Dynamic Structural Changes in Nickel Single-Atom Catalysts During Electrochemical Reduction of CO2 to CO

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Article

**Keywords:** electrochemical CO2 reduction reaction, Ni single-atom catalyst, X-ray absorption spectroscopy

**DOI:** [https://doi.org/10.21203/rs.3.rs-689036/v1](https://doi.org/10.21203/rs.3.rs-689036/v1)

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Abstract

Electrochemical CO₂ reduction reaction (ECO₂RR) is an important route for global carbon abatement. However, a comprehensive picture of the structure evolution of metal active sites is currently lacked in ECO₂RR. Here, we present the first full view of Ni single-atom catalyst for ECO₂RR over a broad potential range. Comprehensive X-ray absorption spectroscopy (XAS) analyses confirmed the Ni coordinated with pyrrole nitrogen in the form of Ni-N₄ attached with an axial O₂ ligand. Operando XAS revealed the precise structure of the Ni single-atom catalyst that dynamically changes with the shift of applied potentials. Such changes ultimately contributed to the CO selectivity variation ranging from 20%-99%. Interestingly, the Ni center was found to move toward the N₄ plane during the ECO₂RR, which played a crucial role of reaching near-unity CO selectivity. Together with theoretical calculations, a clear quantitative correlation between the dynamic configuration and the catalytic properties was established.

Introduction

The electrochemical CO₂ reduction reaction (ECO₂RR) offers a promising approach for curbing anthropogenic CO₂ emissions, storing intermittent power from solar, wind, and thermal sources, and producing value-added chemicals or fuels including carbon monoxide, formic acid, ethylene, and ethanol¹. Owing to the thermodynamic stability of CO₂, a rational catalyst design is required to reduce the activation energy barrier for the ECO₂RR². Over the past decade, numerous efficient catalysts have been developed and various chemicals such as carbon monoxide, ethylene, and ethanol can be produced depending the catalyst types³⁻⁷. The carbon abatement capability has strong dependence on the chemical product. As estimated by Lin et al., CO is the privileged target for ECO₂RR due to the carbon mitigation capability of 616 g CO₂ per kWh, which tops two among various chemical products⁸. CO is widely needed in chemical and metallurgical industries such as alkenes, alcohols, and synthetic oils⁹. Thus, the electrochemical reduction of CO₂ to CO offers a renewable route toward industrial raw materials and can eliminate additional pollution during industrial manufacturing processes.

Recently developed transition-metal single-atom catalysts, which are projected to have high atomic efficiencies, provide an intriguing paradigm for CO₂ electroreduction to CO with Faradaic efficiencies comparable to precious-metal catalysts¹⁰,¹¹ owing to their unique structures and coordination environments¹²⁻¹⁴. Utilizing atomically dispersed Fe³⁺ sites, good performances of CO₂ electroreduction to CO have been obtained at a mild overpotential of 80 mV¹. Various Ni single-atom catalysts have also been successfully prepared¹⁵,¹⁶. For example, Yan et al. developed a Ni single-atom catalyst with coordinatively unsaturated Ni–N active sites prepared by pyrolyzing Ni-substituted zeolitic imidazolate framework-8 (ZIF-8) that exhibited Faradaic efficiencies of 92.0%–98.0% for the ECO₂RR over a wide potential range¹⁷. Although significant progress has been made in the area of single-atom catalysts for the ECO₂RR, many fundamental questions concerning the vital roles played by the dynamic structural changes in active sites induced by applied potentials, adsorbates, and reactants remains to be answered,
since many previous studies just focused on static active sites. Clarifying the catalytic nature of such cost-effective catalysts and the structural origin of their activity is necessary to realize further advancements. The structural transformation of active sites during a reaction lowers the electrochemical energy barrier, which is beneficial for the reaction thermodynamics, and monitoring such changes is critical for building structure–reactivity correlations\textsuperscript{18}. As many unique physical and chemical changes can occur, employing operando characterization under real reaction conditions is especially important. Resorting to operando characterization, more precise local structure has been optimized in more electrochemical systems\textsuperscript{18-20}. Besides, the local atomic structure of catalysts under high polarization voltages and its influence on the competitive reactivity between the \text{ECO}_2\text{RR} and side reactions such as the hydrogen evolution reaction (HER) have gotten rare attention, which limits the further development for catalyst used under broad voltage range. As a powerful tool for determining dynamic atomic and electronic structure, operando XAFS spectroscopy is advantageous for unambiguously identifying the basic structures of active sites. In particular, X-ray absorption near-edge structure (XANES) spectroscopy can reveal oxidation states and is highly sensitive to local structure, including electronic spin state and symmetry\textsuperscript{21}. Importantly, XANES offers a high signal-to-noise ratio owing to strong intensities resulting from multiple scattering, especially in the measurements of dilute systems such as single-atom catalysts in fluorescence mode.

