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Introduction

The electrochemical CO_2 reduction reaction (eCO_2RR) yielding value-added chemicals and fuels, coupled with renewable electricity, offers a sustainable solution to achieve carbon neutrality.¹ The products of the CO₂RR vary from C1 (CO, CH₄, HCOOH, CH₃OH, etc.) to C2+ (CH₃CH₂OH, C₂H₄, etc.).² The high energy barrier for C-C coupling, which is the key step to form C2+ products, generally leads to high overpotential and low selectivity for the eCO2RR toward C2+.3 In contrast, C1 products with fewer electrons transferred (e.g., CO and HCOOH) are economically favorable due to their low overpotential,³ high selectivity, and enhanced energy efficiency.⁴ CO constitutes a crucial raw material in industrial production processes.⁵ Particularly, CO and H_2 (the by-product of the eCO₂RR) with a tunable ratio co-produced by the eCO₂RR can be readily used

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Rearranging spin electrons by axial-ligand-induced hybridization state transition to boost the activity of nickel single-atom-catalysts for electrochemical CO₂ reduction[†]

Mingxia Peng,^a Kai Huang,^b Xiuyuan Hu,^c Andrea Zitolo, ^b ^d Honglai Liu,^{ae} Cheng Lian¹^{*ae} and Jingkun Li^{*}

Single-atom catalysts (SACs) with $M-N_4$ active sites show great potential to catalyze the electrochemical CO₂ reduction reaction (eCO₂RR) toward CO. The activity and selectivity of SACs are determined by the local coordination configuration of central metal atoms in $M-N_4$ sites, which is readily tuned by axial ligands. In this work, we construct axial ligands in situ on two Ni–N₄-type model SACs, NiPc and Ni–N– C, by adding Cl⁻ into the electrolyte taking advantage of the strong chemisorption of Cl⁻ over Ni-N₄. Cl axial ligand lowers the energy barrier of the potential-determining step for the eCO₂RR due to a hybridization state transition of Ni orbitals and the resulting rearrangement of spin electrons. Consequently, both NiPc and Ni-N-C with axial Cl exhibit superior activity for the eCO₂RR toward CO. Finally, we propose the magnetic moment of Ni as a universal descriptor for the eCO₂RR toward CO on $Ni-N_{4}$ with various axial ligands.

> as a feedstock for syngas.6 In addition, cascade eCO2RR systems, which integrate two consecutive steps of CO₂-to-CO and CO-to-C2+ either within one CO2 electrolyzer using a bifunctional cathode or in two tandem CO₂ and CO electrolyzers,7-9 have been reported to boost the current density and faradaic efficiency (FE) for the eCO₂RR toward C2+. Thus, extensive efforts have been devoted to exploring catalysts for the eCO2RR toward CO with outstanding activity and tunable selectivity in the past decades.10,11

> Single-atom catalysts (SACs) with unique electronic and geometric structures exhibit superior activity and selectivity for the eCO_2RR toward CO.^{12,13} The M-N₄ (M = Fe, Co, Ni, Cu, etc.) moieties, in both macrocyclic metal complexes (metal porphyrins, metal phthalocyanines (MPc), etc.) and their analogous metal-nitrogen-carbon (M-N-C) materials, are widely accepted as active sites.14,15 Particularly, nickel SACs deliver extraordinary performance with a FE >90% at a wide potential range.16,17 However, nickel SACs still suffer from insufficient activity in practical CO₂ electrolyzers, leading to a significantly reduced selectivity of the eCO2RR toward CO at high current densities $(e.g., >200 \text{ mA cm}^{-2})$.¹⁷ Thus, it is pivotal to further boost the activity of Ni SACs for the eCO2RR toward CO to promote their feasible implementation in large-scale CO₂ electrolyzers. It is reported that the symmetric D_{4h} square-planar geometry of Ni-N₄ is unfavorable for adjusting the spatial distribution of electrons and, consequently impedes the electron transfer during electrochemical reactions.¹⁷⁻²⁰ Hence, breaking the D_{4h} symmetry of Ni-N4 via geometric distortion modulates their







