Coordination environment engineering on nickel single-atom catalysts for CO2 electroreduction†

Mengbo Ma, Fuhua Li and Qing Tang
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Coordination engineering has recently emerged as a promising strategy to boost the activity of single atom catalysts (SACs) in electrocatalytic CO2 reduction reactions (CO2RR). Understanding the correlation between activity/selectivity and the coordination environment would enable the rational design of more advanced SACs for CO2 reduction. Herein, via density functional theory (DFT) computations, we systematically studied the effects of coordination environment regulation on the CO2RR activity of Ni SACs on C, N, or B co-doped graphene. The results reveal that the coordination environments can strongly affect the adsorption and reaction characteristics. In the C and/or N coordinated Ni–B3C1N2 (B-free, X = 0), only Ni acts as the active site. While in the B, C and/or N coordinated Ni–B3C1N2 (X ≠ 0), the B has transition-metal-like properties, where B and Ni function as dual-site active centers and concertedly tune the adsorption of CO2RR intermediates. The tunability in the adsorption modes and strengths also results in a weakened linear scaling relationship between *COOH and *CO and causes a significant activity difference. The CO2RR activity and the adsorption energy of *COOH/*CO are correlated to construct a volcano-type activity plot. Most of the B, C, and/or N-coordinated Ni–B3C1N2 (X ≠ 0) are located in the left region where *CO desorption is the most difficult step, while the C and/or N coordinated Ni–B3C1N2 (X = 0) are located in the right region where *COOH formation is the potential-determining step. Among all the possible Ni–B3C1N2 candidates, Ni–B2C2N1 and Ni–B1C1N2–N–oppo are predicted to be the most active and selective catalysts for the CO2RR. Our findings provide insightful guidance for developing highly effective CO2RR catalysts based on a codoped coordination environment.

Introduction

With the excessive consumption of non-renewable fossil fuels (coal, oil and natural gas), the increasing emission of carbon dioxide (CO2) into nature has caused severe ecological and environmental problems.1–3 As an alternative way, CO2 can be reduced into useful chemical products, such as carbon monoxide, methane, ethylene and methanol. However, the carbon element in CO2 is in the highest +4 oxidation state and the C=O bond is highly stable, which makes it very difficult to be reduced.4–7 Among the variety of developed solutions, the electrochemical reduction of CO2 is one of the most promising strategies and has attracted widespread attention due to its low energy consumption, mild reaction conditions, and simple operation, which relies on efficient catalysts to accelerate the reaction.8–10 The promising electrocatalysts for the electrochemical CO2 reduction reaction (CO2RR) should be able to operate at a low overpotential and can effectively control the product selectivity, inhibit the competitive hydrogen evolution reaction (HER) and maintain high electrochemical stability.11–14

Among the various types of investigated electrocatalysts,15,16 single-metal-atom catalysts have developed rapidly and emerged as a promising class of catalysts for the CO2RR.17–20 Compared to the metal bulk and nanoparticle counterparts, the atomically dispersed single metal catalysts have largely exposed active sites and exhibit effective atom utilization and high selectivity for the electrochemical CO2RR.21,22 Moreover, their well-defined structures serve as an ideal model to establish the relationship between the structure and catalytic properties at an atomic level. To stabilize the single metal center from agglomeration, the single-metal-atom catalysts are usually coordinated and immobilized on nitrogenated carbon-based conductive substrates, such as carbon nanotubes, graphene and amorphous or porous carbon.23–25 In particular, the graphene matrix has been widely used due to its high electronic conductivity and large surface area for metal loading.
Many transition metals, such as Mn, Fe, Co, Ni, and Cu, have been embedded into nitrogen-doped carbon systems and investigated as CO2RR electrocatalysts. The results demonstrate that the intrinsic CO2RR activity of Fe–N–C and especially Ni–N–C catalysts to yield CO is higher than that of the Co–N, Mn–N, and Cu-based moieties, which even rival the state-of-the-art Au- and Ag-based catalysts. However, the relatively strong binding of CO* over Fe–N and Mn–N sites could lead to lower selectivity for CO formation.

Particularly, apart from being cost effective, Ni single atom catalysts have displayed exceptional activity, selectivity and high stability. Additionally, several recent experimental advances have demonstrated that the CO2RR activity of Ni–N–C entities can be effectively manipulated by controlling the local coordination environment of the Ni active center. For example, Li et al. realized a specific Ni–N4 structure through a topochemical transformation strategy by carbon shell coating, which shows excellent activity and remarkable stability for the CO2RR to CO. Bao et al. reported that coordinatively unsaturated Ni–N sites within porous carbon had higher selectivity and activity for the CO2RR than the Ni–N4 sites. Joo et al. and Lu et al. both showed that the Ni–N–V (V: vacancy) sites with a shrunk Ni–N–C local structure incorporated into the graphene lattice exhibit enhanced CO2RR performance compared to the Ni–N4 sites. Moreover, Jiang et al. prepared a series of Ni single atom catalysts with controlled Ni–N coordination numbers (Ni–N–C, x = 2, 3, 4) by varying the pyrolysis temperature of the polyhydridolite@MgNi-MOF-74 precursor. They revealed that the Ni–N2–C catalyst with Ni coordinated by two N and two C shows far superior CO faradaic efficiency and turnover frequency compared to the Ni–N1–C and Ni–N4–C counterparts. Cheng et al. fabricated Ni-based catalysts with various N/C coordination numbers (Ni@NxCy) through pyrolysis of carbon substrates at different temperatures and achieved an optimal catalytic performance for the Ni@N2C2 catalysts. Theoretically, Zhang et al. suggested that the graphene embedded Ni–N5 site with additional ligated axial N atoms exhibits lower CO2RR onset overpotential than the Ni–N4 site.