Herein, we report the dynamic structural changes in the active site of a Ni single-atom catalyst under \text{ECO}_2\text{RR} conditions, as probed by operando XAFS, and the structure–reactivity correlation. The atomically dispersed Ni single-atom catalyst was prepared and exhibited extremely high \text{ECO}_2\text{RR} performance and excellent robustness. Comprehensive XAS characterization identified the precise basic structure of the active site as disordered pyrrole-type Ni-N_4O_2 with the Ni center out of the N_4 plane. Furthermore, operando XAFS analysis revealed a novel structural transformation concerning the potential–induced Ni species moving toward the N_4 plane, which determined the catalytic activity. We also observe the formation of novel nickel diatomic clusters under extremely negative potential and its effect on reaction performance. These analyses offer a new approach for characterizing the active site geometry and the structural transformations that occur during the \text{ECO}_2\text{RR}, an understanding of which is essential for elucidating the mechanisms of other transition-metal single-atom electrocatalysts and designing more effective catalysts.

Results And Discussion

**Structural characterization of as-prepared catalysts.** A Ni-based heterogeneous catalyst (denoted Ni-N-C) was prepared by pyrolyzing Ni-doped ZIF-8 in Ar at 1000 °C, which resulted in the formation of a N-doped carbon skeleton. Ni-N-C was found to consist of nanopolyhedrons with uniform shapes and sizes, as revealed by scanning electron microscopy (SEM) (Fig. 1a) and transmission electron microscopy (TEM) (Supplementary Fig. 1a), suggesting that Ni-N-C maintains the MOF structure of ZIF-8. Furthermore, high-resolution transmission electron microscopy (HRTEM) revealed the formation of graphene sheets with no nanoparticles (Supplementary Fig. 1b). The aberration-corrected high-angle annular dark-field scanning
transmission electron microscopy (HAADF-STEM) image shows bright spots with sizes of ~0.2 nm, which verify the uniform atomic dispersion of Ni species in Ni-N-C (Fig. 1b). Moreover, the low-resolution HAADF-STEM image and corresponding energy-dispersive X-ray spectroscopy (EDS) mapping indicate that Ni, N, C, and O are homogenously distributed over the graphene sheets (Fig. 1c). For comparison, a catalyst without Ni (denoted N-C) was synthesized to investigate the effects of the Ni species on the catalytic properties. As revealed by SEM and TEM (Supplementary Fig. 2), the absence of Ni and Zn species resulted in considerable shrinkage of the nanopolyhedrons and even destruction of the MOF nanocrystals.

X-ray photoelectron spectroscopy (XPS) was performed to further examine the structure and electronic state of Ni-N-C (Supplementary Fig. 3a, Supplementary Table 1). The full XPS survey scan in Supplementary Fig. 3a verified the elemental composition of Ni-N-C. Moreover, the corresponding elemental contents (Supplementary Table 1) were consistent with the XPS and EDS mapping results. As shown in Supplementary Fig. 3b, the high-resolution Ni 2p XPS spectrum of Ni-N-C contains two main peaks at 855.7 eV (Ni 2p$_{3/2}$) and 872.8 eV (Ni 2p$_{1/2}$) with two corresponding satellite peaks, indicating that the Ni species in Ni-N-C has a valence state of +2 and the sharp peak indicates the single Ni$^{2+}$ feature$^{22-24}$.

