

A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

Accepted Article

Title: Modulating the Leverage Relationship in Nitrogen Fixation Through Hydrogen-Bond-Regulated Proton Transfer

Authors: Shaoce Zhang, Hu Hong, Rong Zhang, Zhiquan Wei, Yiqiao Wang, Dong Chen, Chuan Li, Pei Li, Huilin Cui, Yue Hou, Shengnan Wang, Johnny C. Ho, Ying Guo, Zhaodong Huang, and Chunyi Zhi

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Angew. Chem. Int. Ed.* **2024**, e202412830

Link to VoR: <https://doi.org/10.1002/anie.202412830>

RESEARCH ARTICLE

Modulating the Leverage Relationship in Nitrogen Fixation Through Hydrogen-Bond-Regulated Proton Transfer

Shaoce Zhang,^{[a,b]†} Hu Hong,^{[a]†} Rong Zhang,^[a,b] Zhiqian Wei,^[a] Yiqiao Wang,^[a] Dong Chen,^[a] Chuan Li,^[a] Pei Li,^[a,b] Huilin Cui,^[a,b] Yue Hou,^[a,b] Shengnan Wang,^[a] Johnny C. Ho,^[a] Ying Guo,^{*[c]} Zhaodong Huang,^[a,b] and Chunyi Zhi^{*[a,b,d,e]}

[a] Shaoce Zhang, Hu Hong, Rong Zhang, Zhiqian Wei, Yiqiao Wang, Dong Chen, Chuan Li, Pei Li, Huilin Cui, Yue Hou, Dr. Shengnan Wang, Prof. Johnny C. Ho, Dr. Zhaodong Huang, Prof. Chunyi Zhi

Department of Materials Science and Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong 999077, China.

E-mail: cy.zhi@cityu.edu.hk

[b] Shaoce Zhang, Rong Zhang, Pei Li, Huilin Cui, Yue Hou, Dr. Zhaodong Huang, Prof. Chunyi Zhi

Hong Kong Center for Cerebro-Cardiovascular Health Engineering (COCHE), Shatin, NT, HKSAR, China.

[c] Dr. Ying Guo

College of Materials Science and Engineering, Shenzhen University, 518061, Shenzhen, China.

E-mail: yingguo@szu.edu.cn

[d] Prof. Chunyi Zhi

Centre for Functional Photonics, City University of Hong Kong, Kowloon, Hong Kong.

[e] Prof. Chunyi Zhi

Hong Kong Institute for Clean Energy, City University of Hong Kong, Kowloon 999077, Hong Kong.

[†] These authors contributed equally to this work.

Supporting information for this article is given via a link at the end of the document.

Abstract: In the electrochemical nitrogen reduction reaction (NRR), a leverage relationship exists between NH₃-producing activity and selectivity because of the competing hydrogen evolution reaction (HER), which means that high activity with strong protons adsorption causes low product selectivity. Herein, we design a novel metal-organic hydrogen bonding framework (MOHBF) material to modulate this leverage relationship by a hydrogen-bond-regulated proton transfer pathway. The MOHBF material was composited with reduced graphene oxide (rGO) to form a Ni-N₂O₂ molecular catalyst (Ni-N₂O₂/rGO). The unique structure of O atoms in Ni-O-C and N-O-H could form hydrogen bonds with H₂O molecules to interfere with protons being directly adsorbed onto Ni active sites, thus regulating the proton transfer mechanism and slowing the HER kinetics, thereby modulating the leverage relationship. Moreover, this catalyst has abundant Ni-single-atom sites enriched with Ni-N/O coordination, conducive to the adsorption and activation of N₂. The Ni-N₂O₂/rGO exhibits simultaneously enhanced activity and selectivity of NH₃ production with a maximum NH₃ yield rate of 209.7 μg h⁻¹ mg_{cat}⁻¹ and a Faradaic efficiency of 45.7%, outperforming other reported single-atom NRR catalysts.

Introduction

Ammonia (NH₃) is an essential feedstock in fertilizer and medicine production and a promising energy carrier because of its high hydrogen storage capacity.^[1] Industrial NH₃ synthesis is mainly conducted using the conventional energy-intensive Haber–Bosch approach, which requires high temperature and pressure owing

to the large dissociation energy of nitrogen (N₂), resulting in substantial consumption of fossil fuel and high greenhouse gas emissions.^[2] Next-generation technologies for synthesizing NH₃ must be developed to reduce the associated energy consumption and promote carbon neutrality.^[3] The electrochemical N₂ reduction reaction (NRR) conducted under ambient conditions using a clean proton source, namely H₂O, has become an attractive alternative for synthesizing NH₃.^[4] Unfortunately, the slow kinetics of the NRR and the competing hydrogen evolution reaction (HER) severely limit activity and selectivity during the NRR. This problem might be solved by using high-efficiency electrocatalysts.^[5]

In general, both activity and selectivity are crucial considerations when a state-of-the-art catalyst is designed for the NRR,^[6] however, a leverage relationship often exists between them.^[7] To ensure high NRR selectivity for a specific active site, the active site must be designed to have robust N₂ adsorption capability,^[8] and thus relatively weak proton adsorption. Such an active site hinders hydrogenation and leads to sluggish N₂-to-NH₃ conversion in the NRR, hence resulting in poor activity (Figure 1a). Conversely, if the local environment of the active site has sufficient protons for six proton-coupled electron transfer reactions to occur rapidly,^[9] the excessive proton accessibility contributes to a strongly competing HER.^[7, 10] This phenomenon causes high activity but low selectivity (Figure 1b). Such a leverage relationship poses a challenge to simultaneously improving selectivity and activity.

