NH\textsubscript{2}. Fourier transformation of EXAFS spectra for Ni K-edge of Ni foil, NiO, NiPc, and Ni-N\textsubscript{4}/C-NH\textsubscript{2} (g). Fitting for EXAFS spectrum of Ni-N\textsubscript{4}/C-NH\textsubscript{2}, inset is Ni-N\textsubscript{4}/C-NH\textsubscript{2} structure (h).

structure is observed for Ni-N\textsubscript{4}/C (Figure S4). These results reinforce that Ni atoms still retained atomic dispersion after amino-modification. Noteworthily, Ni-N\textsubscript{4}/C-NH\textsubscript{2} exhibits similar $D_{4h}$ centro-symmetry to that of standard reference sample Ni\textsuperscript{2+}Pc as revealed by the sharp absorption peaks at 8337.5 eV (Figure S5) in XANES spectrum, implying that Ni-N\textsubscript{4}/C-NH\textsubscript{2} has a similar planar local structure with Ni\textsuperscript{2+}Pc, in which Ni atoms are coordinated by four pyrrolic-type N atoms (Figure S17).\textsuperscript{3,5,4} Fitting results of extended XAFS spectra also reveal that Ni center in Ni-N\textsubscript{4}/C-NH\textsubscript{2} adopts a planar structure with an average Ni-N coordination numbers of 3.8 (Figure 1h, Table S1). As shown in XANES spectrum, isolated Ni atoms exhibit a unique electronic structure with valence states between Ni\textsuperscript{0} (Ni foil) and Ni\textsuperscript{2+} (Ni\textsuperscript{2+}Pc) (Figure S4), which is in good
agreement with XPS results (Figure S6).

![Image of Figure 2](image-url)

**Figure 2.** Electrocatalytic activity tests in H-type cell. a) LSVs of Ni-N₄/C and Ni-N₄/C-NH₂ in CO₂/N₂-saturated electrolyte, b) CO FE and c) CO partial current density of Ni-N₄/C and Ni-N₄/C-NH₂, d) Stability test of Ni-N₄/C-NH₂ at an electrolytic potential of -0.8 V.

**CO₂RR in H-type cell.** CO₂ electrocatalytic reduction reaction was first carried out in a gas-tight H-type cell containing 0.5 M KHCO₃ electrolyte, and the gas and liquid products were quantitatively analyzed by on-line GC and HPLC, respectively. Electrocatalytic activity was first investigated by LSV tests (Figure 2a). Apparently, Ni-N₄/C-NH₂ demonstrates a larger current density in CO₂-saturated electrolyte than that in N₂-saturated electrolyte. Moreover, a more positive onset reduction potential and a larger current density of Ni-N₄/C-NH₂ in CO₂-saturated electrolyte than that of Ni-N₄/C was observed, indicating Ni-N₄/C-NH₂ is indeed active for CO₂RR. Then CO₂RR activity was evaluated by potentiostatic electrolysis, and no liquid products were detected in this research. After amino-modification, Ni-N₄/C-NH₂ shows a significant enhanced current density (Figure S7), achieving a total current density ($j_{\text{total}}$) of 76.7 mA cm⁻² at 1.0 V (an overpotential of 0.89 V). It is worth noting that the increase in current density does not result in an obvious decrease in CO FE and an increase in H₂ FE (Figure 2b and Figure S8), Ni-N₄/C-NH₂ achieves a maximum CO FE of 96.2% and that of Ni-N₄/C is 98.1%. Interestingly, CO FE of Ni-N₄/C-NH₂ maintains over 90% in
a wide operating potential window from 0.6 V to 0.9 V, which leads to a significant enhanced CO partial current density ($j_{CO}$, Figure 2c), reaching 63.6 mA cm$^{-2}$ at 1.0 V, which is 2.5 times that of Ni-N4/C. Additionally, a stable current density with CO FE of over 90% was observed for Ni-N4/C-NH2 during a long-term CO$_2$RR of 10 h at -0.8 V (Figure 2d).

To shed light on the effect of amino-modification on other single-atom catalysts, we also modified Fe and Zn single-atom catalysts by the same method. Similar to Ni-N4/C-NH2, CO$_2$ reduction activity of both catalysts, especially CO partial current density, was significantly improved after being amino-modification (Figure S9 and S10), implying that amino-functionalized carbon supports is a generalized strategy for boosting CO$_2$RR activity of single-atom catalysts.

**Figure 3.** a) Schematic of a gas-fed flow cell configuration. b) Electrocatalytic activity of Ni-N4/C-NH2 in flow cell. c) Stability test of Ni-N4/C-NH2 at an electrolytic potential of -1.0 V in flow cell. d) Nyquist plots of Ni-N4/C-NH2 at -1.0 V, and inset is the corresponding fitting equivalent circuit.

