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Low-Valence $Zn^{\delta+}$ ($0 < \delta < 2$) Single-Atom Material as Highly Efficient Electrocatalyst for CO_2 Reduction

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Abstract: Electrochemical CO_2 reduction represents a promising approach to sustainably produce carbon-based chemicals and fuels but has been experiencing challenges in developing low-cost and efficient electrocatalysts. Herein, a nitrogen-stabilized single-atom catalyst containing low-valence zinc atoms ($Zn^{\delta+}-NC$) is reported. It is revealed that $Zn^{\delta+}-NC$ contains a mixture of saturated four-coordinate ($Zn-N_4$) and unsaturated three-coordinate ($Zn-N_3$) sites. The latter makes Zn a low-valence state, as deduced from X-ray photoelectron spectroscopy, X-ray absorption fine structure spectroscopy, electron paramagnetic resonance, and density functional theory (DFT) simulation. As a result, $Zn^{\delta+}-NC$ catalyzes electrochemical reduction of CO_2 to CO with near-unity selectivity in water at an overpotential as low as 310 mV. Importantly, a record-high current density up to 1 A cm^{-2} can be achieved together with high CO selectivity of >95% using $Zn^{\delta+}-NC$ in a flow cell reactor. DFT calculations suggest that the unsaturated $Zn-N_3$ site could dramatically reduce the energy barrier by stabilizing the $COOH^*$ (* represents active sites) intermediate due to the electron-rich environment of Zn. This work sheds light on not only the relationship between coordination number, valence state, and catalytic performance of Zn single-atom sites, but it also succeeds in achieving high current densities relevant for industrial applications.

Introduction

The electrochemical CO_2 reduction reaction (e CO_2 RR) represents a promising solution for mitigation of excessive CO_2 concentration in the atmosphere as well as for utilization and transformation of CO_2 into value-added chemicals and commodities.^[1] This technology, if powered by renewable energy such as solar and wind power, has great potential to reach industrial level and achieve long-term energy storage.^[2] Nonetheless, the inert nature of the CO_2 molecule impedes its direct electrochemical conversion, requiring large overpotential to overcome the high activation barrier. Even worse, the hydrogen evolution reaction (HER) is kinetically more favorable and will unavoidably compete with e CO_2 RR under aqueous conditions. This results in low energy utilization and poor selectivity toward the target products. In general, activity is also severely limited by low solubility and slow diffusion of CO_2 in aqueous media. Thus, it is of paramount importance to improve the scalability of e CO_2 RR by designing affordable catalysts that overcome the challenges regarding activity and selectivity.^[3]

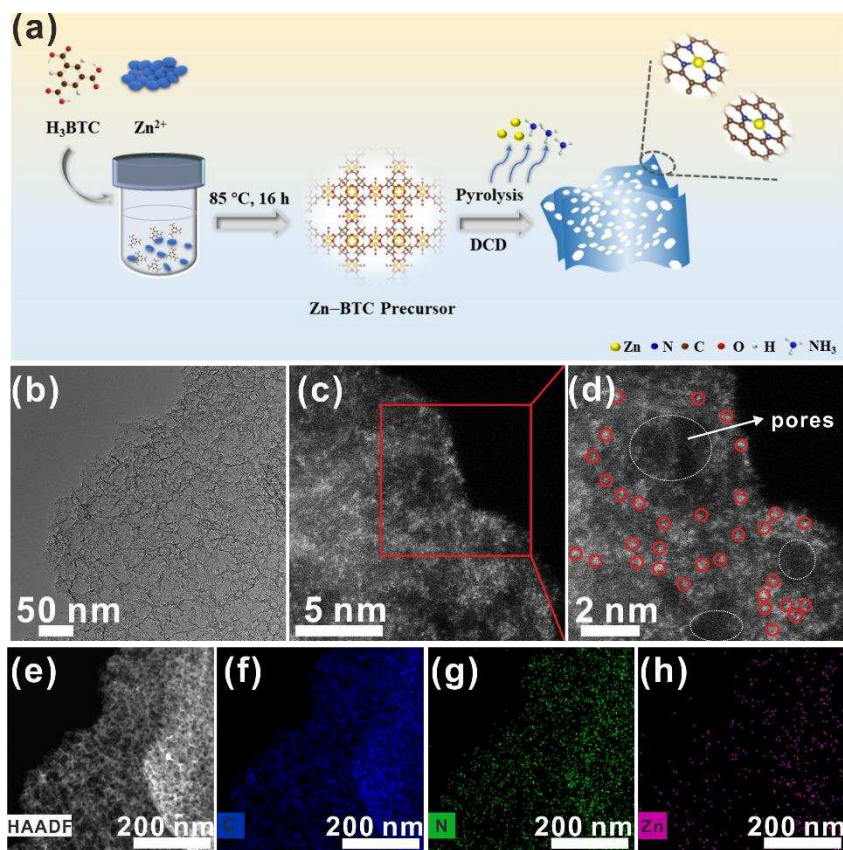


Figure 1. (a) Fabrication protocol of $\text{Zn}^{\delta+}\text{-NC}$ along with (b) TEM, (c,d) aberration-corrected HAADF-STEM, and (e–h) STEM images with corresponding elemental mapping.