Exploring how the activity of the competing HER can be suppressed as much as possible while sufficient protons are

RESEARCH ARTICLE

supplied is critical. Because of their highly exposed active sites and unique quantum size effects, transition metal (TM) single-atom (SA) catalysts exhibit high potential for the NRR.^[11] These catalysts have both occupied and unoccupied d-orbitals; thus, they can donate electrons to the empty π^* orbital of N_2 and accept the lone-pair σ electrons of N_2 , thereby effectively activating N_2 molecules.^[12] However, the electrons in the d-orbitals of TM SA catalysts can also create strong metal–H bonds, which cause the competing HER to be more kinetically dominant than the NRR, leading to poor selectivity for NH_3 synthesis.^[7] A rational strategy for the design of TM SA catalysts is required to modulate the leverage relationship. A hydrogen bond between H_2O molecules is a typical dipole-dipole interaction.^[13] If such a bond can be incorporated into TM SA catalysts, the motion of H_2O molecules in aqueous solutions may be effectively inhibited, thereby modulating the leverage relationship and enhancing the performance of the NRR (Figure 1c); a suitable approach for this purpose has not yet been reported.

In this study, we designed a novel Ni SA molecular catalyst with a metal-organic hydrogen bonding framework (MOHBF), and based on this framework, we fabricated a reduced graphene oxide (rGO)-supported Ni- N_2O_2 molecular catalyst (Ni- N_2O_2 /rGO). Ni with a unique nearly full d orbital makes it promising in NRR. The Ni SA centers in Ni- N_2O_2 /rGO, which have asymmetric O/N coordination, exhibit robust ability in polarizing and activating N_2 molecules. More importantly, the unique structure of O atoms in Ni-O-C and N-O-H can form hydrogen bonds with H_2O molecules and thus weaken the activity of these H_2O molecules, thereby effectively regulating the migration of protons and suppressing the parasitic HER. Consequently, the proposed molecular catalyst enhance both activity and selectivity, with its NH_3 yield rate being $209.7 \mu g h^{-1} mg_{cat}^{-1}$ and Faradaic efficiency (FE) being 45.7% at $-0.30 V$ vs. reversible hydrogen electrode (RHE), which outperforms other reported SA NRR catalysts.

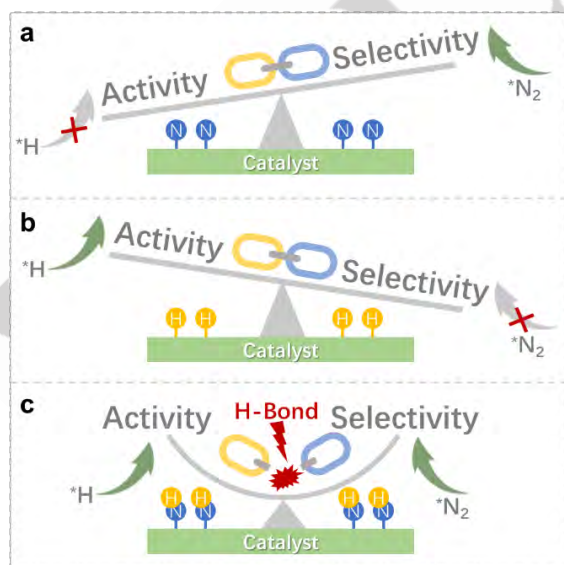


Figure 1. Schematic diagram of the leverage relationship. a,b) Leverage relationship of catalysts with a) low activity and high selectivity and b) high activity and low selectivity. c) The modulated leverage relationship between activity and selectivity in the NRR.

Results and Discussion

We first used $Ni(NO_3)_2 \cdot 6H_2O$ and salicylhydroxamic acid as raw materials to prepare MOHBF (Figure S1). The scanning electron microscopy (SEM) image indicated that the framework comprised nanorods with a smooth surface and uniform size (Figure S2). The Rietveld refinement of X-ray diffraction (XRD) pattern (Figure S3) revealed that the material was monoclinic with the $P2_1/c$ space group (Table S1). The X-ray photoelectron spectroscopy (XPS) results suggested the coexistence of Ni–O (peak at 532.6 eV in the high-resolution O 1s spectra) and Ni–N (peak at 399.0 eV in the high-resolution N 1s spectra) bonds (Figure S4).^[14] The Fourier transform infrared spectroscopy (FTIR) pattern (Figure S5) contained the characteristic peaks of the C=N (1625 cm^{-1}), C=C (1583 and 1539 cm^{-1}), O–H (1413 cm^{-1}), C–O (1306 cm^{-1}), and C–H (1286 and 1147 cm^{-1}) bonds.^[15] The aforementioned results indicated the successful synthesis of the MOHBF. We calculated the electrostatic potential (ESP) of the MOHBF to study its charge distribution. As shown in Figure 2a, the O sites in Ni–O–C and N–O–H in the molecular monomers of the MOHBF had a more negative ESP than the sites of other elements, which favored the formation of hydrogen bonds with H_2O molecules near the Ni active sites. This finding was verified by the reduced density gradient (RDG) isosurface map (Figure S6) and corresponding scatter diagram (Figure 2b), in which the blue peaks located between -0.03 and -0.04 a.u. , demonstrating the ability of intramolecular O sites to form hydrogen bonds.