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^aSchool of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China. E-mail: liancheng@ecust.edu.cn; lijingkun@ecust.edu.cn

^bSchool of Pharmaceutical and Chemical Engineering, Taizhou University, Taizhou, Zhejiang, 318000, P. R. China

No. 2 High School of East China Normal University, 555 Chenhui Rd, Pudong, Shanghai, 201203, P. R. China

^dSynchrotron SOLEIL, L'Orme des Merisiers, Départementale 128, 91190 Saint-Aubin, France

eState Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China

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electronic structures, leading to accelerated electron transfer and enhanced activity of nickel SACs for the eCO₂RR toward CO.²¹

Regulating the planar and axial ligands are two major strategies for tuning the geometric and electronic structures of M-N4.22-25 Planar ligand regulation includes doping with heteroatoms,26,27 engineering surface vacancies,28,29 adjusting coordination numbers,30 and constructing multi-atom sites.6 For example, S. Ji et al.³¹ incorporated P heteroatoms in the second coordination shell of Fe-N4 to break the local symmetry of electron distribution, leading to excellent activity and stability for oxygen reduction and evolution reactions. S. Chen et al.³² doped sulfur in the second coordination shell of Fe-N₄, which induces a pronounced proton-feeding effect to boost the eCO₂RR. However, it remains a great challenge for the precise and site-specific manipulation of the first and/or secondary coordination shell of central metal atoms, resulting in heterogeneous structures of planar coordination particularly for M-N-Cs obtained by high-temperature pyrolysis.^{33,34} In contrast, M-N₄ sites with axial ligands constitute a well-defined proximal coordination configuration with tunable geometric and electronic structures.²² M. Li et al.³⁵ reported an electronic localization enhancement of Ni-N4 induced by the Cl axial ligand, accounting for the superior HER activity of Ni-N₄-Cl. However, electronic-level insights into the axial effect in tuning the eCO₂RR activity of M-N₄ moieties are still lacking, which is crucial for designing highly efficient SACs for the eCO₂RR.

Herein, we systematically investigated the electronic structures and eCO_2RR activities of two Ni–N₄-type model SACs, namely NiPc and Ni–N–C, with and without the axial ligand. The axial ligand is introduced *in situ* by adding Cl⁻ into the electrolyte taking advantage of the strong chemisorption of Cl⁻ on Ni–N₄. The Cl axial ligand induces a transition in hybridization states of Ni orbitals and a rearrangement of spin electrons, leading to the low energy barrier for the formation of key intermediate COOH*. As a result, Ni–N₄ SACs with Cl axial ligands exhibit an enhanced CO partial current density. The magnetic moment of Ni is proposed as a universal descriptor for the eCO₂RR toward CO on Ni–N₄ with various axial ligands. This study provides a feasible strategy for screening highly efficient M–N₄-type SACs with axial ligands for the eCO₂RR toward CO.

Results and discussion

There are two typical classes of SACs extensively investigated for the eCO₂RR: macrocyclic metal complexes (*e.g.*, MPc) with a well-defined square-planar M–N₄ coordination configuration³⁶ and their analogous M–N–Cs consisting of isolated metal atoms anchored on nitrogen-doped carbon.³⁷ M–N–Cs derived from high-temperature pyrolysis generally show heterogeneous structures, with well-recognized structures of bulk-hosted M– N₄–C₁₀ moieties embedded within a graphene sheet (denoted as MN₄ hereafter) and edge-hosted M–N₂₊₂–C₄₊₄ bridging two adjacent graphene sheets (denoted as MN₂₊₂ hereafter).³⁸⁻⁴⁰ Taking into consideration the superior activity and selectivity of Ni–N₄ moieties,^{17,36} we focus on Ni SACs and exploit NiPc, NiN₄ and NiN₂₊₂ as representative model structures (Fig. 1a–c) to investigate the effect of axial ligands on their electrocatalytic activity for the eCO₂RR toward CO *via* density functional theory (DFT) simulations.