This recent progress has evidenced the strong potential of coordination environment regulation in tuning the CO2RR activity of a single metal center. In principle, due to the difference in electronegativity and atomic size, changing the surrounding coordination elements will modify the electronic structure of the metal center, which would essentially affect the adsorption strength of the reaction intermediates and in turn, modify the activity and selectivity. It is noteworthy that, in addition to the widely studied Ni–NxCy catalysts with Ni–N and Ni–C coordination environments, many recent studies have shown that boron can be doped into the carbon matrix and the incorporation of boron can greatly accelerate the electrocatalytic reactions. The boron (~0.82 Å) has a comparable covalent radius with C (~0.77 Å) and N (~0.75 Å), which can form rich compounds with C (e.g., BC), N (BN), and Ni (e.g., NiB, Ni3B, NiB3). Moreover, B, in many cases, functions like a transition metal since the hybridization of its non-fully occupied valence electrons supplies a great chance to accept and donate lone-pair electrons. Hence, B can also be a potential element to dope and adjust the coordination environment.

In this research, we investigate the CO2RR performance of Ni-centered graphene with various B/C/N coordination environments from density functional theory (DFT) calculations. Recently, Goddard and Luo reported a comprehensive study of the CO2RR mechanism on C/N coordinated Ni SAC by taking kinetics, the solvation effect, and experiment comparison into consideration. The CO2RR performance varies remarkably by differences in the number of C or N bonded to Ni. Herein, we used the computational hydrogen electrode model with a number of simplifications and approximations for fast screening the potential catalysts by calculating the thermodynamic energetics. This simplified model, in most cases, allows the reliable alignment of theoretical electrochemical potentials to those measured in experiment. Compared to the prior theoretical studies that mainly focus on the N and C coordination, the hybrid coordination by non-metal C, N and transition-metal-like B leads to more versatile adsorption characteristics and diverse activities. Our results showed that most of the Ni–BxCyNz (x + y + z = 4) catalysts (25 out of 27 possible candidates) have high thermodynamic and electrochemical stability. The adsorption modes of CO2, *COOH and *CO are versatile. In the case of C and/or N coordinated Ni–BxCyNz (B-free, x = 0), the Ni center acts as the active site, and the CO2 hydrogenation to *COOH is the potential-determining step. While in the case of B-coordinated Ni–BxCyNz (x ≠ 0), the B can actively participate in the reaction. As a result, the Ni and B function as dual sites to flexibly tune the adsorption of CO2RR intermediates, which facilitate the CO2 hydrogenation but increase the adsorption strength of *CO, making *CO desorption the most difficult step. Because of the versatile single- and dual-site adsorption modes, the

Qing Tang is a Professor of Chemistry at Chongqing University. She received her B.S. in Chemistry from Shenzhen University in 2009, and her Ph.D. in Chemistry from Nankai University in 2014. After three years of postdoctoral research at the University of California Riverside (UCR), she joined the faculty at the school of chemistry and chemical engineering at Chongqing University in 2018. Her current research interests focus on the application of multi-scale computational methods to understand, design and discover new materials for electrocatalytic applications, such as hydrogen evolution, oxygen reduction and CO2 conversion.
scaling relationship between the adsorption energy of *COOH and *CO is significantly weakened. Moreover, we build the correlation between the adsorption energy and the limiting potential to describe the activity and selectivity. Compared to the pure N-coordinated Ni, the hybrid coordination by C–N, B–N or B–C–N can lead to much higher electrocatalytic activity, and several highly promising candidates stand out with high CO2RR activity and selectivity, including Ni–B3C1N4, Ni–B3C0N4, Ni–B3C0N2–B-hex, Ni–B3C1N2–N-oppo, and Ni–B3C1N2–N-hex. These results provide useful insights into the understanding of the coordination effect on the CO2RR and offer a reference for further research on advanced electrocatalysts.