Subsequently, Ni K-edge X-ray absorption fine structure (XAFS) spectroscopy was performed to gain a deeper understanding of the chemical state and local coordination environment of Ni sites within the MOHBF catalyst. The X-ray absorption near-edge structure (XANES) spectra in Figure 2c indicated that the valence state of Ni fell between 0 for Ni foil and +2 for NiO and more closely to a +2 oxidation state. The Fourier-transformed extended XAFS (FT-EXAFS) curve of the MOHBF (Figure 2d) contained a prominent signal centered at 1.58 \AA , between the peaks corresponding to Ni–N (1.49 \AA) and Ni–O (1.70 \AA) bonds, which suggested that the existence of Ni–N or Ni–O bonds, while no scattering peaks corresponded to the Ni–Ni coordination. This confirmed that Ni was atomically dispersed in the MOHBF. The extended XAFS (EXAFS) spectra fitting was performed in R and k spaces to investigate the coordination configuration of Ni atoms (Figure S7). The fitting results revealed that all fitted curves were consistent with the experimental results and that the Ni sites in the MOHBF were coordinated with N and O atoms (Table S2), which had average bonds of 1.99 \AA for Ni–N and 2.08 \AA for Ni–O. In contrast to the wavelet-transform EXAFS (WT-EXAFS) patterns of Ni foil, NiO, and Ni_2O_3 , that of the MOHBF (Figure 2e) did not contain a WT signal for Ni–Ni bonds, which suggested the atomic dispersion of Ni sites in the MOHBF.

The NRR performance of the MOHBF was evaluated in 0.1 M phosphate buffer solution (PBS) by using an H-type electrolytic cell, and the measured potential was calibrated using an RHE. The linear sweep voltammetry (LSV) curves of the MOHBF (Figure S8) were obtained in N_2 - or Ar-saturated 0.1 M PBS. The current density under N_2 conditions was higher than that under Ar conditions within the potential range, which revealed that the

RESEARCH ARTICLE

MOHBF was active in the NRR. The indophenol blue method (Figure S9) and Watt–Chrisp method (Figure S10) were used to conduct quantitative detection for the electrolysis product NH_3 and the possible by-product N_2H_4 in the electrolyte after a chronoamperometry test (Figure S11). Negligible quantities of N_2H_4 were collected at all potentials (Figure S12). As shown in Figure S13, the NH_3 yield rate and FE increased with negatively

shifted potential, reaching $32.0 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ and 10.5% at -0.3 V vs. RHE, respectively. Nevertheless, the electrocatalytic NRR performance of the MOHBF was unsatisfactory because of the framework's one-dimensional nanorod structure (Figure S2), which may hamper the exposure of O sites, thus cannot form hydrogen bonds to modulate the leverage relationship during the NRR.

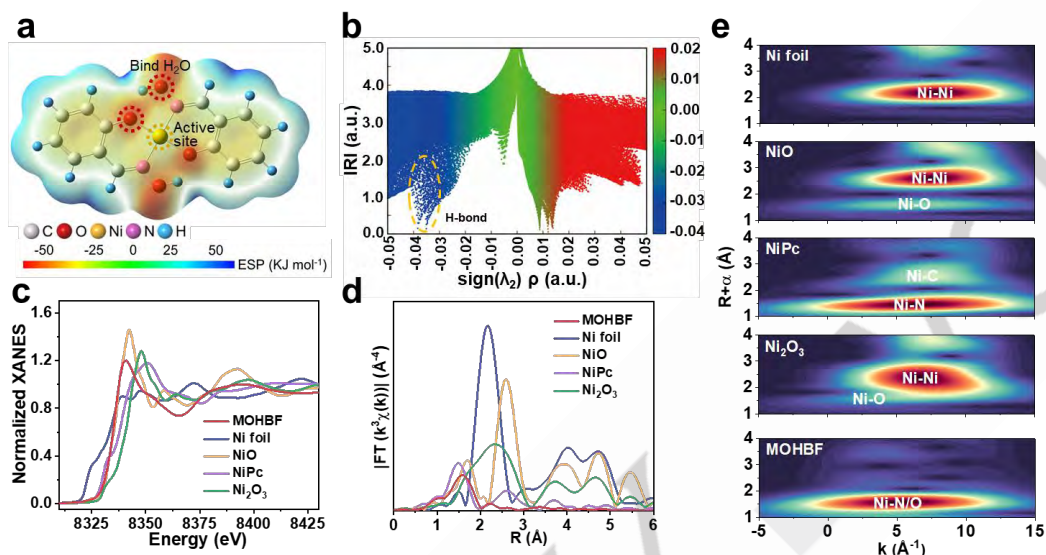


Figure 2. Structural characterization and performance evaluation of the designed MOHBF. a) The ESP diagram and b) RDG scatter diagram for $\text{Ni-N}_2\text{O}_2$ in the MOHBF. c) Ni K-edge XANES, d) FT-EXAFS, and e) WT-EXAFS spectra of MOHBF, Ni foil, NiO, NiPc, and Ni_2O_3 .

To fully utilize the potential of hydrogen bonds for modulating the leverage relationship and enhancing the NRR performance, the created MOHBF was optimized through a melting process, as illustrated in Figure 3a. Specifically, MOHBF nanorods were melted into $\text{Ni-N}_2\text{O}_2$ molecules anchored on an NRR-inert rGO (Figure S14) substrate ($\text{Ni-N}_2\text{O}_2/\text{rGO}$) on the basis of thermogravimetry–differential scanning calorimetry (TG–DSC) curves (Figure S15). This process yielded a sheet-like composite structure (Figure S16). The energy-dispersive X-ray spectroscopy (EDS) mapping presented in Figure S17 revealed that $\text{Ni-N}_2\text{O}_2$ was uniformly distributed across the rGO substrate. The XAFS spectroscopy results for $\text{Ni-N}_2\text{O}_2/\text{rGO}$ (Figure S18 and Table S2) confirmed that the coordination structure of Ni sites was unaffected by the melting process. Furthermore, $\text{Ni-N}_2\text{O}_2$ had a carbon ring that exhibited a high degree of conjugation with the rGO substrate, which was demonstrated by a comparative analysis of the surface potential through Kelvin probe force microscopy (KPFM) measurement performed before and after $\text{Ni-N}_2\text{O}_2$ loading (Figures 3b and S19). Density functional theory (DFT) calculations provided additional confirmation of π – π interactions in the $\text{Ni-N}_2\text{O}_2/\text{rGO}$ composite (spikes between -0.01 and 0.00 a.u., Figure S20). Interactions in the out-of-plane direction promoted interfacial charge transfer, which considerably enhanced the conductivity of the catalyst.^[16]