**CO$_2$RR in flow cell.** Due to the low solubility of CO$_2$ in aqueous electrolysis, current density of CO$_2$RR in an H-type cell is severely limited by mass transfer,$^{55,56}$ so we used a gas-fed flow cell equipped with a gas diffusion electrode (GDE) to electrolyze CO$_2$ (Figure 3a). Specifically, reaction current density of Ni-N4/C-NH2 in flow cell is far
greater than that in H-type cell, evidencing the superiority of this flow cell configuration (Figure S11). A maximum CO FE of 89.3% was observed for Ni-N₄/C-NH₂ at -0.9 V, and especially note that CO FE keeps above 85% over a wide potential range from -0.5 V to -1.0 V (Figure 3b). Accordingly, Ni-N₄/C-NH₂ achieves a remarkable CO partial current density of 447.6 mA cm⁻² at 1.0 V, which is 7.0 times that in an H-type cell. Compared with previously reported catalysts, Ni-N₄/C-NH₂ is one of the state-of-the-art single-atom catalysts for CO₂RR (Detailed results of comparison of catalytic activity are shown in Table S2). Although current density fluctuated regularly and slightly (~20 mA cm⁻², 3.8% of total current density), no significant attenuation of current density and CO FE were observed in a 6-hour electrolysis (Figure 3c), indicating an excellent durability of Ni-N₄/C-NH₂ catalyst in a flow cell configuration. However, it is necessary to point out that during a longer electrolysis process, the entire device will stop operating because of inevitable flooding of carbon paper based GDEs, thus suggesting that using PTFE-based GDEs with greater mechanical strength to replace carbon paper based GDEs or developing engineering methods to achieve longer-term stable operation of the device is crucial before investigating durability of the catalysts.⁵⁵,⁵⁷

Discussion

To shed light on the origin of enhanced activity by amino-modification, we first ruled out the contribution of electrochemical surface area (ECSA) to current density. CO partial current density normalized to ECSA (double layer capacity, C_dl, Figure S12) is shown in Figure S13, and a higher CO partial current density indicates the improved intrinsic activity of Ni-N₄/C-NH₂. Then, the origin of high CO partial current density was explored from the perspective of reaction kinetics by electrochemical impedance spectroscopy (EIS) and Tafel slope. Specifically, Ni-N₄/C-NH₂ exhibits a faster charge transfer rate (a smaller charge transfer resistance, Rct) than that of Ni-N₄/C, especially in flow cell configuration (Figure 3d and Table S3), which is favorable for activation process of adsorbed CO₂ in the first reaction step.⁵⁸ The higher kinetic activity was also evidenced by a lower Tafel slope of Ni-N₄/C-NH₂. Additionally, Tafel slope of Ni-N₄/C-NH₂ is closed to 118 mV dec⁻¹ (Figure S14), suggesting that the first electron-proton coupling process to form COOH* intermediate is rate-determining step (RDS).¹⁸ Finally, we investigated the effect of CO₂ adsorption capacity and adsorption strength of reaction intermediates on the intrinsic catalytic activity. CO₂ isotherm adsorption experiments reveal that CO₂ adsorption capacity of Ni-N₄/C was significantly increased
by amino-modification (Figure S15). Because the dissociative CO$_2$$^{•−}$ intermediate cannot exist stably in electrolyte, OH$^−$ adsorption was used as a surrogate to evaluate binding energy of CO$_2$$^{•−}$ by oxidative LSV experiments in 0.1 M KOH electrolyte.$^{59-61}$ As shown in Figure S16, Ni-N$\text{d}$/C-NH$_2$ demonstrates a negative potential of OH$^−$ adsorption than that of Ni-N$\text{d}$/C, evidencing a stronger adsorption strength of OH$^−$ on catalyst surface, which implies that Ni-N$\text{d}$/C-NH$_2$ can immobilize CO$_2$$^{•−}$*$^*$ intermediates more strongly, finally accelerating reaction rate of CO$_2$RR. Based on the above experimental results, the origin for enhanced catalytic activity by amination modification can be attributed to the faster charge transfer kinetics and stronger adsorption of CO$_2$ and reaction intermediates, which was also demonstrated by DFT calculations from the perspective of catalysts electronic structure (Figure 4b-4e, and Figure S20).