### Computational details

All the spin-unrestricted DFT computations are carried out in the DMOl3 code.53 The generalized gradient approximation (GGA)54 of the Perdew–Burke–Ernzerhof (PBE)55 functional is used to describe the exchange–correlation interactions and the core electrons are treated with semi-core pseudopotentials (DSPPs).56 The double numerical plus polarization (DND) basis is adopted and the global orbital cutoff value is set as 4.0 Å. The convergence tolerance of geometry optimization is set as 2.0 × 10−4 Å in energy, 0.004 Ha Å−1 in force, and the force exerted on each atom is set to be 0.005 Å. To simulate the aqueous solvent environment, a conductor-like screening model (COSMO) with a dielectric constant of 78.54 is used.57 The k-points mesh of 5 × 5 × 1 and 9 × 9 × 1 using the Monkhorst–Pack method58 is utilized for the structural optimization and electronic property calculations, respectively.

The absorption free energy of CO2 on Ni–B3C1N2 is calculated by: \( \Delta G_{\text{ads}} = \Delta E_{\text{ads}} + \Delta ZPE - T \Delta S - \Delta G_U \), where \( \Delta E_{\text{ads}} \) is the adsorption energy obtained by subtracting the total energy of the isolated Ni–B3C1N2 catalyst and free CO2 molecule from the adsorbed system. Due to the inaccurate description of CO2 molecule by the PBE functional, we added a correction of +0.10 eV for CO2.59

The change of Gibbs free energy (\( \Delta G \)) for each elementary reaction step is calculated using the equation: \( \Delta G = \Delta E + \Delta ZPE - T \Delta S + \Delta G_U \), where \( \Delta E \) is the electronic reaction energy of a certain reaction step directly obtained from DFT energies, \( \Delta G_U = -eU \), with \( U \) being the electrode potential of the electrochemical step. \( \Delta ZPE \) and \( T \Delta S \) are the contributions of the zero-point energy and entropy, respectively, which originate from the calculation of vibrational frequencies of the adsorbed intermediates at \( T = 298.15 \) K. The entropy of gas phase molecules is derived from the NIST database. The detailed data are provided in the ESL†

### Results and discussion

#### Catalyst models and stability

As shown in Fig. 1, we use a 6 × 6 × 1 graphene supercell with two C vacancies as the original substrate to construct the model catalysts, and then a single Ni atom is placed into the vacancy center and binds to four pyridine-like coordination atoms (B, C or N). The corresponding catalyst models are named Ni–B3C1N2 (X + Y + Z = 4). Note that there are three possible coordination configurations when X, Y or Z = 2, denoted as Ni–B3C1N2–oppo, Ni–B3C1N2–pen, and Ni–B3C1N2–hex, in which the same two atoms occupy the opposite coordination sites or neighboring coordination sites in penta-atomic and hex-atomic rings, respectively. Ultimately, 27 catalyst structures are constructed.

In order to characterize the thermodynamic stability, we calculated the formation energy (\( E_f \)) of Ni–B3C1N2 systems, defined as \( E_f = E_{\text{total}} - n_{\text{Ni}} \mu_{\text{Ni}} - n_{\text{B}} \mu_{\text{B}} - n_{\text{C}} \mu_{\text{C}} - n_{\text{N}} \mu_{\text{N}} \). Here, \( E_{\text{total}} \) is the total energy of Ni–B3C1N2, \( \mu_{\text{B}}, \mu_{\text{C}} \) and \( \mu_{\text{N}} \) represent the chemical potential of B, C, and N, which corresponds to the energy of a single carbon atom in graphene, a single boron atom in planar hexagonal B36 and half of the energy of the N2 molecules, respectively. While \( n_{\text{B}}, n_{\text{C}} \) and \( n_{\text{N}} \) stand for the number of corresponding coordination atoms in Ni–B3C1N2. \( E_{\text{Ni}} \) is the energy of the isolated Ni atom. From Fig. 1a, one can see that except for the pure carbon coordinated Ni–B3C1N0, the calculated \( E_f \) values of the other 26 Ni–B3C1N2 catalysts are all negative (−0.94 to −5.44 eV), indicating their high thermodynamic stabilities and high synthetic potential in experiments. In addition, the dissolution potential \( U_{\text{diss}} \) is another
important parameter to evaluate the electrochemical stabilities in a realistic electrochemical environment. The $U_{\text{diss}}$ is calculated as $U_{\text{diss}} = U^\text{diss[metal]} - E_f/n$, where $U^\text{diss[metal]}$ is the standard dissolution potential of the Ni metal, $E_f$ is the formation energy, and $n$ is the number of electrons involved in the dissolution (herein $n = 2$). According to this definition, only a catalyst with $U_{\text{diss}} > 0$ V vs. SHE can stably exist under acidic electrochemical conditions (the exact values of $E_f$ and $U_{\text{diss}}$ are listed in Table S1†). Among the 27 Ni–B$_x$C$_y$N$_z$ systems, only Ni–B$_x$C$_1$N$_6$ and Ni–B$_x$C$_4$N$_6$ are excluded due to their negative $U_{\text{diss}}$ and electrochemical instability (Fig. 1b). Finally, after the stability screening, there are about 25 Ni–B$_x$C$_y$N$_z$ structures that both meet the criteria of thermodynamic and electrochemical stability. The corresponding structures of the 25 Ni–B$_x$C$_y$N$_z$ are displayed in Fig. 2, which are further investigated as the candidate catalysts of the CO$_2$RR.