The catalysts with various $\text{Ni-N}_2\text{O}_2$ contents on the rGO substrate were fabricated to regulate the catalyst performance

and investigate the mechanism of $\text{Ni-N}_2\text{O}_2/\text{rGO}$ in the NRR. As illustrated in Figure S21, when N_2 was employed as the feed gas, the current density was positively correlated with $\text{Ni-N}_2\text{O}_2$ content. The heatmaps displayed in Figure 3c,d revealed that the FE and NH_3 yield rates of the catalysts with different $\text{Ni-N}_2\text{O}_2$ contents increased as the potential was negatively shifted and were highest at -0.3 V vs. RHE. Interestingly, as the $\text{Ni-N}_2\text{O}_2$ content was increased at each potential, the NH_3 yield rate showed an upward trend because of the more active sites, while the FE of NH_3 changed negligibly; however, both the FE and yield rate dropped sharply when the loading reached 80 wt.% (Figure S22a,b). This trend was attributable to excessive $\text{Ni-N}_2\text{O}_2$ loading, causing the stacking of molecules and the interlinkage of intermolecular by hydrogen bonds, thus weakening the regulation of proton transfer. Then, the attenuated total reflection (ATR)-FTIR spectroscopy results of the catalysts with different $\text{Ni-N}_2\text{O}_2$ contents confirmed this finding. As shown in Figures 3e and S23, the O–H bending and stretching peaks shifted to higher wavenumbers when the $\text{Ni-N}_2\text{O}_2$ content increased, indicating that the activity of H_2O molecules was inhibited.^[17] However, this inhibitory effect weakened as the $\text{Ni-N}_2\text{O}_2$ content increased beyond 80 wt.%. Two characteristic signals were observed at 2071 and 1979 cm^{-1} in the ATR-FTIR spectroscopy results (Figure 3f); these signals corresponded to N=N stretching and *H adsorption at Ni sites, respectively. Gaussian fitting was conducted to calculate the $S_{\text{N=N}}/S_{\text{*H}}$ content ratio (Figure S24),

RESEARCH ARTICLE

and the curve of this ratio declined suddenly as the loading of Ni-N₂O₂ was increased beyond 80 wt.%. These results are highly consistent with the trend obtained for the FE of NH₃ (Figure 3g). In the NRR, H₂O and N₂ compete for adsorption on Ni sites. O atoms in Ni-N₂O₂ can hydrogen-bind H₂O near a Ni site, thus hindering the direct adsorption of H₂O at the site and facilitating the adsorption of N₂ on the Ni site. Excessive Ni-N₂O₂ loading causes molecules to connect through hydrogen bonds, weakening the control of H₂O molecules by hydrogen bonds near Ni sites and thereby enabling H₂O to adsorb on Ni sites quickly, which inhibits N₂ adsorption.

The aforementioned mechanism was confirmed through electron paramagnetic resonance (EPR) analysis in which 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was used as a trapping reagent. A chronoamperometry test for 10 minutes was conducted to achieve a dynamic balance between the production and consumption of active hydrogen. To eliminate the interference of rGO during the test, EPR was first performed using rGO as the working electrode in the chronoamperometry test; the resultant spectra contained no peaks (Figure S25). In the spectra obtained when Ni-N₂O₂/rGO was employed as the working electrode (Figure 3h), nine peaks with a 1:2 intensity ratio were obtained, which confirmed the presence of DMPO-H.^[18] When the loading of Ni-N₂O₂ was not excessive, lower EPR signal intensity demonstrated greater consumption of active hydrogen in the NRR.

When the loading of Ni-N₂O₂ exceeded 80 wt.%, a large quantity of active hydrogen was competitively adsorbed at Ni sites because of the weakened regulation of hydrogen bonds; thus, the NRR was inhibited. Lower consumption of active hydrogen led to considerably stronger EPR signals corresponding to DMPO-H. LSV tests involving various Ni-N₂O₂ contents were conducted in the Ar atmosphere (Figure S26). Electrochemical active surface area (ECSA) confirmed the more active sites with the increased Ni-N₂O₂ loading (Figures S27 and S28a),^[19] which led to enhanced current density. The ECSA-normalized current densities (Figure S28b) remained stable as the Ni-N₂O₂ loading increased, indicating the catalytic activity for the HER was maintained. However, when the loading reached 80 wt.%, the current densities exhibited an obvious increase, suggesting an enhancement in the HER activity. The Tafel plots (Figure 3i) also indicated that the hydrogen production barrier was negligibly affected by the Ni-N₂O₂ loading until it was increased beyond 80 wt.%. The decreased Tafel slope (inset in Figure 3i) revealed the weakened hydrogen production barrier.^[20] These phenomena were caused by the weakened ability of hydrogen bonds on the catalyst surface to control H₂O molecules near Ni sites. The aforementioned results indicate that hydrogen bonds interfered with the direct adsorption of protons on Ni sites, thus strengthening the barrier to the HER, thereby increasing selectivity for NH₃ generation.