We then utilized NiPc and Ni-N-C as model catalysts to verify the positive effect of Cl axial ligand on the electrolytic activity of Ni-N4 for the eCO2RR toward CO. NiPc was loaded on carbon supports via ball milling to enhance the electronic conductivity, followed by a heat treatment under milder conditions (300 °C) to stabilize NiPc on carbon without altering its structure.41,42 A Ni-N-C material consisting of atomically dispersed nickel sites was synthesized according to our previous work.43 The X-ray diffraction (XRD) pattern of Ni-N-C reveals two characteristic peaks of disordered carbon (Fig. S1a[†]), and the defective structure of carbon is further supported by the high intensity of D band at 1350 cm⁻¹ in the Raman spectrum (Fig. S1b[†]). The scanning electron microscopy (SEM) image indicates a porous structure of Ni-N-C (Fig. 1d), which consists of abundant micropores and mesopores (Fig. S1c and d[†]). The Brunauer-Emmett-Teller surface area of Ni-N-C is 223 m² g⁻¹ (Table S1[†]). The highly microporous and defective structure of the carbon matrix is favorable to anchor single atoms of transition metals.44 The energy-dispersive X-ray spectroscopy (EDX) mappings show a uniform distribution of Ni, N, and C elements in Ni-N-C (Fig. 1e). No metallic particle is observed after an extensive evaluation of high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Fig. 1f), in good agreement with the absence of characteristic peaks arising from nickel-based agglomerates in XRD (Fig. S1a[†]). The isolated nickel atoms are distinctly visible (highlighted by red circles) in the abbreviation-corrected STEM image (Fig. 1g), confirming that nickel in Ni-N-C is present as single atoms.

The atomically dispersed nature of nickel in Ni-N-C is further supported by X-ray absorption spectroscopy (XAS) and Xray photoelectron spectroscopy (XPS) (Fig. 1h-l). The Ni 2p X-ray photoelectron spectroscopy (XPS) spectrum of Ni-N-C delivers only one main peak arising from Ni²⁺ accompanied by several satellite peaks, and Ni⁰ species is not detected (Fig. 1i).45 The XANES spectrum of Ni-N-C significantly deviates from that of NiO (Fig. 1h), suggesting that the Ni²⁺ species detected in XPS is not in the form of oxide. Meanwhile, the Fourier transform of extended X-ray absorption fine structure (EXAFS) exhibits negligible signals at \sim 2.1 and \sim 2.4 Å attributed to the Ni–Ni backscattering in metallic nickel and nickel oxide (Fig. 1j and S3[†]), indicating the absence of nickel-based agglomerates. Thus, XPS, EXAFS, XRD and STEM characterization studies unambiguously demonstrate the atomic dispersion of nickel in Ni-N-C. The nickel content in Ni-N-C is 0.22 at% according to XPS (Table S2[†]).

Then we elucidate the coordination environment of atomically dispersed nickel sites in Ni–N–C with detailed analysis of N 1s XPS and EXAFS spectra. Five nitrogen species are identified in the N 1s XPS spectrum of Ni–N–C, namely, N in M–N_x, pyrrolic N (labeled as N–H), pyridinic N, graphitic N (including N_{gr} and N⁺), and N–O_x (Fig. 1k and Table S3⁺).⁴³ The presence of abundant M–N_x suggests that nickel coordinates with nitrogen defects in the carbon matrix. Thus, we fit the Fourier transform



Fig. 1 The morphology and structure of Ni–N–C. Top views (upper panel) and side views (lower panel) of model structures for (a) NiPc, (b) NiN₄ and (c) NiN₂₊₂ with and without Cl axial ligand. The black, blue, purple, green, and white balls represent C, N, Ni, Cl, and H atoms, respectively. (d) SEM image. (e) HAADF-STEM image and the corresponding EDX mappings. (f and g) Abbreviation-corrected STEM images with different magnifications. (h) Ni K-edge XANES spectrum. The spectra for nickel foil and nickel oxide powders are also presented as references. (i) Ni 2p XPS spectrum. (j) The Fourier transform of experimental and best fit Ni K-edge EXAFS spectra. Inset is the schematic model for the best fit, with nickel and nitrogen atoms represented by purple and blue balls, respectively. No phase-shift correction was applied to the Fourier transforms. (k) N 1s XPS spectrum. (l) Ni K-edge EXAFS analysis: Ni–N, Ni–C γ (2) two-body signals and the N–Ni–N γ (3) three-body signal included in the fit, the total signal (red line) superimposed on the experimental one (black line).