The high-resolution N 1s XPS spectrum of Ni-N-C is deconvoluted into five nitrogen configurations which assigned to pyridinic N at ~398.8 eV, metal-N at ~399.6 eV, pyrrolic N at ~401.1 eV, graphitic N at ~402.1 eV and oxidized N at ~404.4 eV (Fig. 2a and Supplementary Table 2). Compared with the N 1s XPS spectrum of N-C, the pyrrolic N peak of Ni-N-C was shifted 0.4 eV toward higher binding energies, suggesting that the Ni atoms interact with pyrrolic N species$^{25}$. Furthermore, the peak intensity ratio of pyrrolic N to pyridinic N for Ni-N-C is significantly higher than that for N-C, which was ascribed to Ni doping enhancing the content of pyrrolic N. Thus, in Ni-N-C, Ni mainly bonds with pyrrole-type N species.

Element-sensitive synchrotron X-ray absorption spectroscopy (XAS) was conducted to investigate the local coordination environment and electronic states of as-prepared catalysts. In the Ni L-edge XAS spectra of Ni-N-C and nickel phthalocyanine (NiPc) (Supplementary Fig. 4), the intensity of the white line peak assigned to the 2p $\rightarrow$ 3d transition is a direct indicator of the valence state; thus, the Ni species valence state in Ni-N-C is similar to that in NiPc. Besides, the identical peak width of the Ni L-edge XAS spectra of Ni-N-C and NiPc indicates the single site in Ni-N-C which is in agreement with the Ni 2p XPS result$^{12, 26}$. The N K-edge XAS spectra of Ni-N-C and N-C were also obtained to confirm the nitrogen configuration (Fig. 2b). The 1s $\rightarrow$ p$^*$ resonance peaks including a pyridinic N peak (peak A) at 397.8 eV, a pyrrolic N peak (peak B) at 399.1 eV and a graphitic N peak (peak C) at 400.8 eV were detected, as well as the 1s $\rightarrow$ s$^*$ resonance peaks including a broaden peak (peak D) at 407.2 eV. Obviously, compared with N-C, the pyridinic N peak of Ni-N-C is relative weak and just shows as a shoulder. Moreover, the intensity of pyrrolic N peak and the peak intensity ratio of pyrrolic N to pyridinic N for Ni-N-C increase substantially, suggesting that Ni doping facilitate the formation of pyrrole-type N and pyrrole-type N species become predominant, in agreement with the N 1s XPS results$^{27, 28}$. The ex situ Ni K-edge XANES spectra of
pristine Ni-N-C and several reference materials are displayed in Fig. 2c. The main absorption edge near 8347 eV, which corresponds to the 1s ® 4p electric dipole transition, is sensitive to the Ni oxidation state. To precisely determine the absorption edge energy, the derivative of the XANES spectrum was employed (Supplementary Fig. 5), in which the position of the most intense peak represents the energy of the absorption edge. The absorption edge energy of Ni-N-C (8347.5 eV) is similar to that of Ni(OH)\textsubscript{2} (8347.0 eV), indicating that the oxidation state of Ni species in Ni-N-C is approximately +2, which is in agreement with the XPS and Ni L-edge XAS results. In Fig. 2b, the shoulder at ~8340 eV arising from 1s ® 4p\textsubscript{z} shakedown transition is a straightforward fingerprint for a square-planar Ni-N\textsubscript{4} configuration with D\textsubscript{4h} symmetry. However, as this shoulder is relatively weak for Ni-N-C as compared to that for NiPc, the D\textsubscript{4h} symmetry is broken. Moreover, the intensity of the pre-edge peak at ~8333 eV, which corresponds to the dipole-forbidden but quadrupole-allowed transition from 1s to the 3d–4p mixed orbital of Ni, depends on the site symmetry. The inset of Fig. 2c highlights the difference in the integrated intensities of the pre-edge peaks of Ni-N-C and NiPc, further showing that the square-planar configuration is distorted in the pristine catalyst. The coordination environment surrounding Ni in Ni-N-C was then investigated using the Fourier transform (FT) of the phase-uncorrected EXAFS spectrum (Supplementary Fig. 6a). The non-phase-corrected FT curve of Ni-N-C exhibits only one domain peak at 1.33 Å, which originates from the interactions between Ni and light atoms such as C, N, and O, without the Ni–Ni coordination identified for the Ni foil reference, indicating that the Ni species in Ni-N-C are atomically dispersed. The peak at ~2.3 Å can be assigned to the scattering between Ni and C atoms in higher shells or multiple scattering interactions between Ni and surrounding N atoms. Moreover, EXAFS wavelet transform (WT), a powerful tool for discerning the contribution of each pathway in both R-space and k-space, was performed to discriminate the backscattering atoms (Fig. 2d). As compared to Ni foil and Ni(OH)\textsubscript{2}, the observation of a single obvious maximum at ~4 Å\textsuperscript{-1} for Ni-N-C provided unequivocal support for the absence of a Ni–Ni scattering path. For quantitative determination of the coordination configuration around the Ni atoms in Ni-N-C, we performed least-squares FT-EXAFS curve fitting (Supplementary Fig. 6b and Supplementary Table 3). The best-fitting analyses clearly showed that the Ni center is coordinated by one O atom and four N atoms with bond distances of 2.19 and 1.93 Å, respectively.