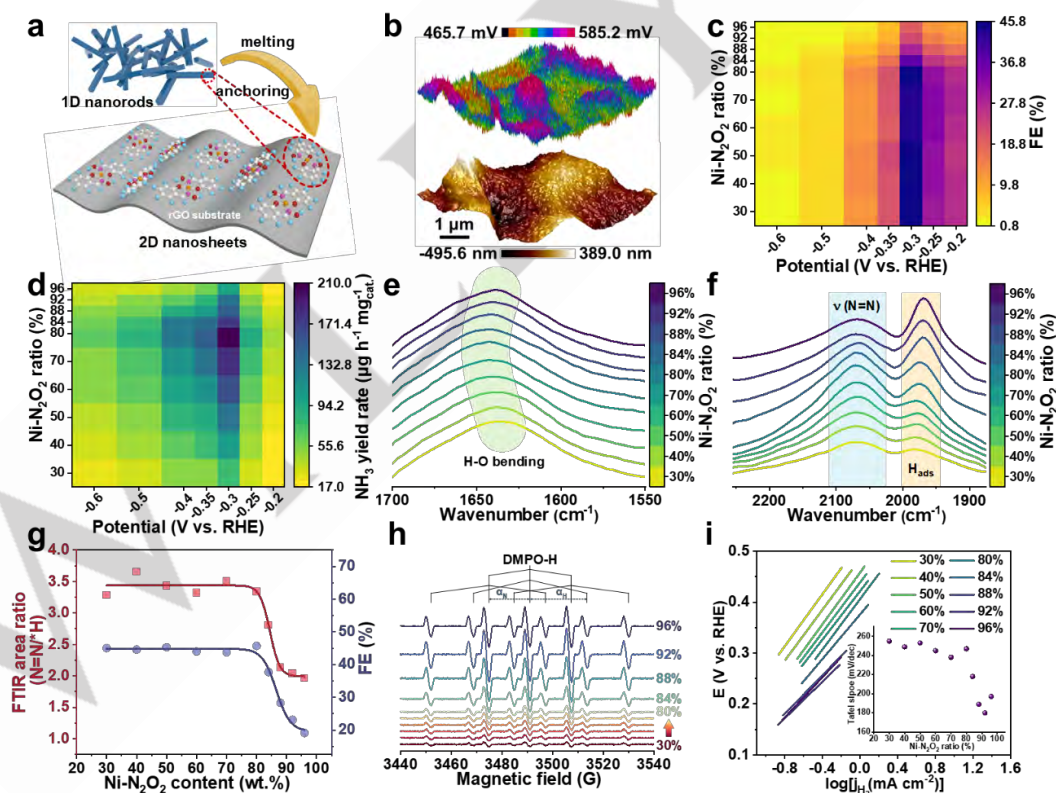


Figure 3. Performance of Ni-N₂O₂/rGO with various Ni-N₂O₂ contents in the NRR. a) Schematic diagram of Ni-N₂O₂/rGO preparation. b) AFM topography and KPFM image of Ni-N₂O₂/rGO. c) FE and d) NH₃ yield rate of Ni-N₂O₂/rGO with various Ni-N₂O₂ contents at each examined potential. ATR-FTIR spectroscopy results of the e) O-H bending mode and f) N=N stretching mode as well as adsorbed *H at -0.3 V vs. RHE for Ni-N₂O₂/rGO with differing Ni-N₂O₂ contents. g) S_{N=N}/S_H ratio based on f) and FE of NH₃ for various Ni-N₂O₂ contents. h) EPR results of DMPO-H at various Ni-N₂O₂ contents under hyperfine coupling constants of a_N = 16.3 G and a_H = 22.5 G. i) Tafel plots obtained in Ar atmosphere. Inset: Tafel slope values of catalysts with various Ni-N₂O₂ contents. In a), the yellow, red, blue, pink, and white spheres represent Ni, O, H, N, and C, respectively.

RESEARCH ARTICLE

Ni-N₂O₂/rGO with a Ni-N₂O₂ loading of 80 wt.% (referred to as 80-Ni-N₂O₂/rGO) was selected for further investigation of the performance in the NRR. The LSV curves displayed in Figure S29 for 80-Ni-N₂O₂/rGO were obtained in N₂- or Ar-saturated 0.1 M PBS. Within the investigated potential range, the current density achieved with N₂-saturated PBS was higher than that obtained with Ar-saturated PBS, which highlighted the considerable activity of 80-Ni-N₂O₂/rGO in the NRR. The quantities of NH₃ product and potential N₂H₄ by-product were determined (Figure S30) after a chronoamperometry test (Figure S31). Notably, a negligible quantity of N₂H₄ was detected at all potentials (Figure S30b), which indicated the excellent NH₃ selectivity of 80-Ni-N₂O₂/rGO in the NRR. Figure 4a shows that the NH₃ yield rate and FE reached 209.7 μg h⁻¹ mg_{cat.}⁻¹ and 45.7% at -0.3 V vs. RHE. At potentials higher than -0.3 V, the NH₃ yield rate and FE decreased because of the strong competition of protons adsorbed on the active sites.^[21] We also obtained LSV curves under different scan rates (Figure S32), which confirmed the presence of a diffusion-limitation feature. The magnetic stirring employed in the electrochemical measurements could effectively mitigate this influence. Figure 4b reveals that the performance of 80-Ni-N₂O₂/rGO was considerably superior to that of catalysts with other Ni-N₂O₂ loading ratios. The NH₃ yield rate and FE of 80-Ni-N₂O₂/rGO were 6.5 and 4.3 times higher than those of the MOHBF, respectively, which indicated the excellent activity and selectivity of 80-Ni-N₂O₂/rGO. In 80-Ni-N₂O₂/rGO, Ni-N₂O₂ molecules dispersed on the rGO substrate could fully utilize hydrogen bonds to bind H₂O molecules near Ni active sites to regulate proton behavior, thereby improving NRR selectivity. The remarkable NRR activity of Ni-N₂O₂ was also elucidated through DFT calculations. Nickel phthalocyanine (NiPc), a commonly used catalyst with a Ni-N₄ coordination structure, was employed as a control sample. The lengths of the bonds in N₂ molecules adsorbed on Ni sites in Ni-N₂O₂ and NiPc were found to be 1.141 Å and 1.130 Å, respectively, longer than that in free N₂ (1.120 Å), demonstrating the activated N₂ molecules (Figure S33).^[6b, 8] Moreover, Bader charge analysis (Figure S34) revealed that the number of electrons acquired by *N₂ was higher in Ni-N₂O₂ (0.31 e) than in NiPc (0.17 e) because of the unique local coordination structure of Ni-N₂O₂. After N₂ adsorption, the projected density of states (PDOS) for Ni sites contained an obvious energy-level overlap between the N orbital and the Ni orbital (Figure S35), which manifested a robust interaction between *N₂ and Ni sites within Ni-N₂O₂. As displayed in Figure S35c, the electrons of *N₂ entered the empty d orbital of Ni. Moreover, the 2π* orbital of *N₂ exhibited a notable shift to lower energy relative to the energy level for free N₂; this shift was due to the transfer of electrons from the Ni d orbital to the unoccupied 2π* orbital of N₂. This "accept-donate" mechanism strengthened the Ni-N bond while weakening the N≡N bond.^[22]