To date, metal-nitrogen co-decorated carbon (M–NC) materials, featured with atomically dispersed metal cations, are emerging heterogeneous catalysts. M–NC materials have the possibility of achieving maximal utilization of metal atoms and good performance in electrocatalysis due to the unique electronic properties of the isolated metal sites.^[4] Among a variety of M–NC catalysts (e.g. Ni–NC, Fe–NC, and Co–NC),^[5] Zn–NC has experienced little progress for two reasons. First, Zn has both low melting (692 K) and boiling (1180 K) points, making it difficult to incorporate it into the carbon structure, as it readily evaporates during pyrolysis.^[6] In fact, Zn-containing precursors are often used to fabricate metal-free porous carbon materials, exploiting the removal of Zn under heat treatment.^[7] Second, unlike other earth-abundant transition metals (i.e. Fe, Co, Ni, and Cu), which have unfilled 3d orbitals with facilitated charge transfer as their characteristic feature, the fully occupied 3d¹⁰ configuration of Zn severely impedes electron movement and diminishes its electrocatalytic activity. The nature of the active site in catalysts comprising isolated Zn atoms is intensely debated. For some Zn-based complexes, the active sites have been suggested to be the ligands or adjacent carbon atoms, instead of the Zn (II) center which is considered to be inactive for electrocatalysis.^[8] In contrast, other studies have shown that Zn-based single-atom catalysts (SACs) can be responsible for CO₂ conversion.^[9] For instance, Zhu et al. studied the coexistence of Zn and Co single atoms on N-doped carbon and put forward evidence that electronic interaction between Zn and Co atoms facilitated COOH* formation on the former to boost CO production in eCO₂RR (to 93%).^[10] Fang et al. and Hao et al. addressed the

curvature of Zn–N_x sites as a way to improve eCO₂RR by increasing the electron density of the Zn 3d orbital.^[11] Although these studies showed significant improvement in eCO₂RR, further development would still be required to make industrial applications of Zn-based SACs viable. Great challenges still remain; how to construct highly efficient catalyst versions of this type, and how to gain fundamental mechanistic understanding of the exact nature of active sites.

Herein, we report a nitrogen-stabilized low-valence Zn-based SAC ($\text{Zn}^{\delta+}\text{-NC}$) prepared by pyrolyzing a Zn-containing precursor in the presence of nitrogen source. On the basis of various experimental techniques, we demonstrate that the $\text{Zn}^{\delta+}\text{-NC}$ catalyst contains a mixture of saturated four-coordinate Zn–N₄ and unsaturated three-coordinate Zn–N₃ sites. The latter kind of sites, which are electron-rich, lowers the oxidation state of Zn. Density functional theory (DFT) calculations corroborate that the 3d orbitals of the unsaturated Zn–N₃ sites are involved in binding the COOH* intermediate to effectively reduce the energy barrier of its formation. In contrast, the 3d orbital of Zn–N₄ is inert during eCO₂RR. Overall, this catalyst exhibits near 100% CO selectivity at a small overpotential (310 mV). Notably, $\text{Zn}^{\delta+}\text{-NC}$ achieves a record-high current density of 1 A cm⁻² when used in a flow cell electrolyzer, showing great prospect for industrial applications.

Results and Discussion

Material synthesis and characterization

Zn^{δ+}-NC electrocatalysts were prepared through consecutive coordination and carbonization processes (**Figure 1a**). The Zn-containing precursor, i.e. Zn-BTC (BTC denotes benzene-1,3,5-tricarboxylic acid) was synthesized following a solvothermal method.^[12] Powder X-ray diffraction (XRD) pattern confirms its good crystallinity, and scanning electron microscopy (SEM) images show a smooth slab structure of Zn-BTC, with a surface area of 23 m² g⁻¹ determined by the Brunauer-Emmett-Teller (BET) method (**Figure S1**). Next, Zn-BTC was pyrolyzed at 1000 °C under Ar atmosphere in the presence of dicyandiamide (DCD) to produce the target material, Zn^{δ+}-NC. Here, DCD serves as nitrogen source to anchor Zn single atoms through Zn-N coordination. This is accomplished as judged from the 1.08 wt% Zn content determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). SEM images of Zn^{δ+}-NC show that pyrolysis leaves the surface less smooth with numerous holes exposed (**Figure S2**). The coarse structure of Zn^{δ+}-NC with coexistence of both micropores and mesopores gives it a high surface area of 332 m² g⁻¹ and good CO₂ adsorption capacity of 34 cm³ g⁻¹ (**Figures S3 and S4**).

Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images reveal that Zn^{δ+}-NC possesses thin nanosheets morphology with large population of through-plane pores (**Figures 1b,e and S5**). Importantly, we observe neither Zn nanoparticles nor clusters across the entire structure of Zn^{δ+}-NC. Instead, we see nicely distributed bright spots, corresponding to Zn atoms, from aberration-corrected HAADF-STEM (**Figure 1c,d**). Moreover, atomization of Zn after pyrolysis could be substantiated by the XRD pattern, showing only diffraction from graphitic carbon ($2\theta = 26^\circ$ and 43°) and no Zn-based crystalline phases (**Figure S6**).^[6a] Finally, elemental mapping by energy-dispersive X-ray spectroscopy reveals uniform distribution of C, N, and Zn (**Figure 1f-h**) which, together with the aberration-corrected HAADF-STEM and XRD pattern, confirms the existence of Zn single atoms in Zn^{δ+}-NC.

For comparative purpose, we synthesized two control samples leaving out either the Zn or N source from the pyrolysis step. In the former case, N-doped carbon (denoted NC) was obtained (**Figures S7-S9**). In the latter case, somewhat surprisingly, the produced material contained no Zn, but only carbon (denoted BTC-C). This substantiates the indispensable role of DCD in preparation of Zn single atoms, serving to prevent Zn evaporation at high temperature by anchoring the atoms.^[13] In addition, a third control sample (DP-ZnNC) was produced by pyrolyzing directly the mixture of zinc nitrate and H₃BTC to verify the importance of using the Zn-BTC framework as precursor in the Zn SAC preparation (**Figure S10**).

Valence state and fine structure of Zn

XPS was employed to characterize chemical composition and elemental state of Zn^{δ+}-NC, using Zn(II) tetraphenylporphine (ZnTPP) containing Zn²⁺ and an intact Zn-N₄ core structure as reference sample (**Figure S11**). The binding energy of Zn 2p_{3/2} in Zn^{δ+}-NC is located at 1021.6 eV, which is slightly lower than that of ZnTPP (1021.9 eV) (**Figures 2a and S12**).^[11a] This would

suggest a low-valence Zn (<2+) in Zn^{δ+}-NC. In addition, Zn Auger LMM kinetic energy spectra reveal a distinct Zn LMM peak (990.0 eV) of Zn^{δ+}-NC located between that of ZnTPP (987.8 eV) and Zn metal (992.0 eV) (**Figure 2b**). This corroborates the low valence state of Zn^{δ+}, suggesting that a certain fraction of Zn(II) atoms have been reduced to Zn(I) during heat treatment because of the strong reductive capacity of NH₃ released from DCD.^[14] The N 1s XPS spectrum of Zn^{δ+}-NC (**Figure 2c**) can be deconvoluted into five types of N, including pyridinic N, Zn-N, pyrrolic N, graphitic N, and oxidized N. The presence of Zn-N species, which is further shown in N K-edge soft X-ray absorption near-edge structures (XANES) (**Figure S13a**), supports the atomic dispersion of Zn.

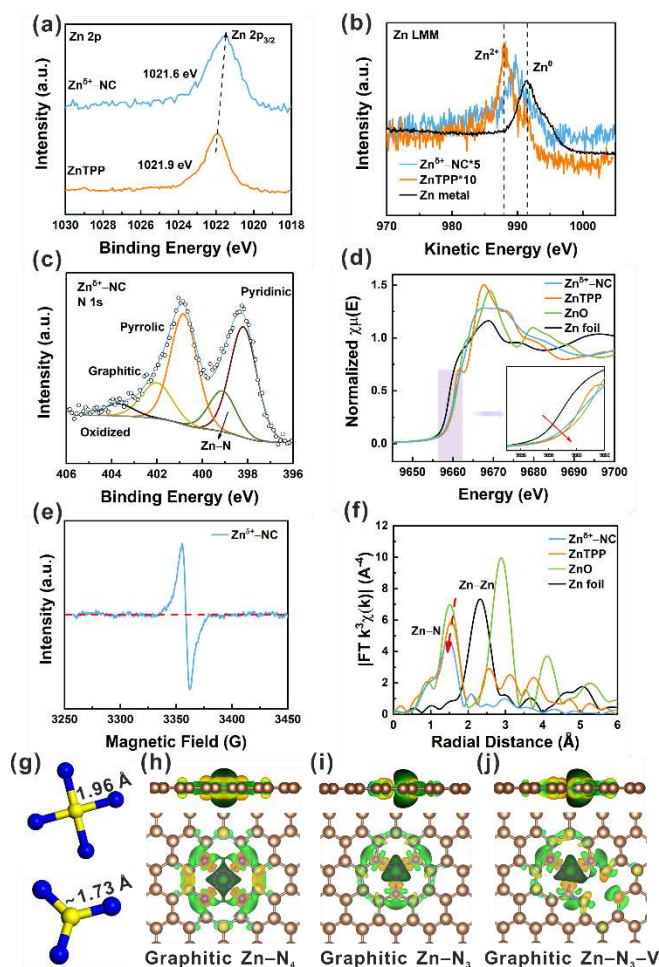


Figure 2. (a) XPS Zn 2p spectra, (b) Zn Auger LMM kinetic energy spectra, (c) N 1s spectrum, (d) Zn K-edge XANES (inset shows enlarged near-edge pattern), (e) EPR spectrum, and (f) Fourier transform of EXAFS spectra of Zn^{δ+}-NC. (g) Interatomic distance between Zn center (yellow) and surrounding N atoms (blue) in graphitic Zn-N₄, Zn-N₃ (or Zn-N₃-V where V denotes vacancy) model simulated from DFT calculations. (h-j) Calculated spatial distribution of charge density for graphitic Zn-N₄, Zn-N₃, and Zn-N₃-V (yellow and green iso-surfaces denote depletion and gain of electron density, respectively, with an iso-surface value of 0.003 e Å⁻³; brown color represents C atoms).