**Adsorption of reaction species**

The activation of CO$_2$ as well as the adsorption of reaction intermediates (e.g., *COOH, *CO) onto the surface of catalysts plays a critical role during the electrocatalytic CO$_2$RR. Hence, we firstly investigated the adsorption behaviors, and the most stable adsorption configurations for *CO$_2$, *COOH and *CO are shown in Fig. 3 (the detailed adsorption free energy and charge transfer values are listed in Table S2†). From Fig. 3a, the *CO$_2$ adsorption has two types of adsorption modes: physical adsorption and chemical adsorption. Among them, about 22 Ni–B$_x$C$_y$N$_z$ compositions form physisorption. On Ni–B$_x$C$_1$N$_z$ ($X = 0$), Ni–B$_x$C$_y$N$_z$ ($X = 1$, 2[pen]; $Y = 0$), Ni–B$_x$C$_y$N$_z$ ($X = 1$; $Y = 2$; $Z = 1$) and Ni–B$_x$C$_y$N$_z$ ($X = 1$; $Y = 1$; $Z = 2$[hex]), the CO$_2$ is physically adsorbed with the C atom of CO$_2$ pointed above the Ni center. While for Ni–B$_x$C$_y$N$_z$ ($X = 2$[oppo, hex], 3, 4; $Y = 0$), Ni–B$_x$C$_y$N$_z$ ($Y = 1$, 2; $Z = 0$) and Ni–B$_x$C$_y$N$_z$ ($X = 2$[oppo, hex]; $Y = 1$; $Z = 1$), the CO$_2$ is physically adsorbed with the O atom of CO$_2$ pointed above the Ni center. In the case of physical adsorption, the calculated CO$_2$ adsorption free energy is around $-0.09$ to $-0.20$ eV, and the charge transfer between CO$_2$ and Ni–B$_x$C$_y$N$_z$ is around 0.004 to 0.019 e from Bader charge analysis. In the case of chemical adsorption, there also exist two types of binding modes. On Ni–B$_x$C$_1$N$_1$-b[pen], CO$_2$ is chemically bonded with both the C and O atoms bonded to the Ni atom, leading to a favorable adsorption free energy of $-0.18$ eV, substantial charge transfer of 0.36 e, and curved O–C–O bond angle of 145.8°. Differently, on Ni–B$_x$C$_2$N$_2$-oppo and Ni–B$_x$C$_1$N$_2$-N-[pen], the C atom of chemisorbed CO$_2$ is bonded to the Ni atom, while the O atom is bonded to the coordinated B atom. The dual-site activation of CO$_2$ results in stronger adsorption energies ($-0.25$ and $-0.39$ eV), larger charge transfer ($0.76$ and $0.96$ e), and stronger deviation of the O–C–O bond angle from linearity (130.8° and 129.3°). The charge density difference of Ni–B$_x$C$_1$N$_1$-b[pen], Ni–B$_x$C$_2$N$_2$-oppo and Ni–B$_x$C$_1$N$_2$-N-[pen] with chemically captured CO$_2$ is shown in Fig. S1†. One can see that the Ni center and the directly coordinated N, C or B atom are the main player in the activation and orbital interaction with the CO$_2$ reactant.

From Fig. 3b, the *COOH has versatile adsorption modes, which can be divided into five types. Specifically, (i) on Ni–B$_x$C$_y$N$_z$ ($X = 0$), Ni–B$_x$C$_y$N$_z$ ($X = 2$[hex], 3; $Y = 0$) and Ni–B$_x$C$_y$N$_z$ ($X = 2$[hex]; $Z = 0$), the C atom of *COOH is singly bonded to the Ni active center; (ii) on Ni–B$_x$C$_y$N$_z$, Ni–B$_x$C$_1$N$_z$, Ni–
B_{2}C_{2}N_{0,-oppo} and Ni–B_{2}C_{2}N_{0,-pen}, both the C and O atoms of *COOH are co-adsorbed onto the Ni atom; (iii) on Ni–B_{3}C_{1}N_{1,-oppo}, the C atom of *COOH is bonded to a B atom while the O atom is bonded to the Ni atom; (iv) conversely, on Ni–B_{2}C_{0}N_{2,-B,-pen} and Ni–B_{2}C_{1}N_{1,-B,-pen}, the C of *COOH is bonded with Ni while the O atom binds with the B atom; (v) on Ni–B_{X}C_{Y}N_{Z} (X = 1, 2(oppo, pen); Y = 1, 2; Z = 1), Ni–B_{X}C_{Y}N_{Z} (X = 1; Y = 1; Z = 2) and Ni–B_{X}C_{Y}N_{Z} (X = 0; Y = 1; Z = 2), the C atom of *COOH is singly bonded to the B atom, which indicates that the B acts as the active center. Moreover, from Fig. 3c, the *CO can have three types of adsorption modes. (i) On Ni–B_{3}C_{3}N_{4}, the *CO is physically adsorbed on the catalyst; (ii) on Ni–B_{X}C_{Y}N_{Z} (X = 0; Z = 1, 2, 3), Ni–B_{X}C_{Y}N_{Z} (X = 2(hex), 4; Y = 0), Ni–B_{X}C_{Y}N_{Z} (Y = 1; Z = 0) and Ni–B_{X}C_{Y}N_{Z} (X = 1; Y = 1; Z = 2(oppo)), the *CO is chemically adsorbed at the Ni center forming Ni–C single bonds; (iii) on Ni–B_{2}C_{1}N_{2} (X = 1, 2(oppo, pen); Y = 0), Ni–B_{2}C_{1}N_{2} (X = 2; Y = 1; Z = 1), Ni–B_{X}C_{Y}N_{Z} (X = 1; Y = 2; Z = 1) and Ni–B_{X}C_{Y}N_{Z} (X = 1; Y = 1; Z = 2(pen, hex)), the *CO forms bridging coordination with the Ni and B atoms. These flexible and versatile adsorption modes of CO_{2}, *COOH and *CO indicate that not only the Ni center but also the non-metal coordination atoms, B, in particular, play a vital role in tuning and stabilizing the reaction intermediates.