XANES is much more sensitive to the symmetry of the local environment and the atomic arrangement of the absorber. To precisely identify the coordination structure of Ni-N-C, we implemented the FDMNIES code to simulate Ni K edge XANES spectra based on NiN\textsubscript{4}O configuration following the fitting result. In accordance with the N 1s XPS and N K-edge XAS results, various planar pyrrole-type Ni-N\textsubscript{4} moieties with or without axial oxygen were constructed (Supplementary Fig. 7a–c). However, the extreme disagreement between the theoretical and experimental spectra, especially in terms of the energy position of feature d and the intensity ratio of feature b to feature c (I\textsubscript{b}/I\textsubscript{c}), indicated that more detailed structural parameters should be considered. In the case of feature d, the energy position is related to the metal–ligand bond distance in the first shell according to Natoli’s rule: DE = \text{constant}, where DE represents the threshold energy. Accordingly, the bond length between Ni and the ligand atoms should be shortened to improve
the fitting. Thus, disordered pyrrole-type Ni-N₄ moieties with shorter bonds between Ni and the ligand N/O atoms \((R_{\text{Ni-N/O}})\), corresponding to feature d shifting toward high energies, were built and simulated (Supplementary Fig. 7d–f). As a result, better alignment between the features in the theoretical and experimental spectra was achieved, although the position of feature d was still offset, perhaps because \(R_{\text{Ni-N/O}}\) was too short. Furthermore, increasing the number of axial oxygen atoms caused \(I_b/I_c\) ratios in the theoretical and experimental spectra to become more similar. Accordingly, the Ni atom was pulled away from the N₄ plane to lengthen \(R_{\text{Ni-N/O}}\), and the corresponding spectra in Supplementary Fig. 8 and Fig. 2e show excellent alignment between the experimental and theoretical energy positions of the observed features. Given that additional axial oxygen atoms can influence these features, the good agreement observed over the entire XANES energy range when an oxygen atom is absorbed to form a dioxygen structure demonstrates that the as prepared Ni-N-C catalyst adopts a NiN₄O₂ configuration with the Ni atom offset from the N₄ plane and an axial dioxygen unit absorbed on the raised side. To further identify the type of ligand nitrogen species, various planar and disordered pyridine-type Ni-N₄ moieties were built and simulated (Supplementary Fig. 9). The resulting poor agreement between the theoretical and experimental spectra confirmed that the Ni atoms are bonded to pyrrolic N, which is consistent with the N 1s XPS and N K-edge XAS results.