To further elucidate the origin for high activity of Ni-N$\text{d}$/C-NH$_2$, DFT calculations were performed by using CP2K package, and the structural model of Ni-N$\text{d}$/C-NH$_2$ is shown in Figure S17. We first calculated the effect of amino-modification on free

![Figure 4. DFT calculated results of CO$_2$RR. a) Free-energy diagram of CO$_2$ electroreduction to CO over Ni-N$\text{d}$/C and Ni-N$\text{d}$/C-NH$_2$. Differential charge diagram of b) Ni-N$\text{d}$/C-NH$_2$ and c) Ni-N$\text{d}$/C, yellow and cyan represent the dissipation and aggregation of electrons, respectively. d) Adsorption energies of reaction intermediates. e) Projected DOS of Ni 3d in Ni-N$\text{d}$/C-NH$_2$ and Ni-N$\text{d}$/C.](image-url)
energies of intermediates in the reaction path. It can be seen that electrocatalytic
reduction of CO₂ to CO includes a two-step electron-proton transfer process, involving
the key intermediate COOH* (protonation of oxygen atom in CO₂) (Figure 4a).
Encouragingly, after being modified with amino groups, free energy (ΔG) for COOH*
formation decreases by 0.57 eV, whereas ΔG to form H* formation (intermediate for
H₂ formation) increased by 0.38 eV (Figure 4a and Figure S18), demonstrating Ni-
N₄/C-NH₂ is favorable for CO formation, which coincides well with our experimental
results. A higher energy barrier to form COOH* than to form CO* are observed for
both catalysts, indicating CO₂ activation to form COOH* is the RDS, which agrees well
with the Tafel slope (Figure S14). Furthermore, a higher selectivity to CO of Ni-N₄/C-
NH₂ also can be inferred from a more positive difference value of limiting potentials
(ΔPₗımₐₜ) for CO₂RR and HER (Figure S19). Besides, we calculated charge distribution
to investigate the effect of amino-modification on electronic structure of catalysts.
Differential charge diagrams demonstrate the charge redistribution in Ni-N₄/C-NH₂ and
Ni-N₄/C (Figure 4b and 4c), which directly leads to increase of electron mobility and
change of adsorption energies of reaction intermediates.62-64 Interestingly, a more
negative adsorption energies of CO₂* and COOH* is observed for Ni-N₄/C-NH₂,
evidencing the stronger binding strength to absorbate (Figure 4d), which will enhance
the directionality of CO₂ electroreduction toward CO* formation. Although Ni-N₄/C-
NH₂ exhibits slightly stronger binding strength of CO* than that of Ni-N₄/C (a negative
adsorption energy of CO* of -0.03 V, Figure 4d), the free energy path of CO* desorption
from the catalysts surface is thermodynamically downhill (Figure 4a). Specifically, the
conventional scaling relations between COOH* and CO* intermediates was broken.32, 65-68 Finally, we further explored the origin of effect of electronic structure on adsorption
energy from the difference in density of electronic state (DOS). The calculated -2.30
eV d-band center of Ni 3d DOS in Ni-N₄/C-NH₂ is positive than that of -3.35 eV in Ni-
N₄/C (Figure 4e), which is favorable to enhance adsorption strength of reaction
intermediates because of decreased occupation caused by the positive shift of d-band
center,25 coinciding well with the experimental results of CO₂ and OH⁻ adsorption
(Figure S15 and S16). Additionally, the enhanced adsorption energy of COOH* can be
well-explained by the difference of Ni 3d DOS of Ni-N₄/C-NH₂ and Ni-N₄/C after
adsorbing COOH* species. The highest peak of Ni 3d DOS of Ni-N₄/C-NH₂ adsorbed
COOH* is closer to the Fermi level than that of Ni-N₄/C adsorbed COOH* (Figure
S20), indicating a stronger adsorption strength of Ni-N₄/C-NH₂ for COOH*. Overall,
we can draw a conclusion that amino-modification effectively regulated the catalysts electronic structure to enhance the adsorption energies of reaction intermediates and accelerate the charge transfer rate, thus promoting the CO2 activation and transformation process.

In conclusion, we provided an ingenious amino-modification method for significantly increasing the current density of CO2RR of Ni single-atom catalyst at industrial level, demonstrating a remarkable CO partial current density of 447.6 mA cm⁻² with a nearly 90% CO FE. Even more remarkably, amino-modification can not only increase the current density of Ni single-atom catalyst but also has been identified as a general strategy to enhance the current density of other single-atom catalysts, such as Fe-N/C and Zn-N/C. Both experimental and theoretical calculations demonstrate that the enhanced catalytic activity by amino-modification origins from changes in the catalysts electronic structure, which leads to stronger adsorption of reaction intermediates and faster charge transfer rate. Our work provides a new method for significantly increasing the current density at industrial-relevant level for CO2RR of single atom catalysts.