To elucidate the fine electronic structure of Zn^{δ+}-NC, the Zn K-edge spectrum from XANES was analyzed with ZnTPP, ZnO, and Zn foil serving as references (**Figures 2d and S14**). Notably, the adsorption edge position of Zn^{δ+}-NC is far away from that of Zn foil but also at somewhat lower energy than that of ZnTPP. Second, the white line intensity of Zn^{δ+}-NC lies in between Zn foil

and ZnTPP/ZnO. Third, the typical D_{4h} symmetry fingerprint peak of Zn–N₄ at 9661.8 eV, as seen in the ZnTPP spectrum, disappears in Zn^{δ+}–NC, indicative of a non-centrosymmetric Zn–N configuration.^[15] In addition, electron paramagnetic resonance (EPR) spectroscopy shows a distinct signal (**Figure 2e**), which is attributed to the unpaired electron of Zn (I) in Zn^{δ+}–NC,^[8c,15] as the coordinately saturated Zn (II) would be EPR silent.^[8c] All these observations point toward low valency of Zn^{δ+} ($0 < \delta < 2$) in Zn^{δ+}–NC.

Figure 2f compares phase-uncorrected Fourier transformed (FT) EXAFS spectra of Zn^{δ+}–NC, ZnTPP, ZnO, and Zn foil. In the radial distribution function from k^3 -weight Zn K-edge EXAFS, no Zn–Zn bonding at 2.32 Å is detected in Zn^{δ+}–NC. This excludes presence of metallic Zn in Zn^{δ+}–NC and underlines good atom dispersion of Zn sites. Furthermore, because Zn–C and Zn–O bonds are excluded from C and O K-edge XANES spectra (**Figure S13b,c**) and C and O 1s XPS spectra (**Figure S15**), the first-shell main peaks at 1.47 and 1.55 Å for Zn^{δ+}–NC and ZnTPP, respectively, are attributed to Zn–N coordination. The slightly shorter Zn–N interatomic distance of Zn^{δ+}–NC, relative to that of ZnTPP, unveils a contracted Zn–N–C local center in Zn^{δ+}–NC. Moreover, the fact that Zn^{δ+}–NC displays lower peak intensity than that of the four N-coordination (Zn–N₄) in ZnTPP, suggests that the coordination number is lower than four. Taking together, XANES and EXAFS spectra consistently suggest the existence of non-centrosymmetric and unsaturated Zn–N centers in Zn^{δ+}–NC.

We conducted EXAFS fitting using ZnTPP as Zn–N₄ core structure to identify the local structure of Zn^{δ+}–NC (**Figure S16**). **Table S2** summarizes the fitting parameters. Notably, the average coordination number of Zn–N in Zn^{δ+}–NC after first-shell fitting is 3.47, which is far less than four. It should be noted that the fitting result becomes less satisfactory using Zn–N₃ as model (with vacancy nearby or not), as evidenced from the larger *R*-factor (percentage misfit) and unmatched coordination number. These results would suggest that Zn^{δ+}–NC consists of a mixture of Zn–N₄ and Zn–N₃. Furthermore, Zn–N₄, Zn–N₃, and Zn–N₃–V (V denotes vacancy) were modelled up in the graphene plane to simulate the active site structure in the viewpoint of DFT (**Figure 2g**); presence of vacancies was considered due to the observation of pores in Zn^{δ+}–NC (**Figure 1**). The DFT optimized Zn–N bond distance of ~1.73 Å in both Zn–N₃ and Zn–N₃–V, is shorter than that of Zn–N₄ (1.96 Å), matching well with the radial distance in EXAFS results and fitting analysis.