of the experimental EXAFS spectrum of Ni–N–C with a variable number of in-plane nitrogen atoms binding the Ni²⁺ center (inset of Fig. 1j), and the best-fit result shows a coordination number of 4.3 and a Ni–N bond distance of 1.92 Å (Table S4†). The dominant contribution is given by Ni–N first shell coordination (Fig. 1l), leading to the major peak at 1.5 Å in the Fourier transform of the EXAFS spectrum (Fig. 1j). In contrast, Ni–C second shell coordination contributes to the minor peak in the range of 2–3 Å (Fig. 1j and l).⁴⁰ The intensity of the N–Ni–N signal is insufficient to determine the bond angle and, consequently, the geometric structure of the Ni–N₄ moiety. Therefore, the nickel single atoms in Ni–N–C are mainly present in the form of Ni–N₄ moieties, with either square-planar or distorted geometry. The eCO₂RR toward CO undergoes four elementary steps (written for acidic solutions): (1) CO₂(g) + * \rightarrow CO₂*, (2) CO₂* + H⁺ + e⁻ \rightarrow COOH*, (3) COOH* + H⁺ + e⁻ \rightarrow CO* + H₂O(g), and (4) CO* \rightarrow CO(g) + *,⁴⁶ with a debatable potential-determining step (PDS) of either COOH* formation or CO₂* adsorption.^{46,47} The configurations of all elementary steps on NiPc, NiN₄ and NiN₂₊₂ models are shown in Fig. S3.† The free energy (*G*) diagrams for the eCO₂RR toward CO over three models show that the Gibbs free energy change (ΔG) of COOH* formation is the highest among four elementary steps (Fig. 2a–c and Table S5†). Thus, we can infer that the first proton coupled electron transfer to form COOH* is the potential-determining step (PDS) for the eCO₂RR toward CO over Ni–N₄. The changing current densities with pH on an absolute scale (*vs.* normal hydrogen



Fig. 2 The effect of Cl axial ligand on the energy barrier of PDS for the eCO_2RR toward CO over Ni–N₄. Free energy diagrams of the eCO_2RR to CO for (a) NiPc, (b) NiN₄ and (c) NiN₂₊₂ with and without the Cl axial ligand. Experimental current densities plotted against potential vs. NHE for (d) NiPc and (e) Ni–N–C. (f) Comparison of the ΔG of PDS for NiPc, NiN₄ and NiN₂₊₂ with and without the Cl axial ligand.

electrode (NHE)) over NiPc and Ni-N-C (with NiN₄ and NiN₂₊₂ structures) indicate that proton participates in the PDS (Fig. 2d and e), further confirming COOH* formation as PDS for the eCO2RR toward CO. Pinpointing Cl axial ligand on Ni-N4 does not alter the PDS (Fig. 2a-c), but lowers its energy barrier for all three model structures (Fig. 2f). Moreover, NiN_{2+2} exhibits the lowest ΔG among three models without the axial ligand due to the strong adsorption of *COOH. However, the strong adsorption of *CO over NiN2+2 as a consequence of linear scaling relationship⁴⁸ leads to an uphill *CO desorption ($\Delta G > 0$), in contrast to the spontaneous *CO desorption over Ni-N4 and NiPc ($\Delta G < 0$). Interestingly, Cl axial ligand not only strengthens *COOH adsorption over NiN₂₊₂, but also weakens the adsorption of *CO, leading to a reduced energy barrier of PDS and a downhill *CO desorption. Thus, Cl axial ligand breaks the linear scaling relationship over NiN₂₊₂,⁴⁸ probably due to the synergistic effect of the axial ligand and defects in the edges. Overall, the Cl axial ligand lowers the energy barrier of PDS for the eCO₂RR toward CO over Ni-N₄, boosting the catalytic activity of Ni single atoms.