Scaling relations
The reduction of CO_{2} to CO is a two-electron reaction, which includes two step hydrogenations of carbonaceous intermediates, i.e., *CO_{2} + H^{+} + e^{-} → *COOH and *COOH + H^{+} + e^{-} → *CO + H_{2}O. On the traditional metal surfaces, the adsorption energies of *COOH and *CO are usually linearly correlated, and the weak *COOH or *CO adsorption (*COOH formation becomes unfavorable) can lead to a low CO_{2}RR activity, while a strong *COOH or *CO adsorption makes the release of the CO product become difficult. Therefore, how to break or weaken the linear scaling relationship between *COOH and *CO has
long been pursued in the CO2RR study. In our case, we also
examined the correlation between *COOH and *CO. The
adsorption energy ($E_{\text{ads}}$) of *COOH and *CO on Ni–B$_x$C$_y$N$_z$ is
calculated using the equation:

$$E_{\text{ads}}(\text{*COOH}) = E(\text{Ni–B}_x\text{C}_y\text{N}_z + \text{COOH}) - E(\text{Ni–B}_x\text{C}_y\text{N}_z) - E_{\text{CO}(g)}$$

$$- 1/2E_{\text{H}_2}$$

$$E_{\text{ads}}(\text{*CO}) = E(\text{Ni–B}_x\text{C}_y\text{N}_z + \text{CO}) - E(\text{Ni–B}_x\text{C}_y\text{N}_z) - E_{\text{CO}(g)}$$

The calculated adsorption energies are provided in Table S3,† and the correlation between $E_{\text{ads}}$ (*COOH) and $E_{\text{ads}}$ (*CO) is shown in Fig. 4. From Fig. 4, the adsorption energy of *COOH and *CO follows a fitted linear relationship $E_{\text{ads}}$ (*COOH) = 0.95$E_{\text{ads}}$ (*CO) – 1.86, and the scaling relations ($R \approx 0.87$) between them are slightly weakened with scattered points compared to those of pure metal surfaces ($R \approx 0.96$).63

A special case is Ni–B$_x$C$_y$N$_z$-N-oppo, which deviates greatly from the overall linear correlation. Note that on the pure metal surfaces, the *COOH and *CO are uniformly adsorbed to the surface metal atoms via single coordination mode (C–M bond). However, in our Ni–B$_x$C$_y$N$_z$ systems, the change of coordination environment, especially with the introduction of B, leads to versatile coordination modes (e.g., single or dual-site coordination) that vary greatly with the type and number of coordination elements. The versatility in the adsorption structures could be the main reason for the weakened linear scaling between *COOH and *CO in Ni–B$_x$C$_y$N$_z$.