Next, we employed Bader charge analysis to characterize the Zn–surface interaction using the above models (**Figure 2h–j**). Green and yellow regions refer to electron accumulation and depletion, respectively. The Zn atom possesses 10.82, 11.00, and 10.90 valence electrons after combining with N atoms in Zn–N₄, Zn–N₃, and Zn–N₃–V, respectively. Thus, the Zn atom in Zn–N₃ or Zn–N₃–V possesses an electron-rich environment compared to that in Zn–N₄, leading to lower valence state in Zn^{δ+}–NC. Thus, together with the structural characterization of XAS and XPS, these results reveal the relationship between coordination number and valence state. Zn^{δ+}–NC consists of a mixture of Zn(II)–N₄ and Zn(I)–N₃ sites, leading to a mix-coordinated and low-average-valence Zn–N_x ($3 \leq x \leq 4$) structure. Meanwhile, the Zn–N₃ and/or Zn–N₃–V could hold enough delocalized electrons to facilitate electron transfer and affect the intermediate adsorption/desorption steps during eCO₂RR.^[15]

eCO₂RR performance in H-cell

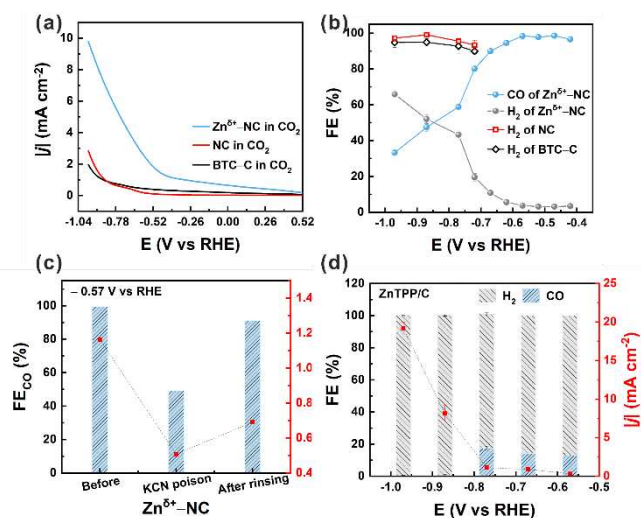


Figure 3. (a) Linear sweep voltammograms at sweep rate = 10 mV s⁻¹ and (b) FE of H₂ and CO measured after 15 min electrolysis at various potentials for Zn^{δ+}–NC, NC, and BTC–C. (c) FE_{CO} and $|j|$ recorded at –0.57 V vs RHE for Zn^{δ+}–NC in the absence and presence of 25 mM KCN (as well as after rinsing) after 15 min electrolysis. (d) FE and $|j|$ measured at various potentials for ZnTPP/C after 15 min electrolysis. Electrolyte is CO₂-saturated 0.5 M KHCO₃.

To test electrocatalytic properties of the as-prepared Zn^{δ+}–NC, NC, and BTC–C, linear sweep voltammograms were recorded under both CO₂ and Ar atmosphere in 0.5 M KHCO₃ (**Figures 3a** and **S17**). Increase of the absolute cathodic current density, $|j|$, recorded on Zn^{δ+}–NC is evident upon purging CO₂ into the catholyte. Moreover, it is comparatively larger than that for the NC and BTC–C materials under the same conditions, implying that Zn^{δ+}–NC exhibits much better catalytic performance for eCO₂RR.

Next, eCO₂RR activity and selectivity of the materials were evaluated in an H-cell at selected potentials between –0.97 and –0.42 V vs the reversible hydrogen electrode (RHE). CO and H₂ are the only products detected (**Figure S18**). **Figure 3b** shows that Zn^{δ+}–NC gives the largest CO selectivity in the entire potential range, presenting a maximum CO faradaic efficiency (FE_{CO}) as high as 99% at –0.47 V vs RHE. However, DP–ZnNC produced via direct pyrolysis of the precursors performs significantly poorer, emphasizing the importance of the Zn–BTC template for obtaining a highly active Zn-based SAC (**Figure S19**).

Moreover, CO formation on Zn^{δ+}–NC starts already at –0.42 V vs RHE, corresponding to a fairly low overpotential of 310 mV, given that the equilibrium potential for CO₂ to CO is –0.11 V vs RHE. In contrast, NC and BTC–C are both inactive for CO₂ reduction, with only H₂ being detected during electrolysis. Notably, Zn^{δ+}–NC exhibits much higher $|j|$ and, in particular, $|j_{CO}|$ compared with NC and BTC–C (**Figure S20**), underlining the catalytic activity of Zn-based active sites in eCO₂RR. To a minor extent only, this enhancement can be attributed to a higher electrochemical active surface area (ECSA) of Zn^{δ+}–NC, evaluated from the double-layer capacity (*C_{dl}*) of all electrodes (**Figure S21**). In this manner, *C_{dl}*, which is proportional to ECSA, was found to be 19.4, 1.9 and 9.7 mF cm⁻² for Zn^{δ+}–NC, NC, and BTC–C, respectively.