**Methods**

**Synthesis of Ni-N₄/C.** In a typical synthesis procedure, Zn(NO₃)₂·6H₂O (4.76 g) and nickel(II) acetylacetonate (Ni(acac)₂, 0.41 g) were dissolved in 60 mL of methanol, which was subsequently added into 60 mL methanol containing 2-methylimidazole (MeIM, 5.26 g) under vigorously stirring for 60 min at room temperature, and then the mix solution was grown under static at room temperature for 24 h. Next, the as-obtained precipitates were centrifuged and washed with methanol three times and dried in vacuum at 60 °C for 12 h. Finally, the as-prepared Ni-doped ZIF-8 was pyrolyzed at 1000 °C for 3 h with a heating rate 5 °C min⁻¹ in a stream (25 sccm) of Ar to yield Ni-N₄/C. During the pyrolysis process, Zn would be evaporated away (melting point of 420 °C, boiling point of 907 °C) and Ni ions would be reduced by carbonized organic linkers, leaving atomically dispersed Ni atoms anchored on nitrogen-doped carbon.

**Synthesis of Ni-N₄/C-NH₂.** In a general procedure, as-prepared Ni-N₄/C (0.10 g) was firstly mechanically mixed with carbamide (5.00 g) by an agitated mortar for 30 min, and then the fine powder mixture was pyrolyzed at 450 °C for 3 h with a heating rate 5 °C min⁻¹ in a stream (15 sccm) of NH₃. Next, the as-obtained catalyst was impregnated with the mixed solution of ammonia (25%) and ethanol (V:V=2:1, 50 mL) and stirred for 24 h. Subsequently, the obtained precipitate was dispersed in ammonia water (35 mL) and then was sealed in a Teflon-lined stainless steel autoclave and heated to 150 °C for 12 h. Finally, the suspension was centrifuged, and then the
precipitate was washed with deionized water and dried in vacuum at 60 °C for 24 h to obtain Ni-N₄/C-NH₂ catalyst. As-prepared catalysts were directly used without any post-treatment.

**Preparation of working electrodes.** The substrate electrode using in H-type cell was fabricated by carbon cloth (1×1 cm), which was sonicated in hydrochloric acid (10 M), acetone, and deionized water for 30 min, respectively. Typically, powder catalysts (12.0 mg) were dispersed in Nafion perfluorinated resin solution (5 wt%, 120 μL) and isopropanol (600 μL) by ultrasonication for 30 min to form homogeneous catalysts ink. Then the as-prepared catalyst ink was sprayed onto the carbon cloth several times with a 20 μL pipette, using 360 μL for each electrode. Finally, the obtained composite electrodes were dried at 50 °C for 12 h, and the catalyst loading is 3.0 ± 0.1 mg cm⁻¹.

Carbon paper (Freudenberg H14C9) with a Micro Porous layer (MPL) and hydrophobic treatment (PTFE) was used as gas diffusion layer (GDL). Powder catalyst was coated on the MPL face of GDL by the same method as the carbon cloth electrode using in H-type cell, and the catalyst-supported GDL was used as GDE in flow cell.

**Electrochemical experiments in H-type cell.** Electrochemical experiments were performed in a gas-tight H-cell containing 25 mL of electrolyte, which was separated by a proton exchange membrane (Nafion N117). Ag/AgCl (saturated KCl) electrode and Pt plate (1×1 cm) were used as reference and counter electrodes, respectively. Electrochemical data were recorded on a CHI660E electrochemical workstation. Before each experiment, CO₂ (99.999%) was continuously bubbled into electrolyte for 30 minutes to eliminate O₂, and saturate electrolyte with CO₂. Electrochemical experiments were measured at room temperature (25±3 °C), and all potentials reported in this paper are referenced to reversible hydrogen electrode (RHE, \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.0591 \times \text{pH} \)), and an automatic iR compensation (85%) was used. The pH of N₂ and CO₂-saturated 0.5 M KHCO₃ electrolyte in this study is 8.56 and 7.33, respectively. Linear sweep voltammetry (LSV) was carried out in CO₂-saturated or N₂-saturated 0.5 M KHCO₃ electrolyte with a scan rate of 50 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was recorded at -1.0 V in CO₂-saturated 0.5 M KHCO₃ electrolyte with an amplitude of 5 mV, and the frequency range is from 0.1 Hz to 10000 Hz. Tafel plot (overpotential versus log \( j_{\text{CO}} \)) was derived from the controlled potential electrolysis results. Electrocatalytic reduction of CO₂ was investigated for 30 min at each applied potential by controlled potential electrolysis method. Prior to each new electrolysis, 50 cycles of cyclic voltammetry (CV) were used to activate the catalysts. Stirring (1000 rpm) was applied during CO₂ electrocatalytic reduction.