**ECO₂RR performance evaluation.** The electrocatalytic activity of the as-prepared catalyst for the ECO₂RR was evaluated in a gas-tight H-type cell containing a CO₂-saturated KHCO₃ solution. Liquid and gas products were analyzed by nuclear magnetic resonance (NMR) spectroscopy and gas chromatography (GC), respectively. All the data were repeated three times and averaged. No liquid products were detected and \(H_2\) and CO were the sole conversion products formed. As shown by the linear sweep voltammetry (LSV) curves of Ni-N-C and N-C in CO₂- and Ar-saturated 0.5 M KHCO₃ solution (Fig. 3a), Ni-N-C has much higher activity from −0.5 to −1.3 V (vs. the reversible hydrogen electrode (RHE)). The measurement results of FE with regard to CO and \(H_2\) are displayed in Fig. 3b and Supplementary Fig. 10b. At a potential of -0.4 V (vs. RHE), CO was detected with poor FE of 53.6%. As the applied potential increased, the competing HER was greatly suppressed, and the production of CO became predominant in the range of −0.5 to −0.9 V (vs. RHE) with Faradaic efficiencies of more than 90%. The highest CO Faradaic efficiency of 99% was achieved at a potential of −0.67 V (vs. RHE). At more negative potentials, the \(H_2\) Faradaic efficiency exceeded the CO Faradaic efficiency. By contrast, the N-C catalyst exhibited relatively poor ECO₂RR performance because the HER played a dominant role over the entire range of applied potentials (Supplementary Fig. 10). The stability of Ni-N-C was evaluated by performing CO₂ electrolysis at a constant potential of −0.6 V (vs. RHE). Ni-N-C exhibited remarkable stability with negligible decays in current density (20 mA cm⁻²) and CO Faradaic efficiency (96%) over 24 h (Fig. 3c). Furthermore, constant potential electrolysis at various potentials confirmed the long-term stability of Ni-N-C (Supplementary Fig. 11).

**Operando XAFS measurements of Ni-N-C during the ECO₂RR.** In an attempt to gain insights into the intrinsic origin of the catalytic activity of Ni-N-C, we conducted operando XAFS measurements under real
electrochemical conditions. Ni K-edge XAFS spectra were collected for a dry sample and wet samples immersed in a sufficient amount of CO$_2$-saturated 0.5 M KHCO$_3$ at the open circuit potential (OCP) and at potentials decreasing in steps from −0.17 to −1.37 V (vs. RHE). The XANES spectra of Ni-N-C along with that of Ni foil as a reference are displayed in Fig. 4a. The spectra of the dry sample and the catalyst at the OCP show nearly identical features, indicating the structural stability of Ni-N-C in the absence of an applied potential. As previously mentioned, the pre-edge peak at ~8333 eV, attributable to the 1s® d–p hybridized orbital transition, is sensitive to the oxidation state and acts as a fingerprint for local symmetry. The inset in Fig. 4a clearly shows a gradual decrease in the intensity of the pre-edge peak with increasing negative applied potentials, suggesting a continuous reduction in the oxidation state of the Ni species with a concomitant enhancement in the structural symmetry of the active center. With regard to the multiple scattering resonances, when the potential was changed from the OCP to −0.67 V (vs. RHE), the intensity of feature b was weakened, whereas that of feature c was strengthened, resulting in a reduction of I$_b$/I$_c$. When the applied potential became more negative (−0.77 V vs. RHE), the key spectral features were aligned with those in the spectrum at −0.67 V (vs. RHE), despite a small change in I$_b$/I$_c$, demonstrating that the structure was consistency in the range of −0.67 to −0.77 V (vs. RHE). As mentioned in the previous section, the energy position of feature d is related to the metal–ligand bond distance in the first shell following Natoli’s rule$^{39}$. The shift in the position of feature d towards higher energies when the applied potential decrease from OCP to −0.67 V (vs. RHE) implied that the Ni–ligand bond was shortened. Interestingly, the spectra obtained at −1.27 and −1.37 V (vs. RHE) exhibited inconsistent behavior with an increase in I$_b$/I$_c$ but the position of feature d corresponding to that in the spectra collected between −0.67 and −0.77 V (vs. RHE). These results indicated that an intriguing local geometry emerges under more negative potentials, which could be related to the HER. Corresponding trends were observed in the XANES difference spectra (Dm) (Fig. 4b), obtained by subtracting the spectrum at OCP, with the feature at 8346 eV indicating that the structure remains unchanged from −0.67 to −0.77 V (vs. RHE), whereas a new moiety is formed at −1.27 and −1.37 V (vs. RHE).