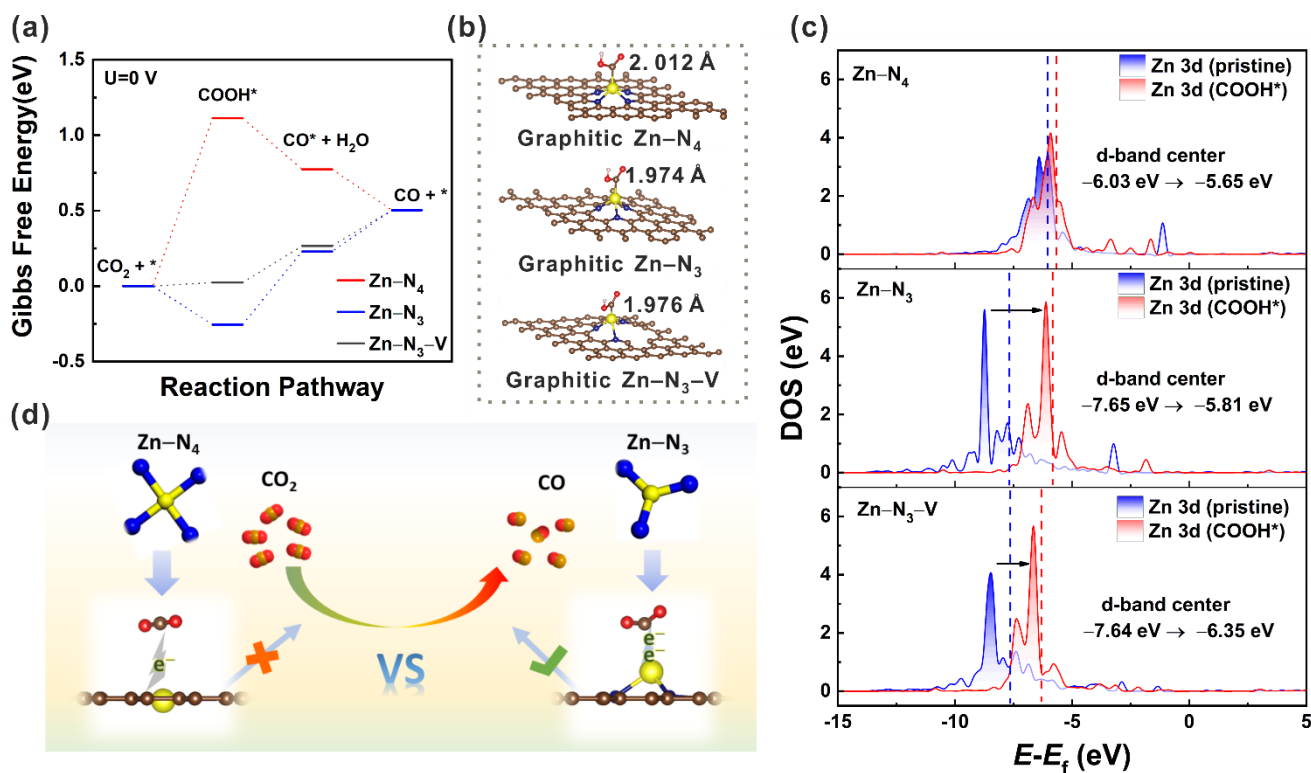


Figure 4. (a) Calculated Gibbs energy diagram for CO₂-to-CO conversion using graphitic Zn-N₄, Zn-N₃ and Zn-N₃-V models at U = 0 V and pH = 0. (b) DFT calculated geometry of graphitic Zn-N₄, Zn-N₃ and Zn-N₃-V sites with key intermediate COOH* adsorbed species. (c) Projected electron density of states (DOS) of the Zn-N₄, Zn-N₃, and Zn-N₃-V models before and after COOH* interaction. (d) Comparison of the active site of electron-rich Zn-N₃ with that of Zn-N₄. Note that Zn, N, C, O, and H atoms are represented by yellow, blue, brown, red, and pink colors, respectively.

To gain deeper insight into the outstanding performance of Zn^{δ+}-NC, poisoning experiments involving cyanide ions (blocking Zn atoms to suppress its reaction with CO₂) were carried out in the H-cell setup. **Figure 3c** shows that both FE_{CO} and |j| display distinct decreases once CN⁻ is introduced to the electrolyte. After removing CN⁻ by washing in Milli-Q water, the activity of Zn^{δ+}-NC is partially recovered, validating that isolated Zn atoms are the active sites for eCO₂RR. It is also interesting to compare the catalytic performance of Zn^{δ+}-NC with that of a composite material comprising ZnTPP supported on carbon black (ZnTPP/C) (**Figures 3d**, **S22**, and **S23**). As seen, such Zn-N₄-containing supported catalyst with Zn oxidation state of 2+ exhibits high HER activity and produces much less CO. On this basis, we propose that the superior CO selectivity of Zn^{δ+}-NC should be ascribed to its coordinatively unsaturated configuration, resulting in a distorted charge distribution (*vide infra*).

Finally, long-term stability of Zn^{δ+}-NC was examined by carrying out continuous CO₂ reduction at -0.57 V vs RHE for 12 h (**Figure S24**). Encouragingly, both FE_{CO} (≈ 95.3%) and |j| (≈ 0.9 mA cm⁻²) remain stable over the entire period. XPS spectra, TEM, and elemental mapping of post-electrolysis Zn^{δ+}-NC give evidence of negligible changes to the Zn oxidation state, coordination characteristics, porous structure, and distribution of active sites (**Figures S25** and **S26**). These results validate the superior durability and stability of single-atom Zn sites for eCO₂RR.