**Electrochemical experiments in flow cell.** Electrochemical experiments in flow cell was performed in a four-part self-made microflow cell (Figure 3a) using constant potential electrolysis method, and an automatic iR compensation (85%) was used. Catalyst-supported GDE, Ag/AgCl
(saturated KCl) electrode equipped with a salt bridge, and squashed nickel foam (0.2 mm thickness, 400 mesh) were used as cathode (for CO\textsubscript{2} reduction), reference electrode and anode (for O\textsubscript{2} evolution), respectively. Cathode and anode are respectively connected with copper tape (current collector). Three chambers of catholyte, anolyte and CO\textsubscript{2} gas diffusion were made of polytetrafluoroethylene (PTFE), and the depth of each chamber is 0.3 cm. Each chamber had an inlet and an outlet for electrolyte or CO\textsubscript{2} gas, and reference electrode was fixed in catholyte chamber. Cathode were placed between CO\textsubscript{2} gas diffusion chamber and electrolyte chamber, and an anionic exchange membrane (Fumasep FAB-PK-130) was interposed between anolyte and catholyte chamber. Cathode area was controlled to 1 cm\textsuperscript{2} (2.0×0.5 cm) when assembling the cell, and a silicone gasket was placed between each GDE, anionic exchange membrane and electrolyte chamber for sealing. 300 mL of catholyte (1 M KOH) was circulated in cathode chamber by means of a peristaltic pump at a constant flow 35 mL min\textsuperscript{-1}. It should be emphasized that anolyte (1 M KOH) was circulated through anode chamber by using a specially-made gas-liquid mixed flow pump instead of conventional peristaltic pump, which can effectively remove O\textsubscript{2} produced in anode chamber in time, and this is one of key conditions for obtaining ultra-high current density in this flow cell configuration. High purity CO\textsubscript{2} was purged in the back chamber of catholyte chamber at a constant flow 30 sccm by mean of a digital mass flow controller, and CO\textsubscript{2} output was connected to a GC system. Due to the limitation of current range of electrochemical workstation, the actual area of GDEs was controlled to 0.5 cm\textsuperscript{2} (1.0×0.5 cm) when catalytic activity was tested at potentials of -0.9 and -1.0 V.

References

1. Appel, A. M. et al. Frontiers, opportunities, and challenges in biochemical and chemical catalysis of CO\textsubscript{2} fixation. \textit{Chem. Rev.} \textbf{113}, 6621-6658 (2013).

2. Lu, Q. & Jiao, F. Electrochemical CO\textsubscript{2} reduction: Electrocatalyst, reaction mechanism, and process engineering. \textit{Nano Energy} \textbf{29}, 439-456 (2016).

3. Yang, H. B. et al. Atomically dispersed Ni (I) as the active site for electrochemical CO\textsubscript{2} reduction. \textit{Nat. Energy} \textbf{3}, 140-147 (2018).

4. Vasileff, A., Zheng, Y. & Qiao, S. Z. Carbon Solving Carbon's Problems: Recent Progress of Nanostructured Carbon-Based Catalysts for the Electrochemical Reduction of CO\textsubscript{2}. \textit{Adv. Energy Mater.} \textbf{7}, 1700759 (2017).

5. Wang, Y., Han, P., Lv, X., Zhang, L. & Zheng, G. Defect and interface engineering for aqueous electrocatalytic CO\textsubscript{2} reduction. \textit{Joule} \textbf{2}, 2551-2582 (2018).

6. Luc, W. et al. Two-dimensional copper nanosheets for electrochemical reduction of carbon monoxide to acetate. \textit{Nat. Catal.} \textbf{2}, 423-430 (2019).

7. Chen, Z. et al. Grain-Boundary-Rich Copper for Efficient Solar-Driven Electrochemical CO\textsubscript{2} Reduction to Ethylene and Ethanol. \textit{J. Am. Chem. Soc.} \textbf{142}, 6878-6883 (2020).

8. Deng, P. et al. Metal-Organic Framework-Derived Carbon Nanorods Encapsulating Bismuth Oxides for Rapid and Selective CO\textsubscript{2} Electroreduction to Formate. \textit{Angew. Chem. Int. Ed.} \textbf{59},
1. Liu, S. et al. Efficient Electrochemical Reduction of CO₂ to HCOOH over Sub-2nm SnO₂ Quantum Wires with Exposed Grain Boundaries. *Angew. Chem. Int. Ed.* 58, 8499-8503 (2019).