We then measured the activity and selectivity of the eCO₂RR toward CO over NiPc and Ni–N–C, and evaluated the effect of Cl axial ligand by adding KCl in the electrolyte. The metal center in the M–N₄ site tends to be occupied by a H₂O molecule in the backside axial position,^{49–51} and Cl⁻ in the electrolyte replaces H₂O due to the significantly higher binding energy of Cl than that of H₂O adsorbed on Ni–N₄ (including NiPc, NiN₄ and NiN₂₊₂) according to DFT simulations (Fig. 3a–c). Further charge analysis shows that Cl atoms transfer 0.14–0.15|*e*| charges to Ni atoms, indicative of a strong chemisorption of Cl on Ni–N₄ (insets of Fig. 3a–c). In contrast, the charge transfer from H₂O molecules to Ni atoms is only 0.00–0.03|*e*|, suggesting

a physisorption of H_2O on Ni–N₄ (insets of Fig. 3a–c). Thus, we can infer that Ni–N₄ binds with the Cl axial ligand by simply adding Cl⁻ in the electrolyte.

The CO and H_2 partial current densities vs. potential (*iR*corrected) over NiPc and Ni-N-C catalysts in electrolytes measured in 1 M KHCO₃ electrolyte with 0, 10 and 100 mM KCl are presented in Fig. 3d-g. CO₂ electrolysis was conducted for 30 minutes at constant current densities from 10 mA cm⁻² to 60 mA cm⁻² in a flow cell with Ag/AgCl as the reference electrode. The total faradaic efficiencies (FEs) of CO and H₂ for NiPc and Ni–N–C are \sim 100% (Fig. S4†), indicating negligible liquid products formed during the eCO2RR. Thus, we didn't measure liquid products for this study. Both NiPc and Ni-N-C exhibit enhanced CO partial current densities in a wide potential range after adding trace amount of Cl⁻ (10 mM), and the enhancement increases with an increasing Cl⁻ concentration (Fig. 3d and e). The improvement in the catalytic activity of Ni-N4 for the eCO2RR toward CO induced by the Cl axial ligand is consistent with the reduced energy barrier of PDS (Fig. 2a-c). In contrast, the H₂ partial current densities of NiPc and Ni-N-C are not affected by the addition of Cl⁻ (Fig. 3f and g). The above results demonstrate that the Cl axial ligand enhances the intrinsic activity of Ni-N4 for the eCO2RR toward CO without altering its HER activity, leading to an increase in the total current density (Fig. S5[†]). Moreover, during the 8-hour chronoamperometry (CA) tests in 1 M KHCO₃ electrolyte with 100 mM KCl, both Ni-N-C and NiPc maintained stable CO faradaic efficiency (FE) and current density, as shown in Fig. S6.[†] The Cl 2p spectra of the Ni-N-C and NiPc after stability tests exhibit a characteristic peak at ~198.0 eV attributed to Ni-Cl species (Fig. S7[†]),⁵² with Cl as the axial ligand considering the absence of high-temperature required to form planar coordinated Cl.24 In addition, a new





Fig. 3 The effect of Cl axial ligand on the activity of Ni–N₄ for the eCO₂RR toward CO. The binding energies of Cl and H₂O adsorbed on the Ni center in (a) NiPc, (b) NiN₄, and (c) NiN₂₊₂. The insets are the charge density differences of Cl and H₂O on Ni–N₄ sites. The cyan and yellow regions represent loss and accumulation of charge density, respectively, and the isosurface value is ± 0.002 e bohr⁻³. CO partial current densities vs. potential (*iR*-corrected) for (d) NiPc and (e) Ni–N–C. H₂ partial current densities vs. potential (*iR*-corrected) for (f) NiPc and (g) Ni–N–C. The above electrochemical characterization is measured in 1 M KHCO₃ electrolyte with 0, 10 and 100 mM KCl (the data shown in (d–g) are the average of three repeated experiments).

peak at 858.3 eV assigned to Ni³⁺ emerges in the Ni 2p XPS spectra of Ni–N–C and NiPc after stability tests (Fig. S8†), further confirming the formation of Ni–N₄–Cl with Cl as the axial ligand.⁵³ The postmortem XPS studies unambiguously demonstrate the successful introduction and high stability of the Cl axial ligand. Approximately 37% and 18% of Ni³⁺ species are detected in Ni–N–C and NiPc after the stability tests (Fig. S8†), suggesting that Ni–N₄ is partially coordinated with axial Cl ligands.