Origin of electrocatalytic activity

The EXAFS fitting results suggested that Zn-N₄ and Zn-N₃/Zn-N₃-V sites would be the central structures to consider in Zn^{δ+}-NC. Thus, these three Zn-N coordinated models were used to simulate the active site structures for eCO₂RR by means of DFT calculations. In general, the reaction pathway for the CO₂-to-CO conversion is a two-electron/two-proton transfer process, in which generation of key intermediates such as COOH* and CO* (* represents active sites) is recognized as the important steps affecting eCO₂RR performance. We calculated the relative energy of the key intermediates at Zn-N₄, Zn-N₃, and Zn-N₃-V sites. **Figures 4a** and **S27** show that formation of COOH* (CO₂* + e⁻ + H⁺ → COOH*) at Zn-N₄ is highly endothermic and becomes the rate-limiting step in eCO₂RR while the same process is less demanding on Zn-N₃ or Zn-N₃-V. Even if the specifically applied potential and electrolyte pH were to be taken into account in the calculations, the formation of COOH* would become thermodynamically even more favorable on the unsaturated Zn-N₃ and Zn-N₃-V sites than on Zn-N₄ (**Figure S28a**). In comparison, the competing HER becomes more energy-demanding, leading to sluggish kinetics of H₂ evolution on these sites (**Figure S28b**).

Furthermore, the crucial intermediate COOH* (**Figure 4b**) has Zn-C bond length on Zn-N₄, Zn-N₃ and Zn-N₃-V of 2.012, 1.974, and 1.976 Å, respectively. The decrease in Zn-C bond length with the Zn coordination indicates the strength of interaction and charge transfer between Zn atoms and COOH*. It verifies that unsaturated Zn-N₃ and/or Zn-N₃-V sites effectively smooth the pathway toward COOH* formation. Focusing on the whole energy

pathway on Zn–N₃ and/or Zn–N₃–V, the narrow energy gap between each step indicates less energy requests to trigger eCO₂RR, which could therefore explain the experimentally observed low overpotential of 310 mV. Besides, we found from Bader charge distribution (**Figure 2h–j**) that unsaturated Zn sites hold more electrons. Thus, we ascribe the low free energy of COOH* formation to the electron-rich environment, which enhances electron movement to accelerate the COOH* step and through this boost overall eCO₂RR.

Up to this point, we systemically identified the unsaturated Zn–N₃ (and/or Zn–N₃–V) active sites for eCO₂RR. To understand the inactivity of Zn–N₄ sites, we introduced projected electron density of states (DOS) analysis to investigate the electronic interaction between the Zn center and the COOH* intermediate (**Figures 4c** and **S29**). Comparison of the Zn 3d orbital in the pristine Zn–N₄, Zn–N₃, and Zn–N₃–V models before and after interacting with COOH* reveals that the change of the d-band center of Zn 3d in Zn–N₄ is negligible. In contrast, it shows upshift in both Zn–N₃ and Zn–N₃–V, corresponding to electron transfer from Zn to the adsorbate. These results imply that there is almost no electron movement from the Zn 3d orbitals of Zn–N₄ to the antibonding orbitals of *COOH, thus being inert toward eCO₂RR. This is also consistent with results reported elsewhere that the 3d orbital of Zn (II) is resistant to participate in catalytic reactions due to the fulfilled electron configuration.^[8b,8c,15] Conversely, accompanying the large upshift of the d-band center of Zn–N₃ and Zn–N₃–V, more electrons in the 3d orbital participate in stabilizing COOH* to promote eCO₂RR in these cases. Thus, it is the coordinately unsaturated Zn sites in Zn^{δ+}–NC that effectively accelerate electron movement and prompt the catalytic activity, playing a main active role throughout the whole process (**Figure 4d**).

eCO₂RR performance in flow cell–toward industrial applications

To assess the potential of the Zn^{δ+}–NC catalyst for industrial applications, we fabricated a custom-designed flow cell (**Figures S30** and **S31a**) to scale up eCO₂RR to industrially relevant current densities (>100 mA cm⁻²).^[16] First, we assembled the Zn^{δ+}–NC catalyst on a gas diffusion electrode (GDE) with mass loading of 1 mg cm⁻². Unlike the H-cell, where the catalysis occurs in a two-phase interphase (electrode/electrolyte), the flow cell configuration creates a three-phase interface of CO₂ (gas), protons (liquid), and catalyst (solid). Notably, CO₂ is directly fed to the cathode in the gas phase to overcome the issue of inherently low mass transport of CO₂ reagents in aqueous media.^[17] In addition, highly alkaline electrolyte (1 M KOH) was employed to suppress the competing HER during eCO₂RR.