2. Dinh, C.-T. et al. CO₂ electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. *Science* 360, 783-787 (2018).

3. Wang, H. et al. Efficient Electrocatalytic Reduction of CO₂ by Nitrogen-Doped Nanoporous Carbon/Carbon Nanotube Membranes: A Step Towards the Electrochemical CO₂ Refinery. *Angew. Chem. Int. Ed.* 56, 7847-7852 (2017).

4. Chen, Z., Mou, K., Yao, S. & Liu, L. Highly Selective Electrochemical Reduction of CO₂ to Formate on Metal-Free Nitrogen-Doped PC61BM. *J. Mater. Chem. A* 6, 11236-11243 (2018).

5. Zhang, S. et al. Polyethylenimine-enhanced electrocatalytic reduction of CO₂ to formate at nitrogen-doped carbon nanomaterials. *J. Am. Chem. Soc.* 136, 7845-7848 (2014).

6. Cui, X., Pan, Z., Zhang, L., Peng, H. & Zheng, G. Selective Etching of Nitrogen-Doped Carbon by Steam for Enhanced Electrochemical CO₂ Reduction. *Adv. Energy Mater.* 7, 1701456 (2017).

7. Duan, X. et al. Metal-Free Carbon Materials for CO₂ Electrochemical Reduction. *Adv. Mater.* 29, 1701784 (2017).

8. Qu, Y. et al. Direct transformation of bulk copper into copper single sites via emitting and trapping of atoms. *Nat. Catal.* 1, 781-786 (2018).

9. Zheng, T. et al. Large-scale and highly selective CO₂ electrocatalytic reduction on nickel single-atom catalyst. *Joule* 3, 265-278 (2019).

10. Gu, J., Hsu, C.-S., Bai, L., Chen, H. M. & Hu, X. Atomically dispersed Fe(3+) sites catalyze efficient CO₂ electroreduction to CO. *Science* 364, 1091-1094 (2019).

11. Lin, L. et al. Synergistic Catalysis over Iron-Nitrogen Sites Anchored with Cobalt Phthalocyanine for Efficient CO₂ Electroreduction. *Adv. Mater.* 31, 1903470 (2019).

12. Zhao, C. et al. Ionic Exchange of Metal-Organic Frameworks to Access Single Nickel Sites for Efficient Electroreduction of CO₂. *J. Am. Chem. Soc.* 139, 8078-8081 (2017).

13. Yang, F. et al. Highly efficient CO₂ electroreduction on ZnN₄-based single-atom catalyst. *Angew. Chem. Int. Ed.* 57, 12303-12307 (2018).

14. Li, X. et al. Exclusive Ni-N₄ Sites Realize Near-unity CO Selectivity for Electrochemical CO₂ Reduction. *J. Am. Chem. Soc.* 139, 14889-14892 (2017).

15. Zhang, C. et al. Electrochemical CO₂ Reduction with Atomic Iron-Dispersed on Nitrogen-Doped Graphene. *Adv. Energy Mater.*, 1703487 (2018).

16. Jiang, H.-L. et al. Regulating Coordination Environment of Single-Atom Ni Electrocatalysts Templated by MOF for Boosting CO₂ Reduction. *Angew. Chem. Int. Ed.* 59, 2705-2709 (2019).

17. Wang, X. et al. Regulation of coordination number over single Co sites: triggering the efficient electroreduction of CO₂. *Angew. Chem. Int. Ed.* 57, 1944-1948 (2018).

18. Jiang, K. et al. Transition-metal single atoms in a graphene shell as active centers for highly efficient artificial photosynthesis. *Chem* 3, 950-960 (2017).

19. Gao, S. et al. Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel. *Nature* 529, 68-71 (2016).

20. Han, N. et al. Ultrathin bismuth nanosheets from in situ topotactic transformation for selective electrocatalytic CO₂ reduction to formate. *Nat. Commun.* 9, 1320 (2018).