Various controlled experiments were conducted to identify the source of N in the NH₃ produced through the NRR. A chronoamperometry test was conducted at the open-circuit potential with N₂ as the feed gas or at various potentials with Ar as the feed gas (Figure S36). No NH₃ was present in these post-electrolytes, which eliminated environmental interference. The ¹H nuclear magnetic resonance (NMR) spectra obtained after a

chronoamperometry test in which ¹⁴N₂ or ¹⁵N₂ was employed as the feed gas revealed the characteristic peaks of triplet coupling for ¹⁴NH₄⁺ (with a spacing of 52 Hz) and doublet coupling for ¹⁵NH₄⁺ (with a spacing of 72 Hz), which corresponded well to the characteristic signals of standard samples (Figure S37a); thus, N₂ feed gas was the only source of N in the NRR for NH₃ generation.^[23] In addition, quantitative NMR was performed using maleic acid as the internal standard (Figure S37). As shown in Figures 4c and S37d, there were negligible differences in the yield rate and FE for NH₃ generation obtained from the quantitative NMR and ultraviolet-visible (UV-Vis) spectroscopy methods; thus, the NH₃ generated in the NRR was confirmed to originate from N₂ feed gas. The electrocatalytic stability of 80-Ni-N₂O₂/rGO for the NRR was investigated by performing a chronoamperometry test at -0.3 V vs. RHE; the electrolyte was replaced every 2 h. As illustrated in Figure 4d, the NH₃ yield rate and FE did not change considerably during 10 consecutive cycles. Only a slight decrease in the current density was discovered in a 40-h chronoamperometry measurement (Figure S38), after which the 80-Ni-N₂O₂/rGO catalyst exhibited an essentially stable NH₃ yield rate and FE (Figure S39), and negligible differences in the FTIR results (Figure S40), which indicated its excellent stability.

In addition, we summarized and compared the NRR performance of recently reported SA catalysts (Figure 4e, Table S3), which could be classified into three types that show: i) both low yield rate and FE (green zone); ii) high yield rate and low FE (red zone); iii) low yield rate and high FE (purple zone). This result suggested the leverage relationship between activity and selectivity in the NRR. Benefiting from the introduction of hydrogen bonds, 80-Ni-N₂O₂/rGO in our work modulated this relationship, thus achieving simultaneously enhanced activity and selectivity of NH₃ production.

Based on the aforementioned analyses, we propose a hydrogen-bond-regulated proton transfer process in the NRR. As illustrated in Figure 4f, this process involves three steps. Step I: hydrogen bonds modulate the adsorption priority between proton and N₂. The O atoms in Ni-O-C and N-O-H form hydrogen bonds with H₂O molecules at the solid-liquid interface, thus regulating the proton transfer process in the NRR. The unique bonding structure of Ni atoms creates a suitable electronic environment for adsorption, and the activity of H₂O molecules is inhibited by the hydrogen bonds. Overall, these features result in a lower barrier for N₂ molecule adsorption on Ni active sites and a simultaneous decrease in proton accessibility. The step is conducive to the designed catalyst's excellent activity and selectivity. Step II: hydrogenation reaction and hydrogen bond breaking. Subsequently, the remote hydrogen of the bound H₂O molecule participates in the hydrogenation of the NRR intermediate, and electrostatic interaction causes OH⁻ to be released; the released OH⁻ enters the PBS electrolyte and is then neutralized. This phenomenon was proven using different electrolytes. When 0.1 M PBS was used, the pH changed negligibly, whereas when 0.1 M K₂SO₄ was employed, the pH clearly increased over 3600 s (Figure S41). The hydrogen bond breaking noted in the DFT calculation also indicated OH⁻ release (Figure S42). Step III: NH₃ generation. Finally, after the continual repetition of steps I and II, the conversion from N₂ to NH₃ is complete.