**CO2RR activity and selectivity**

As discussed above, the adsorption characteristics of CO$_2$, *COOH and CO varied with the change of coordination environments, which indicates that the activity and product selectivity would be significantly affected. Thus, we further explored the activity of the CO$_2$RR to CO. The CO$_2$RR pathways can be divided into four elementary steps (Fig. 5a): (i) CO$_2$ adsorption: CO$_2$ (g) + * → *CO$_2$; (ii) *COOH formation: *CO$_2$ + H$^+$ + e$^-$ → *COOH; (iii) CO formation: *COOH + H$^+$ + e$^-$ → *CO; (iv) CO$_2$ reduction: *CO + H$^+$ + e$^-$ → H$_2$.
*CO + H₂O; and (iv) *CO desorption: *CO → CO (g) + *. The Gibbs free energy changes (ΔG) for each reaction step are provided in Tables S4–S6, and the ΔG (ΔG = max (ΔGii, ΔGiii, ΔGiv)) of the most difficult step, or the most sluggish step, dictates the reaction activity. The activity as a function of the binding energy of COOH and CO is shown in Fig. 5b. It is worth noting that the activity diagram is divided into two regions. In the right region, the *CO adsorption is relatively weak, and the activity is determined by the potential-dependent protonation of *CO2 to *COOH (step ii); while in the left region, the *CO adsorption is strong, and the activity is determined by the thermodynamic-dependent *CO desorption (*CO → * + CO(g), step iv). Clearly, most of the B-coordinated BₓCᵧNₐ (X ≠ 0) catalysts are located in the left region, where ΔG (*CO) varies from ~0.35 to ~1.42 eV, and the *CO desorption becomes the most difficult step. While Ni-BₓCᵧNₐ-N-oppo, Ni-BₓCᵧNₐ-C-hex and all the C and/or N coordinated Ni-BₓCᵧNₐ (X = 0) systems are located in the right region, where the *COOH formation becomes the potential-determining step, and the corresponding free energy change of *CO₂ hydrogenation to *COOH varies from 0.36 to 1.49 eV. Note that for the B-free Ni-BₓCᵧNₐ (X = 0), the CO₂RR activity is gradually decreased as the number of coordinated nitrogen atoms increases (Ni-BₓCᵧNₐ > Ni-BₓCᵧNₐ-N-oppo ≈ Ni-BₓCᵧNₐ-N-pen > Ni-BₓCᵧNₐ-N-hex) as Ni-BₓCᵧNₐ-N-pen > Ni-BₓCᵧNₐ-N-hex). Moreover, from the volcano plot, Ni-BₓCᵧNₐ (the bottom of the right region) and Ni-BₓCᵧNₐ-N-oppo (the bottom of the left region) stand out as the most active catalysts for the CO₂RR. Along the right region, the Ni-BₓCᵧNₐ has the lowest free energy (0.36 eV) for the reaction-limiting step (*CO₂ + H² + e⁻ → *COOH); and along the left region, the Ni-BₓCᵧNₐ-N-oppo has the lowest desorption energy for *CO release (~0.35 eV). The detailed free energy diagram of CO₂ reduction on Ni-BₓCᵧNₐ and Ni-BₓCᵧNₐ-N-oppo is shown in Fig. 5c.

Furthermore, to compare the computational accuracy of DMol³ with the plane-wave basis method in the VASP code, we choose the six Ni/C coordinated Ni-BₓCᵧNₐ (X = 0) systems to calculate the free energy diagram for CO evolution (Fig. S2†), and the free energy change for the potential-determining step (*COOH formation) is summarized in Table S7.† The free energy change predicted by the two methods differs by about 0.06–0.2 eV, and the trend of the predicted activity is similar except for Ni-BₓCᵧNₐ and Ni-BₓCᵧNₐ (DMol³ predicts a higher activity of Ni-BₓCᵧNₐ-N-oppo/Ni-BₓCᵧNₐ-N-pen over Ni-BₓCᵧNₐ, while VASP predicts the opposite). Recent studies by Luo et al.23 applied a grand canonical potential kinetics method to predict the reaction mechanism and rates for the CO₂RR over Ni-NₓCᵧ, Ni-NₓCᵧ, and Ni-Nₓ sites in graphene. They revealed that Ni-NₓCᵧ leads to the lowest onset potential (~0.84 V to achieve 10 mA cm⁻² current density), followed by Ni-NₓCᵧ (~0.92 V) and Ni-Nₓ (~1.03 V). Moreover, Liu et al.52 applied a “slow-growth” sampling approach to evaluate the reaction barriers and showed that the Ni-atom coordinated with one N and three C atoms (Ni-NₓCᵧ) is most active and selective for the CO₂RR. These indicate that the CO₂RR activity tends to decrease with the increase of coordinated nitrogen, which is qualitatively in good agreement with our DMol³ results based on the simplified computational hydrogen electrode model.