21. Zhang, Y. et al. Controllable synthesis of few-layer bismuth subcarbonate by electrochemical exfoliation for enhanced CO₂ reduction performance. *Angew. Chem. Int. Ed.* 130, 13467-13471
30. Wu, Y., Jiang, Z., Lu, X., Liang, Y. & Wang, H. Domino electroreduction of CO₂ to methanol on a molecular catalyst. *Nature* **575**, 639-642 (2019).
31. Cheng, Y., Yang, S., Jiang, S. P. & Wang, S. Supported single atoms as new class of catalysts for electrochemical reduction of carbon dioxide. *Small Methods* **3**, 1800440 (2019).
32. Wu, J., Sharifi, T., Gao, Y., Zhang, T. & Ajayan, P. M. Emerging Carbon-Based Heterogeneous Catalysts for Electrochemical Reduction of Carbon Dioxide into Value-Added Chemicals. *Adv. Mater.* **31**, 1804257 (2019).
33. Gong, J. Enhanced CO₂ Electroreduction on Neighboring Zn/Co Monomers by Electronic Effect. *Angew. Chem. Int. Ed.* **59**, 12664-12668 (2020).
34. Cheng, Y. et al. Unsaturated edge-anchored Ni single atoms on porous microwave exfoliated graphene oxide for electrochemical CO₂. *Appl. Catal. B-Environ.* **243**, 294-303 (2019).
35. Cheng, Y. et al. Atomically Dispersed Transition Metals on Carbon Nanotubes with UltraHigh Loading for Selective Electrochemical Carbon Dioxide Reduction. *Adv. Mater.* **30**, 1706287 (2018).
36. Guan, A. et al. Boosting CO₂ Electroreduction to CH₄ via Tuning Neighboring Single Copper Sites. *ACS Energy Lett.* **5**, 1044–1053 (2020).
37. Huan, T. N. et al. Electrochemical reduction of CO₂ catalyzed by Fe-NC materials: A structure–selectivity study. *ACS Catal.* **7**, 1520-1525 (2017).
38. Chen, Z., Mou, K., Yao, S. & Liu, L. Zinc-Coordinated Nitrogen-Codoped Graphene as an Efficient Catalyst for Selective Electrochemical Reduction of CO₂ to CO. *ChemSusChem* **11**, 2944-2952 (2018).
39. Bi, W. et al. Surface Immobilization of Transition Metal Ions on Nitrogen-Doped Graphene Realizing High-Efficient and Selective CO₂ Reduction. *Adv. Mater.* **30**, 1706617 (2018).
40. Pan, Y. et al. Design of Single-Atom Co-N₅ Catalytic Site: A Robust Electrocatalyst for CO₂ Reduction with Nearly 100% CO Selectivity and Remarkable Stability. *J. Am. Chem. Soc.* **140**, 4218-4221 (2018).
41. Li, F. et al. Molecular tuning of CO₂-to-ethylene conversion. *Nature* **577**, 509-513 (2020).
42. Zhang, J. et al. Polyethylenimine promoted electrocatalytic reduction of CO₂ to CO in aqueous medium by graphene-supported amorphous molybdenum sulphide. *Energy Environ. Sci.* **9**, 216-223 (2016).
43. Wang, Y., Han, P., Lv, X., Zhang, L. & Zheng, G. Defect and Interface Engineering for Aqueous Electrocatalytic CO₂ Reduction. *Joule* **2**, 1-32 (2018).
44. Zhang, A. et al. Nickel doping in atomically thin tin disulfide nanosheets enables highly efficient CO₂ reduction. *Angew. Chem. Int. Ed.* **130**, 11120-11124 (2018).
45. De Arquer, F. P. G. et al. CO₂ electrolysis to multicarbon products at activities greater than 1 A cm⁻². *Science* **367**, 661-666 (2020).
46. Xia, C. et al. Continuous production of pure liquid fuel solutions via electrocatalytic CO₂ reduction using solid-electrolyte devices. *Nat. Energy* **4**, 776-785 (2019).
47. Yang, H. et al. Carbon dioxide electroreduction on single-atom nickel decorated carbon membranes with industry compatible current densities. *Nat. Commun.* **11**, 593 (2020).
48. Möller, T. et al. Efficient CO₂ to CO electrolysis on solid Ni-N-C catalysts at industrial current densities. *Energy Environ. Sci.* **12**, 640-647 (2019).
49. Wang, D., Ma, X., Sentorun-Shalaby, C. & Song, C. Development of carbon-based “molecular
basket” sorbent for CO₂ capture. Ind. Eng. Chem. Res. 51, 3048-3057 (2012).
50. Chen, Z. et al. Activated carbons and amine-modified materials for carbon dioxide capture—a review. Front Environ Sci Eng 7, 326-340 (2013).
51. Zhao, L. et al. Carbon dioxide capture on amine-rich carbonaceous materials derived from glucose. ChemSusChem 3, 840-845 (2010).
52. Chen, Z., Mou, K., Wang, X. & Liu, L. Nitrogen-Doped Graphene Quantum Dots Enhance the Activity of Bi₂O₃ Nanosheets for Electrochemical Reduction of CO₂ in a Wide Negative Potential Region. Angew. Chem. Int. Ed. 57, 12790-12794 (2018).