Quantitatively, EXAFS curve fitting analysis was conducted to investigate the coordination environment around Ni atom for Ni-N-C during ECO$_2$RR under several typical potentials (Supplementary Fig. 12 and Supplementary Table 3). The best-fitting analyses demonstrate that the axial oxygen atoms are replaced by a C atom which may originate from the absorbed CO$_2$ molecule with the potential applied. The EXAFS spectra and fitting results at −0.17 V and −0.77 V (vs. RHE) show the similar coordination configuration, despite the slightly shrinkage of Ni-N and Ni-C bond length at −0.77 V (vs. RHE). However, the extraordinarily strong peak at ~2.3 Å under -1.37 V (vs. RHE) implied the formation of novel local structure. Accordingly, the presence of Ni–Ni scattering path in fitting results with the coordination number of 1 indicates the Ni diatomic clusters were formed under extremely negative potentials. Besides, the appearance of Ni clusters was also illustrated by WT-EXAFS analysis since the additional intensity maximum at approximately 7.4 Å$^{-1}$ corresponds to the Ni-Ni scattering in Ni foil (Supplementary Fig. 13). To further trace the detail dynamic changes in the active center, we used the FDMNES code to simulate representative XANES spectra at the OCP, −0.17 V, −0.77 V, and −1.37 V (vs. RHE). The best simulation results were obtained by optimizing the input structure and parameters. Fig. 4c–e display comparisons
between simulated and experimental spectra with the corresponding satisfactory computed models displayed in the insets. As discussed in the previous section, the active center of the dry sample was formed by the displacement of the Ni atom from the N₄ plane and the absorption of additional axial dioxygen. When the wet sample was measured at the OCP, the structure remained consistent with that of the dry sample. As shown in Fig. 4c, at −0.17 V (vs. RHE), the ECO₂RR proceeds with the desorption of axial dioxygen and the absorption of a CO₂ molecule. Furthermore, the Ni atom shifts toward the N₄ plane, resulting in a displacement of Ni atom out of N₄ plane of 0.3 Å, indicating the shortening of R_{Ni–N} (Supplementary Table 3). With a decrease of the applied potential to −0.77 V (vs. RHE), the absorption/desorption behavior remains unchanged but the Ni atom continues to move toward the N₄ plane with an offset of 0.2 Å (Fig. 4d). However, decreasing the applied potential further to −1.37 V (vs. RHE) should result in large structural changes owing to the previously mentioned novel features. Given the appearance of metallic features at the white line position, an excessively negative potential could break the original structure, resulting in the formation of a Ni diatomic cluster. Combined with EXAFS fitting analyses, we built new moieties with an additional axial Ni atom (Fig. 4e). Note that the basic coordination configuration remains NiN₄ obtained from EXAFS fitting result, which means that the additional whole NiN₄ moieties are detached from graphene sheets and absorbed onto the Ni center (Supplementary Fig. 17). The presence of a hydroxyl group instead of a CO₂ molecule on the opposite side resulted in better agreement between the theoretical and experimental spectra, in agreement with the HER becoming dominant at more negative potentials (Supplementary Fig. 14). In addition, we also considered the form of adsorbate adsorbed on Ni. As shown in Supplementary Fig. 15 and Fig. 16, the unsatisfactory agreement between operando spectra and theoretical spectra based on *CO₂ (bent), *CO and *COOH indicates that the adsorbate adsorbed on NiN₄ sites prefer linear *CO₂. Moreover, aberration-corrected HAADF-STEM was conducted to track the morphological changes after electrolysis. As shown in Supplementary Fig. 17, no aggregation of Ni species was observed in the used catalysts after electrolysis at −0.77 and −1.37 V (vs. RHE) for 1 h, indicating the robust structural restorability and stability of Ni-N-C. Furthermore, negligible differences were observed between pristine Ni-N-C and the used catalysts after electrolysis at −1.37 V (vs. RHE) (Supplementary Fig. 18), further confirming that the dynamic structural transformation only occurs under electrolysis conditions and is triggered by an applied potential (Supplementary Fig. 19). Furthermore, the structural changes in the region of from −0.77 V to −1.37 V (vs. RHE), in which the catalytical performance significantly changed was also investigated. The regular changes in XANES spectra and the well-reproduced fitting data suggesting that the change in spectra from optimal reaction potential to extremely negative reaction potential is linear and the corresponding structure is mixed (Supplementary Fig. 20).