In addition, since the HER usually competes with the CO₂RR, it is thus also important to evaluate the selectivity between CO₂ reduction and HER by comparing their limiting potential (Uᵢ), which is defined as −ΔG/e (ΔG refers to the most sluggish step). According to this definition, a more positive ΔUᵢ (ΔG(CO₂) − ΔG(H₂)) means a higher selectivity toward the CO₂RR (the limiting free energy change of the competitive HER, ΔGHER, is provided in Table S6†). From Fig. 5d, most of the Ni-BₓCᵧNₐ catalysts are selective to the HER except for Ni-BₓCᵧNₐ, Ni-BₓCᵧNₐ, Ni-BₓCᵧNₐ, Ni-BₓCᵧNₐ-B-oppo/Ni-BₓCᵧNₐ-N-oppo/Ni-BₓCᵧNₐ-N-hex, and Ni-BₓCᵧNₐ-B-hex/pen. Among the 7 CO₂RR selective catalysts, Ni-BₓCᵧNₐ and Ni-BₓCᵧNₐ are potentially determined by *CO₂ hydrogenation. However, the ΔG for *COOH formation on Ni-BₓCᵧNₐ is very high (1.49 eV), making Ni-BₓCᵧNₐ selective but less active for the CO₂RR. A recent report by Zhang et al.64 showed that single Ni₇⁺ atoms fourfold coordinated by N and dispersed over a carbon black support displayed excellent CO Faraday efficiency (above 90%) and a low faradaic efficiency to H₂. The higher CO selectivity of the Ni-Nₓ catalyst over the HER is in agreement with our predictions of the CO₂RR selective Ni-BₓCᵧNₐ. Moreover, for the screened Ni-BₓCᵧNₐ, Ni-BₓCᵧNₐ-B-oppo, Ni-BₓCᵧNₐ-B-hex, Ni-BₓCᵧNₐ-N-oppo, Ni-BₓCᵧNₐ-N-hex, and Ni-BₓCᵧNₐ-B-pen, the *CO desorption is the most sluggish step, and the corresponding ΔG (*CO) is ~0.48 eV, ~0.63 eV, ~0.35 eV, ~0.64 eV, and ~1.25 eV, respectively. Since the CO₂RR process requires rapid desorption of *CO to improve the CO selectivity, Ni-BₓCᵧNₐ-B-pen is thus excluded as a viable CO₂RR catalyst due to its over strong *CO adsorption. Note that CO₂ electroreduction can produce many possible products. Previous experimental studies have verified that the N/C coordinated Ni produces CO as the main product, hence we only focus on the CO pathway for the B-free Ni-BₓCᵧNₐ (X = 0). With regard to the B-coordinated systems, we select the 5 CO₂RR selective catalysts (Ni-BₓCᵧNₐ, Ni-BₓCᵧNₐ-B-oppo, Ni-BₓCᵧNₐ-B-hex, Ni-BₓCᵧNₐ-N-oppo, Ni-BₓCᵧNₐ-N-hex and Ni-BₓCᵧNₐ-B-pen) to further examine the possible HCOOH pathway. From Fig. S3,† the limiting potential required for HCOOH formation is much higher, which indicates that CO is the more preferred product. In addition, since the *CO adsorption on Ni-BₓCᵧNₐ-B-pen is very strong (~1.25 eV), we further studied its potential to produce more deep-reduced products. From Fig. S3e,† the *CO can be further reduced to CH₄ and CH₃OH, and the potential-determining step corresponds to hydrogenation of *CHO to *OCH₂ (0.92 eV).

**Activity origin**

The activity of an electrocatalyst is known to be governed by its intrinsic electronic structure. To decode the underlying activity origin, we first analyzed the electronic structures, and the projected density of states (PDOS) of Ni and the coordination atoms (B, C and N) on pure Ni-BₓCᵧNₐ catalysts is shown in Fig. S4.† Since all the investigated 25 catalysts are non-magnetic, there is no spin-polarization in the calculated electronic states; we thus only plotted one of the spin channels. In the C-
and N-coordinated Ni–BₓCᵧNₗ (B-free, X = 0), the electronic states around the Fermi level are mainly contributed by the Ni atom for Ni–BₓCᵧNₗ, Ni–BₓCᵧNₗ,N-oppo, Ni–BₓCᵧNₗ,N-pen, and Ni–BₓCᵧNₗ,N-hex (Fig. S4a, 2b, 2c and 2d†). While in the case of Ni–BₓCᵧNₗ (Fig. S4e†) and Ni–BₓCᵧNₗ (Fig. S4f†), the Ni electronic states shifted downward, and the Fermi levels are mainly contributed by the N atoms. This can qualitatively explain why Ni–BₓCᵧNₗ and Ni–BₓCᵧNₗ with higher N-content show lower CO₂RR activity. We further analyzed the Bader charge of the Ni active center in Ni–BₓCᵧNₗ (B-free, X = 0) (Table S8†), where the Ni atom carries positive charge between +0.625e and +0.830e. Particularly, we note that the charge of the Ni atom in Ni–BₓCᵧNₗ (+0.625e) is the lowest, indicating that the Ni atom has more electrons in the outer shell. The previous research studies reveal that the larger magnitude of electrons in the outer shell would facilitate the adsorption of CO₂ and *COOH intermediates thereby accelerating the CO₂RR.