Strong chemisorption of the axial ligand on $M-N_4$ sites pulls single metal atoms away from the carbon plane, which breaks the D_{4h} symmetry of square-planar $M-N_4$, and consequently promotes the electron transfer during electrochemical reactions.^{19,20} The distance of Ni atom from the carbon plane $(d_{\rm Ni})$ and the Ni–N bond distance $(d_{\rm Ni-N})$ (insets in Fig. 4a and b) describe the degree of geometric distortion of Ni–N₄ sites upon adsorption of Cl axial ligand. Thus, we explore the relationship between the energy barrier of PDS ($\Delta G_{\rm p}$) for the eCO₂RR and $d_{\rm Ni}/d_{\rm Ni-N}$ (Fig. 4a and b). For comparison, weak adsorption of H₂O axial ligand on three models are considered (Fig. S9, S10 and Table S6†). In contrast to H₂O molecules ($d_{\rm Ni} = 0.02-0.08$ Å), Cl atom with a strong binding energy on Ni–N₄ pulls Ni atom further away from the carbon plane ($d_{\rm Ni} = 0.10-0.33$ Å), resulting in a larger $d_{\rm Ni-N}$ (Fig. 4a, b and Table S7†). There is a positive



Fig. 4 The effect of Cl axial ligand on the geometric and electronic structure of Ni–N₄. The relationship between ΔG_p and (a) d_{Nir} (b) d_{Ni-N} (c) The partial density of states and d-band center of Ni atoms in NiN₄, NiN₄–Cl, and NiN₄–H₂O. (d) Schematic diagram of orbital hybridization of Ni atoms in Ni–N₄ with and without axial ligands.

correlation between $d_{\rm Ni}$ and $\Delta G_{\rm p}$: the further away the Ni atoms are from the carbon plane, the lower the $\Delta G_{\rm p}$ (Fig. 4a). The relationship between $d_{\rm Ni-N}$ and $\Delta G_{\rm p}$ falls into two linear lines for NiPc and Ni–N–C (NiN₄ and NiN₂₊₂), respectively (Fig. 4b). It is noteworthy that both the change of $d_{\rm Ni}$ and $d_{\rm Ni-N}$ of NiPc–Cl are smaller than those of NiN₄–Cl and NiN₂₊₂–Cl due to the more rigid structure of NiPc (Fig. 4a and b). Moreover, the periodic boundary conditions on the *xy* plane of molecular NiPc and periodic NiN₄/NiN₂₊₂ are different for DFT simulations. Thus, it is reasonable that the linear coefficient for the correlation between the geometric parameters and $\Delta G_{\rm p}$ of NiPc differs from that of Ni–N–C. In summary, Cl axial ligand induces geometric distortion of Ni–N₄ sites, and the geometric parameters, $d_{\rm Ni}$ and $d_{\rm Ni–N}$, are strongly correlated with the energy barrier of PDS, and consequently the electrocatalytic activity for the eCO₂RR toward CO.

Then we evaluate the effect of Cl axial ligand on the electronic structures of Ni atoms in Ni–N₄. The partial density of states (PDOS) show that the up and down spin images of Ni 3d orbitals of NiN₄ and NiPc (with/without H₂O ligands) are symmetrical (Fig. 4c and S11a[†]), indicating the symmetrical arrangement of the up and down spin electrons of 3d orbitals for Ni–N₄ without geometric distortion (Fig. 4d). In contrast, the geometric distortion induced by Cl axial ligand results in the asymmetric up and down spin electron arrangement of Ni 3d orbitals, and thus the magnetic properties of NiN₄–Cl (Fig. 4c, d and S11a[†]). The empty 3d, 4s and two 4p orbitals of Ni undergo dsp² hybridization to interact with the sp² orbitals of