53. Chen, Z. et al. Engineering Electronic Structure of Stannous Sulfide by Amino-Functionalized Carbon: Toward Efficient Electrocatalytic Reduction of CO₂ to Formate. Adv. Energy Mater. 10, 1903664 (2020).
54. Colpas, G. J. et al. X-ray spectroscopic studies of nickel complexes, with application to the structure of nickel sites in hydrogenases. Inorg. Chem. 30, 920-928 (1991).
55. Kai et al. Introductory Guide to Assembling and Operating Gas Diffusion Electrodes for Electrochemical CO₂ Reduction. ACS Energy Lett. 4, 639-643 (2019).
56. Endrödi, B., Kecsenovity, E., Samu, A. A., Darvas, F. & Janáky, C. Multi-Layer Electrolyzer Stack Converts Carbon Dioxide to Gas Products at High Pressure with High Efficiency. ACS Energy Lett. 4, 1770-1777 (2019).
57. Gregorio, G. L. D., Burdyny, T., Loiudice, A., Iyengar, P. & Buonsanti, R. Facet-Dependent Selectivity of Cu Catalysts in Electrochemical CO₂ Reduction at Commercially Viable Current Densities. ACS Catal. 10, 4854-4862 (2020).
58. Asadi, M. et al. Nanostructured transition metal dichalcogenide electrocatalysts for CO₂ reduction in ionic liquid. Science 353, 467-470 (2016).
59. Zhang, S., Kang, P. & Meyer, T. J. Nanostructured Tin Catalysts for Selective Electrochemical Reduction of Carbon Dioxide to Formate. J. Am. Chem. Soc. 136, 1734-1737 (2014).
60. Liu, K., Wang, J., Shi, M., Yan, J. & Jiang, Q. Simultaneous Achieving of High Faradaic Efficiency and CO Partial Current Density for CO₂ Reduction via Robust, Noble-Metal-Free Zn Nanosheets with Favorable Adsorption Energy. Adv. Energy Mater. 9, 1900276 (2019).
61. Lei, F. et al. Metallic tin quantum sheets confined in graphene toward high-efficiency carbon dioxide electroreduction. Nat. Commun. 7, 12697 (2016).
62. Zhao, S. et al. Enhanced activity for CO₂ electroreduction on a highly active and stable ternary Au-CDots-C₃N₄ electrocatalyst. ACS Catal. 8, 931-937 (2017).
63. Fu, J. et al. Low Overpotential for Electrochemically Reducing CO₂ to CO on Nitrogen-Doped Graphene Quantum Dots-Wrapped Single Crystalline Gold Nanoparticles. ACS Energy Lett. 3, 946-951 (2018).
64. Yang, F. et al. Solid-state synthesis of Cu nanoparticles embedded in carbon substrate for efficient electrochemical reduction of carbon dioxide to formic acid. Chem. Eng. J. 400, 125879 (2020).
65. Lee, C. W. et al. Defining a Materials Database for the Design of Copper Binary Alloy Catalysts for Electrochemical CO₂ Conversion. Adv. Mater., 1704717 (2018).
66. Yoo, J. S., Christensen, R., Vegge, T., Nørskov, J. K. & Studt, F. Theoretical insight into the trends that guide the electrochemical reduction of carbon dioxide to formic acid. ChemSusChem 9, 358-363 (2016).
67. Vasileff, A., Xu, C., Jiao, Y., Zheng, Y. & Qiao, S.-Z. Surface and interface engineering in
copper-based bimetallic materials for selective CO$_2$ electroreduction. *Chem 4*, 1809-1831 (2018).

68. Li, Y. & Sun, Q. Recent advances in breaking scaling relations for effective electrochemical conversion of CO$_2$. *Adv. Energy Mater.* 6, 1600463 (2016).

**Acknowledgements**

This work was supported by the National Natural Science Foundation of China (Grant No. 21676288), China Post doctoral Science Foundation (2020M672158), Dalian National Laboratory For Clean Energy (DNL) Cooperation Fund, CAS (DNL 180406) and QIBEBT (Grant: QIBEBT ZZBS 201805).

**Author contributions**

L. L contributed to the conception of the study, supervised the project, and approved the final version. Z. C. conceived the study, designed experiments, carried out most of experiments, and wrote the manuscript. Xinxin. Z., M, J, K. M, X. M, F. C. assisted Z. C. in conducting experiments and data analysis. W. L performed TEM and HAAD-STEM experiments and analyzed data. Z. W performed FTIR spectroscopy measurements and analyzed data. Xiangping Z., helped with discussions and revised the manuscript.

**Competing interests**

The authors declare no competing interests.