Remarkably, FE_{CO} remains at 95 ± 4% while increasing $|j|$ from 0.2 to 1.0 A cm⁻² (**Figures 5a** and **S31b**). In addition, the Zn 2p XPS spectrum of Zn^{δ+}–NC after electrolysis at 1 A cm⁻² (**Figure S32**) shows that the Zn oxidation state is left unchanged under these conditions, indicating superior stability of low-valence Zn sites. The turnover frequency of Zn^{δ+}–NC catalyst in flow cell is more than hundred times higher than that in the H-cell, reaching over 1.1 × 10⁵ h⁻¹ at $|j|$ = 1.0 A cm⁻² on the assumption that all Zn sites participate in the reaction (**Figure S33**). In addition, a longer-term galvanostatic test performed at $|j|$ = 0.5 A cm⁻² with Zn^{δ+}–NC for 1.5 h shows stable WE potential with FE_{CO} > 90%. In other words, the Zn^{δ+}–NC catalyst exhibits excellent performance

in terms of both CO production and current density, thus showing the superiority of the gas-fed configuration compared with the H-cell setup. After 1.5 h, cell stability issues become evident with the WE potential becoming more negative and FE_{CO} experiencing severe decrease (**Figure 5b**). Furthermore, if $|j|$ is enhanced beyond 1 A cm⁻², severe flooding of the GDE happens, resulting in large fluctuations in WE potential and sharp decay of FE_{CO} from 99% to 32% within the first hour (**Figure S34**). Such lack of durability at high operating current density is fully consistent with literature,^[18] and it shows that further optimization would be requested of both the GDE and cell configuration to expand the operational time window.^[19] This being said, the successful demonstration of a flow-cell setup for Zn^{δ+}–NC with $|j|$ = 1 A cm⁻² is an important first step toward scaling of eCO₂RR. In fact, the performance reported herein is superior when compared with recently reported SACs applied in the GDE reactor (**Figure 5c**, **Table S3**). In conclusion, the record-large $|j|$ = 1 A cm⁻², together with high FE_{CO} > 95% for CO₂-to-CO conversion, provides great prospect for industrial applications.

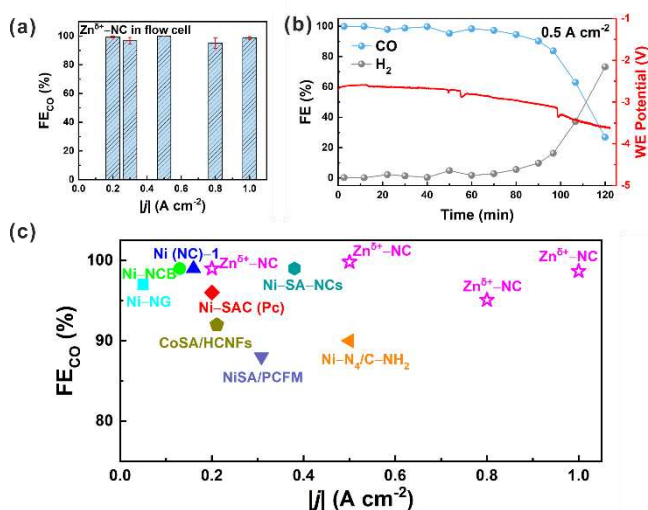


Figure 5. Recording of FE on Zn^{δ+}–NC with (a) $|j|$ varying from 0.2–1.0 A cm⁻² for 10 min electrolysis and with (b) $|j|$ = 0.5 A cm⁻² for 2 h electrolysis of CO₂ using a gas-fed flow-cell reactor (not *iR*-corrected) in 1 M KOH. (c) Comparison of FE_{CO} and $|j|$ for state-of-the-art SACs using flow or membrane electrode assembly cells (**Table S3**).

Conclusion

We successfully synthesized a nitrogen-anchored low-valence Zn-based SAC (Zn^{δ+}–NC) showing excellent performance for electrochemical CO₂-to-CO conversion in aqueous medium. Comprehensive characterizations of Zn^{δ+}–NC consistently reveals the specific fine structure of Zn single atoms, consisting of both Zn–N₄ and Zn–N₃ sites. The latter structure (or with a vacancy, i.e., Zn–N₃–V) holds enough electrons to reduce the average valence of Zn in Zn^{δ+}–NC (i.e., less than 2+). DFT calculations disclose that the main effect of the partial unsaturated Zn–N₃ (and/or Zn–N₃–V) sites is to lower the energy reaction pathway for forming the crucial COOH* intermediate. Importantly, the mix-coordinated Zn SACs display excellent selectivity for CO production (~99%) at a fairly small overpotential (310 mV) during electrochemical CO₂ reduction. From an industrial perspective,

the Zn^{δ+}-NC catalyst achieves a remarkable current density of 1 A cm⁻² with high CO selectivity using a flow cell reactor. Overall, this work reveals the relationship between coordination number, valence state, and catalytic performance, serving as guidelines for designing and developing atomically dispersed active sites for electrocatalytic CO₂ reduction at industrially relevant activity.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: CO₂ reduction • zinc single atoms • electrocatalysis at scale • low valence • coordination environment

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Graphical Abstract

Nitrogen-anchored low-valence Zn single-atom catalyst, containing coordinately unsaturated Zn-N₃ active sites, can boost electrochemical CO₂ reduction to industrial application level.