**DFT calculations and ECO₂RR mechanism.** To gain further theoretical insights into the origin of the ECO₂RR activity and the reaction mechanism of Ni-N-C, DFT calculations were carried out. As a straightforward depiction of the reaction pathway, a catalytic cycle for the ECO₂RR on Ni-N-C was proposed (Fig. 5a). The initial model was built based on Ni-N₄ configuration with an average Ni–N bond length of 2.03 Å, in agreement with the XANES simulation result and EXAFS fitting parameters. Initially, a
*COOH intermediate is formed via a proton-coupled electron-transfer step for CO2 activation and it needs much more energy to overcome the barrier of 1.67 eV (Fig. 5b). After CO2 activation, an energetically facile second proton-coupled electron-transfer step occurs with the formation of absorbed *CO and the desorption of H2O. The subsequent free energy change of 0.42 eV downhill demonstrates the thermodynamic favorability for the desorption of CO.

Subsequently, we used the projected density of state (PDOS) to investigate the electronic properties of Ni-N-C during the ECO2RR under various applied potentials. As illustrated in Fig. 5c–e, the density of states for Ni around the Fermi level is dramatically reduced and the d-band center is shifted away from the Fermi level after the absorption of *COOH compared with that after the absorption of CO2, indicating that the delocalization of electrons in the Ni 3d orbital and spontaneous charge transfer to the absorbed CO2 molecule facilitate the formation of *COOH40-43. Under an applied potential of −0.77 V (vs. RHE), the d-band center of Ni-N-C showed a larger downward shift of 2.42 eV compared with those of 2.27 and 2.39 eV at −0.17 and −1.37 V (vs. RHE), respectively, suggesting that the formation of *COOH on Ni-N-C was favored at −0.77 V (vs. RHE). At −0.17 V (vs. RHE), the decreased overlap between the C+2O 2p state in *COOH and the Ni 3d state gave rise to a weaker binding energy between *COOH and Ni-N-C with the Ni atom offset by 0.3 Å from the N4 plane41. Despite OH absorption being more favorable at −1.37 V (vs. RHE), we calculated the electronic structure of Ni-N-C at this potential after the absorption of CO2 and *COOH to further explore the underlying correlation between ECO2RR performance and the local configuration triggered by the applied potential. As illustrated in Fig. 5e (top), the reduced density of states for the Ni 3d orbital below the Fermi level suggests that the formation of Ni diatomic clusters is not beneficial for subsequent CO2 activation and the absorption of intermediates44. In short, the applied potentials trigger dynamic structural changes in the off-plane Ni atom and modulate the electronic properties, which play a vital role in determining the reaction process.

**Conclusions**

We systematically investigated the dynamic structural changes in the active site of an atomically dispersed Ni-N-C catalyst with a disordered pyrrole-type NiN4O2 configuration during the ECO2RR. Using operando XAFS spectroscopy combined with XANES simulations based on the FDMNES code, the unique phenomenon of the Ni atom moving toward the N4 plane following the application of a potential was demonstrated, which provided a beneficial basis for elucidating the nature of the ECO2RR activity and building a correlation between the actual configuration and the reaction mechanism. These results will motivate further work on the rational design and synthesis of more effective catalysts for the ECO2RR.