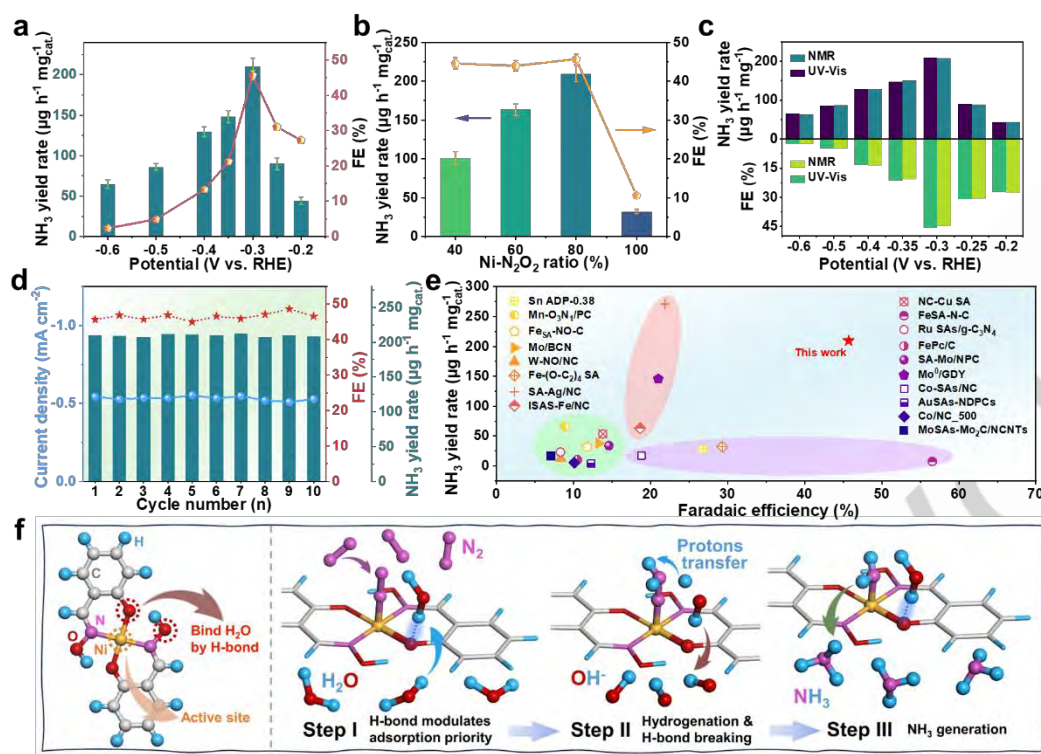


Figure 4. Performance of 80-Ni-N₂O₂/rGO. a) NH₃ yield rate and FE at each potential. b) NH₃ yield rate and FE of Ni-N₂O₂/rGO with various Ni-N₂O₂ contents at -0.3 V vs. RHE. c) Comparison of the NH₃ yield rate and FE by using UV-Vis and NMR methods over 80-Ni-N₂O₂/rGO. d) Stability of 80-Ni-N₂O₂/rGO at -0.3 V vs. RHE during a recycling test involving 10 cycles (2 h per cycle). e) NRR performance of 80-Ni-N₂O₂/rGO and other SA catalysts. Green zone: catalysts with both low yield rate and FE; Red zone: catalysts with high yield rate and low FE; Purple zone: catalysts with low yield rate and high FE. f) Proposed reaction mechanism of hydrogen-bond-regulated proton transfer during the NRR. The yellow, red, blue, pink, and white spheres represent Ni, O, H, N, and C, respectively. The abbreviations in e) are defined as follows: ADP, atomically dispersed protuberance; PC, porous carbon; NC, N-doped carbon; ISAS, isolated single atomic site; NPC and NDPCs, N-doped porous carbon; GDY, graphdiyne; and NCNTs, N-doped carbon nanotubes.

In-situ ATR-FTIR spectroscopy was adopted to explore possible intermediates in the NRR. As shown in Figures 5a–d, within the test potential range, distinct signals corresponding to O–H stretching and bending were obtained at 3450 and 1643 cm⁻¹, respectively. In addition, characteristic peaks of N=N stretching and N–H bending were found at 2071 and 1460 cm⁻¹, respectively. Notably, the intensity of these bands achieved the highest intensity at -0.3 V vs. RHE; this result agreed favorably with the NH₃ yield rate results for 80-Ni-N₂O₂/rGO. Moreover, the Ni–H peak located at 1986 cm⁻¹ exhibited an increase in intensity and a negative shift with decreasing potential, which agrees with previous studies.^[24] In the ATR-FTIR test in which Ar was used as the feed gas, no characteristic peaks corresponding to N=N stretching or N–H bending were obtained. In Ar- and N₂-saturated electrolytes, hydrogen bonds interfered with the direct adsorption of hydrogen on Ni. However, the intensity of the Ni–H signal under the N₂ condition was considerably lower than that under the Ar condition, and a N=N peak was discernible, indicating the excellent NRR activity of 80-Ni-N₂O₂/rGO. More importantly, hydrogen bonds could modulate site adsorption priority by binding H₂O molecules around Ni sites to improve selectivity. Online differential electrochemical mass spectrometry (DEMS) was

employed to study the electrochemical NRR and investigate its intermediates and products.^[25] Figure S43 shows the DEMS results obtained for 80-Ni-N₂O₂/rGO at -0.3 V vs. RHE in N₂-saturated electrolyte. No signal was obtained at mass-to-charge ratios (*m/z*) of 27, 30, 31, or 33 in comparison with the standard mass spectra depicted in Figure S44; thus, no fragments of N₂H₄ were obtained, as confirmed using the Watt–Chrisp method (Figure S30). Consequently, the distinctive signal at *m/z* = 15 proved the generation of NH₃. Furthermore, Figure S45a suggests that the ion current of NH₃ at *m/z* = 17 increased with a decrease in the potential and peaked at a potential of -0.3 V vs. RHE, which is in accordance with the NH₃ yield rate results shown in Figure 4a. Finally, Figure S45b indicates that the ion current was stable during the NRR. No signal was obtained when a potential was not applied, which reconfirmed that N₂ feed gas was the source of the NH₃ generated in the NRR.

DFT calculations were used to investigate the reaction pathway. The differential charge density distributions (Figure S46) revealed a notable interaction between the distal N of the N₂ molecule adsorbed on the Ni site and the hydrogen atom within the H₂O molecule. We constructed a free energy diagram to delve deeper into the NRR. The two primary pathways were studied,

RESEARCH ARTICLE

namely associative distal and associative alternating routes (Figures S47 and S48). Figure 5e indicates that the rate-determining step (RDS) in both routes is $*\text{NN} \rightarrow *\text{NNH}$ (0.78 eV). In the processes involved in the transformations from $*\text{NNH}$ to $*\text{NHNH}$ and from $*\text{NHNH}_2$ to $*\text{NH}_2\text{NH}_2$, the associative alternating pathway demands more energy than the associative distal pathway does. Based on these results, we concluded that the NRR predominantly follows the associative distal pathway.