the four-coordinated N ligands in Ni–N₄ with square planar geometry,⁵⁴ whereas Ni–N₄ with Cl axial ligand exhibits a d^2sp^3 hybridization with an octahedral coordination environment (Fig. 4d). The d^2sp^3 hybridization of Ni leads to the rearrangement of spin electrons, which activates Ni–N₄ sites and boosts their intrinsic activity for the eCO₂RR.⁵⁴ Particularly, the up and down spin PDOS image of Ni 3d orbitals in NiN₂₊₂ is asymmetric (Fig. S11b†), leading to a lower energy barrier for PDS of NiN₂₊₂ than those of NiPc and NiN₄ (Fig. 2f). The Cl axial ligand further intensifies the degree of asymmetry for the PDOS image of Ni 3d orbitals in NiN₂₊₂ (Fig. S11b†), indicating the enhanced activity of NiN₂₊₂-Cl for the eCO₂RR toward CO.

We then analyzed the d-electron distribution of Ni atoms in NiPc, NiN₄ and NiN₂₊₂ with/without the Cl axial ligand (Fig. S12†). For all three models without Cl axial ligand, the peak of partial density of states (PDOS) below the Fermi level is mainly contributed by the d orbital components containing the *z*-axis direction (such as d_{yz} , d_{xz} , and d_{z^2}), indicating that the electrons involved in the eCO₂RR are mainly provided by the d orbitals in the *z*-direction. Stronger the electron donating capability of

d orbitals, better the eCO₂RR activity we achieve. NiPc only provides electrons through d_{z^2} and d_{xz} , while all the d_{yz} , d_{xz} , and d_{z^2} of NiN₄ donate electrons. Moreover, the structural symmetry of NiN₂₊₂ has been disrupted, enabling d_{xy} to donate electrons in addition to d_{yz} , d_{xz} , and d_{z^2} . The above results are in good agreement with the superior eCO₂RR activity of Ni–N–C to that of NiPc. Introducing Cl axial ligands further breaks the structural symmetry of NiPc, NiN₄ and NiN₂₊₂, which not only leads to asymmetric up and down spin images, but also brings the peak of d orbital components containing the *z*-axis direction closer to the Fermi level (Fig. S12†). As a result, the introduction of Cl axial ligands induces the strong electron donating capability and, consequently, enhances the eCO₂RR activity of Ni–N₄.

Since the asymmetric up and down spin electron arrangements of Ni 3d orbitals in Ni–N₄–Cl are crucial for their enhanced eCO₂RR activity, we then explore the relationship between ΔG_p and $\Delta \varepsilon_d$ (the difference in the d-band center of Ni between down and up spin). $\Delta \varepsilon_d$ delivers a good linear relationship with ΔG_p (Fig. S13a†). The change of $\Delta \varepsilon_d$ induced by Cl axial ligands for three model structures follows the trend of



Fig. 5 Universal descriptors for the eCO_2RR activity of Ni–N₄ with various axial ligands. The relationships between ΔG_p and (a) d_{Ni} , (b) d_{Ni-N} , (c) $\Delta \varepsilon_{d}$, u_{Ni} (the circular symbol represent $\Delta \varepsilon_d$, and the triangular symbol represents u_{Ni}). (d) The relationship between $\Delta \varepsilon_d$ (the difference in the d-band center of Ni between down and up spin) and u_{Ni} (the magnetic moment of Ni atoms).

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NiPc (0.207 eV) > NiN₂₊₂ (0.114 eV) > NiN₄ (0.094 eV), perfectly matching the trend for the change of ΔG_p induced by Cl axial ligands (NiPc > NiN₂₊₂ > NiN₄). Therefore, although the effect of axial ligands on the geometric structure of NiPc is the lowest among all three model structures due to its rigid structure, that on the electronic structures is the highest, resulting in the most significant decrease in ΔG_p for NiPc induced by Cl axial ligands. Since $\Delta \varepsilon_d$ is directly correlated with the electronic asymmetry of Ni–N₄ as discussed above, we can safely conclude that the electronic symmetry breaking, which originates from the geometric symmetry breaking, is the primary factor in enhancing the eCO₂RR activity.