On the other hand, the electronic structures of B-coordinated Ni–BₓCᵧNₗ (X ≠ 0) are much more complicated (Fig. S4g–2y†). Depending on the various coordination environments, the electronic states at the Fermi level are mainly contributed by the Ni atoms (Ni–BₓCᵧNₗ, Ni–BₓCᵧNₗ,N-oppo, Ni–BₓCᵧNₗ,N-hex, Ni–BₓCᵧNₗ,N-pen and Ni–BₓCᵧNₗ,N-hex), the B atoms (Ni–BₓCᵧNₗ,N-oppo, Ni–BₓCᵧNₗ,N-hex and Ni–BₓCᵧNₗ,N-pen), the Ni and B atoms (Ni–BₓCᵧNₗ, Ni–BₓCᵧNₗ,N-oppo, Ni–BₓCᵧNₗ,N-hex, Ni–BₓCᵧNₗ,N-pen, Ni–BₓCᵧNₗ,N-hex and Ni–BₓCᵧNₗ,N-pen), or the Ni and C atoms (Ni–BₓCᵧNₗ,C-oppo, Ni–BₓCᵧNₗ,C-pen, Ni–BₓCᵧNₗ,C-pen and Ni–BₓCᵧNₗ,C-hex), respectively. In the B-coordinated systems, both the Ni and B atoms are positively charged (except for Ni–BₓCᵧNₗ where the Ni atom has a negative charge of −0.0411e), and Ni is found to carry much less positive charge (+0.07e to +0.49e) than B (+1.22e to +1.51e). Compared to the B-free Ni–BₓCᵧNₗ (X = 0) (Ni atomic charge: +0.625e to +0.830e),

![Figure 6](image-url)

Fig. 6 Bader charge analysis of active sites (Ni or B atom) on *COOH and *CO adsorbed Ni–BₓCᵧNₗ. Correlations of the adsorption free energy of *COOH (a) and *CO (b) intermediates with Ni Bader charge on B-free Ni–BₓCᵧNₗ (X = 0). Correlations of the adsorption free energy of *COOH and *CO intermediates with Ni (c, e) and B Bader charge (d, f) on B-coordinated Ni–BₓCᵧNₗ (X ≠ 0).
the charge of the Ni atom is significantly reduced with the introduction of B (Table S8†). It is known that B behaves like a transition metal and can be the active site in electrocatalysis. The valence electronic configuration of B atoms is 2s2p1 and the sp3 hybridization of these orbitals can accept and donate the lone-pair electron, which is similar to the d orbital of transition metals.45,67,68 In addition, the electronegativity of B (2.04) is close to that of Ni (1.91) and lower than C (2.55) and N (3.04), which also means that the B has transition-metal-like properties. This indicates that Ni and B can work synergistically to function as dual-active sites, which can explain the dual-site adsorption of CO2, *COOH and *CO in some of the Ni–BxC3Nz (X ≠ 0) catalysts, leading to more favorable *COOH formation and stronger *CO adsorption.

Fig. 6 shows the correlation between the calculated Bader charge of the active center and the adsorption free energy of *COOH and *CO species. In the B-free Ni–BxC3Nz (X = 0), only the Ni acts as the active site, and both the ΔG (*COOH) and ΔG (*CO) display linear correlation (K2(*COOH) ≈ 0.83 and K2(*CO) ≈ 0.78) with the Ni Bader charge (Fig. 6a and b). However, in the B-coordinated BxC3Nz (X ≠ 0), the active site varies with the coordination environment, and either the single Ni site, single B site or dual Ni–B site can be the catalytic active center. Due to the complexity in the bonding behaviors between CO2RR intermediates and the active sites, the correlation between the atomic charge of Ni or B (Table S9†) with the adsorption free energy of *COOH and *CO is very poor (Fig. 6c–f). Compared to the single metal atom catalyst, the dual-site or multifunctional site catalysts need a more complex descriptor to explain the intrinsic activity, which would stimulate the future research on the dual- or multi-site electrocatalysts.

Conclusion

In summary, based on DFT computations, we explored the coordination effect on the electrocatalytic activity of Ni SACs towards CO2 reduction, where the coordination atoms are C, N or B. Our results showed that the coordination environments of the metal atom have a remarkable influence on the adsorption and reaction characteristics. In the C and/or N coordinated Ni–BxC3Nz [B-free, X = 0], only the Ni atom acts as the active site, which features as a single-site adsorption mode for CO2RR intermediates. Differently, with the introduction of B [Ni–Bx–C3Nz, X ≠ 0], the coordinated B atom and the Ni metal function as a dual-site and lead to versatile coordination modes of reaction species (single or dual-site adsorption) that varies with the type and number of coordination elements. The versatility in the adsorption modes also results in a weakened linear scaling relationship between *COOH and *CO. Moreover, we established the volcano-type activity plot. It is found that most of the B-coordinated Ni–BxC3Nz (X ≠ 0) catalysts are located in the left region where *CO desorption becomes the most difficult step, while all the C and/or N coordinated Ni–BxC3Nz (X = 0) are located in the right region where the *COOH formation becomes the potential-determining step. Our results predict that Ni–B4C3N4 and Ni–B4C3N2,N-opp stand out as the most active catalysts for the CO2RR and have high selectivity over the HER. Hence, by precisely controlling the coordination environment, the experimentally available Ni SACs can be utilized as highly active and selective CO2RR electrocatalysts. This work provides significant inspiration on boosting the electrocatalytic CO2RR activity of Ni or other metal catalysts by regulating the coordination environment.

Conflicts of interest

The authors declare no competing financial interests.

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