**Declarations**

Author Contributions
Z.J. and B.M. co-supervised the entire work. Z.J., B.M., and X.D. designed the experiments. B.M., C.L. and L.M. performed most of the experiments and the characterizations. B.M., S.Y., Y.Y., H.Z., and F.S. performed the X-ray structure characterization and analysis. Q.W., F.S., W.X., B.M., X.D. and Z.J. participated in the analysis of the results. C.A. and S.L. performed the DFT calculations. B.M. wrote the manuscript. All the authors contributed to the overall scientific interpretation and edited the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (U1732267). Authors would like to thank Prof. Wensheng Yan from the National Synchrotron Radiation Laboratory (NSRL) for the help on the measurement and discussion of sXAS.

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**Figures**

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**Figure 1**

Morphological characterizations of Ni-N-C. a, SEM image of Ni-N-C. b, Aberration-corrected HAADF-STEM image of Ni-N-C. c, Low-resolution HAADF-STEM image of Ni-N-C and corresponding EDS mapping of Ni, C, N, and O.
Figure 2

Local geometric and electronic configurations of Ni-N-C. a, High-resolution N 1s XPS spectra of Ni-N-C and N-C. b, N K-edge XAS spectra of Ni-N-C and N-C. c, Ni K-edge XANES spectra of Ni-N-C, Ni foil, NiPc, and Ni(OH)2 (inset: enlargement of the pre-edge peaks of Ni-N-C and NiPc, where the colored areas represent peak intensity). d, Wavelet transforms of the k3-weighted Ni K-edge EXAFS spectra of Ni foil, Ni(OH)2, and Ni-N-C. e, Comparison between the K-edge XANES experimental spectrum of Ni-N-C and the theoretical spectrum of a disordered pyrrole-type Ni-N4O2 moiety (inset: schematic model of a disordered pyrrole-type Ni-N4 moiety; Ni (light blue), N (blue), O (red), and C (gray); D represents the distance from offset Ni atom to N4 plane).
Figure 3

CO2 electrochemical reduction performance. a, LSV curves of Ni-N-C and N-C in Ar- and CO2-saturated 0.5 M KHCO3. b, CO Faradaic efficiencies of Ni-N-C and N-C. c, Chronoamperometric current (black) and CO Faradaic efficiency (red) of Ni-N-C at −0.6 V (vs. RHE) in CO2-saturated 0.5 M KHCO3.

Figure 4

Operando XAFS characterization of Ni-N-C. a, Ni K-edge XANES spectra of Ni-N-C at various applied voltages vs. RHE in CO2-saturated 0.5 M KHCO3 at room temperature. b, Ni K-edge XANES difference
spectra (Δμ) of Ni-N-C at various voltages vs. RHE (obtained by subtracting the XANES spectrum at OCP from the XANES spectra at various potentials). c–e, Comparisons between the experimental Ni K-edge XANES spectra of Ni-N-C at −0.17 V (c), −0.77 V (d), −1.37 V (vs. RHE) (e) and the theoretical spectra for the corresponding moieties shown schematically in the insets (Ni (light blue), N (blue), O (red), and C (gray); D represents the distance from offset Ni atom to N4 plane).

**Figure 5**

DFT calculations. a, Reaction pathway of the ECO2RR on Ni-N-C (Ni (light blue), N (blue), O (red), and C (gray)). b, Calculated free energy diagram for Ni-N-C (the asterisk denotes the adsorption site). c–e, PDOS for Ni 3d, CO2 2p, and (C+2O) 2p in *COOH for Ni-N-C after the absorption of CO2 (top) and *COOH (bottom) at −0.17 V (vs. RHE) (c), −0.77 V (vs. RHE) (d), and −1.37 V (vs. RHE) (e).

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