Furthermore, the asymmetric up and down spin electron arrangements of Ni 3d orbitals will cause changes in the magnetic moment of Ni atoms $(u_{\rm Ni})$, and the linear relationship between $\Delta \varepsilon_{\rm d}$ and $u_{\rm Ni}$ is shown in Fig. 5d. Therefore, we further investigate the relationship between $\Delta G_{\rm p}$ and $u_{\rm Ni}$, which also exhibit a good linear correlation: larger the $u_{\rm Ni}$, lower the $\Delta G_{\rm p}$ (Fig. S13b†). Thus, $u_{\rm Ni}$ and $\Delta \varepsilon_{\rm d}$ are possible descriptors of the eCO₂RR activity of Ni–N₄-type SACs with axial ligands. The separate linear relationships for NiPc and Ni–N–C systems are unified when using $\Delta \varepsilon_{\rm d}$ and $u_{\rm Ni}$ as descriptors since electronic properties circumvent the fundamentally different geometries of NiPc and Ni–N–C.

To demonstrate the universality of the above geometric and electronic descriptors, we further extend axial ligands over NiN4 from Cl⁻ to -NO, -SCN, and -CH₃, and investigate the relationship between $\Delta G_{\rm p}$ and geometric/electronic parameters $(d_{\text{Ni}}, d_{\text{Ni-N}}, u_{\text{Ni}}, \Delta \varepsilon_d)$. The configurations of all elementary steps on NiN₄ models are shown in Fig. S14.[†] The free energy diagrams indicate that all axial ligands over NiN₄ investigated exhibit reduced $\Delta G_{\rm p}$, and thus promote the electrocatalytic CO₂RR to CO (Fig. S15, S16 and Table S7[†]). There are linear correlations between $\Delta G_{\rm p}$ and $d_{\rm Ni}$, $d_{\rm Ni-N}$, $u_{\rm Ni}$, $\Delta \varepsilon_{\rm d}$ for NiN₄ with various ligands (Fig. S17[†]), which fit well in the linear lines we have described in Fig. 4a, b and S13^{\dagger} (Fig. 5). Therefore, $u_{\rm Ni}$ and $\Delta \varepsilon_{d}$ are universal descriptors for evaluating the eCO₂RR activity of Ni-N₄-type SACs with a variety of axial ligands, and, most probably, can be extended to other M-N₄-type SACs. The spin electron rearrangement in M-N₄ SACs induced by axial ligands is the key for boosting eCO₂RR activity.

Conclusions

In summary, we investigated the effect of axial ligand on the eCO_2RR activity of two Ni–N₄-type model catalysts (NiPc and Ni–N–C), and both theoretical and experimental studies demonstrate that Cl axial ligand is beneficial for the eCO_2RR . The Cl axial ligand induces a hybridization state transition of nickel orbital from dsp² to d²sp³ and, consequently, a rearrangement of spin electrons, accounting for the superior activity of Ni–N₄–Cl for the eCO_2RR . The low energy barrier of PDS for the eCO_2RR exhibits a strong correlation with the geometric (d_{Ni} and d_{Ni-N}) and electronic ($\Delta \varepsilon_d$ and u_{Ni}) parameters of Ni–N₄. Furthermore, we propose the magnetic moment of Ni as a universal descriptor for the eCO_2RR toward CO on Ni–N₄ with various axial ligands (–H₂O, –Cl, –NO, –SCN, and –CH₃). Our

work provides valuable insights on regulating the geometric configuration and electronic structure of SACs to boost their electrocatalytic activities for various energy and environmental applications.

Data availability

All experimental and computational procedures and associated data are provided in the ESI.†

Author contributions

M. P., K. H., and J. L. conceived the project. M. P. prepared materials, performed measurements and analysed the data. K. H. performed the DFT calculations. X. H. and A. Z. helped with some of the experiments and characterization. All authors discussed the results and commented on the manuscript. M. P., K. H., and J. L. wrote the draft, revised and finalized the manuscript.

Conflicts of interest

There are no conflicts to declare.

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