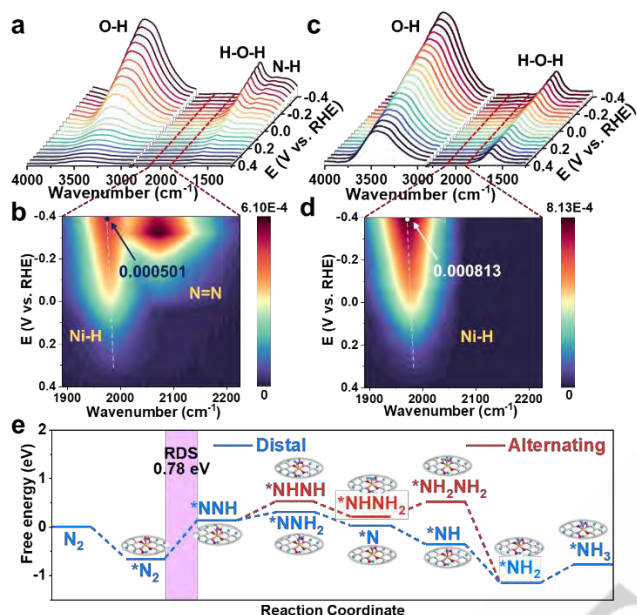


Figure 5. In-situ ATR-FTIR spectroscopy and DFT calculations. a–d) In-situ ATR-FTIR spectroscopy results of 80-Ni-N₂O₂/rGO in a) N₂-saturated and c) Ar-saturated electrolyte, and b,d) corresponding contour maps of the selected part in a,c). e) Free energy diagram in the NRR process and the corresponding adsorption configurations in associative distal and associative alternating pathways. The yellow, red, blue, pink, and white spheres represent Ni, O, H, N, and C, respectively.

Conclusion

In summary, to modulate the leverage relationship between activity and selectivity in the NRR, we designed a novel molecular catalyst based on the MOHBF, namely Ni-N₂O₂/rGO. This catalyst can bind H₂O molecules through hydrogen bonds, thus reducing the activity of H₂O molecules and modulating the priority of adsorption for N₂ molecules versus protons. Ni SA sites coordinated by N/O atoms with a suitable surrounding electron environment ensure high activity. Therefore, Ni-N₂O₂/rGO can simultaneously achieve high selectivity and activity, modulating the leverage relationship. The NRR was found to occur through the following steps in sequence: N₂ molecules were adsorbed and activated on highly active Ni sites, while H₂O molecules were adsorbed through hydrogen bonds, followed by the participation of distal protons in bound H₂O molecules in the hydrogenation reaction, and eventually, NH₃ was generated. The as-prepared Ni-N₂O₂/rGO achieved a favorable NH₃ yield rate of 209.7 μg h⁻¹ mg_{cat.}⁻¹ and an FE of 45.7%, outperforming previously reported

SA NRR catalysts. This novel catalyst design strategy is a promising approach for simultaneously improving the yield and FE of catalytic reactions involving the hydrogenation process.

Acknowledgements

This work is supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China [Project No. T23-713/22-R] and InnoHK Project on [Project 1.3-Flexible and Stretchable Technologies (FAST) for monitoring of CVD risk factors: Sensing and Applications] at Hong Kong Centre for Cerebro-cardiovascular Health Engineering (COCHE). BL11B is acknowledged for its support in measurements and data analyses.

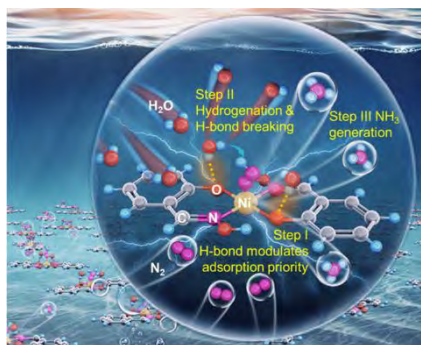
Keywords: electrochemical nitrogen reduction reaction • leverage relationship • hydrogen bond • proton transfer • molecular catalyst

- [1] a) P. Li, R. Li, Y. Liu, M. Xie, Z. Jin, G. Yu, *J. Am. Chem. Soc.* **2023**, *145*, 6471–6479; b) X. Zhang, Y. Lyu, H. Zhou, J. Zheng, A. Huang, J. Ding, C. Xie, R. De Marco, N. Tsud, V. Kalinovich, S. P. Jiang, L. Dai, S. Wang, *Adv. Mater.* **2023**, *35*, 2211894; c) R. Zhang, C. Li, H. Cui, Y. Wang, S. Zhang, P. Li, Y. Hou, Y. Guo, G. Liang, Z. Huang, C. Peng, C. Zhi, *Nat. Commun.* **2023**, *14*, 8036.
- [2] a) S. Liu, T. Qian, M. Wang, H. Ji, X. Shen, C. Wang, C. Yan, *Nat. Catal.* **2021**, *4*, 322–331; b) L. Li, C. Tang, X. Cui, Y. Zheng, X. Wang, H. Xu, S. Zhang, T. Shao, K. Davey, S. Z. Qiao, *Angew. Chem.* **2021**, *133*, 14250–14256.
- [3] a) H. Zhong, M. Wang, M. Ghorbani-Asl, J. Zhang, K. H. Ly, Z. Liao, G. Chen, Y. Wei, B. P. Biswal, E. Zschech, I. M. Weidinger, A. V. Krashennnikov, R. Dong, X. Feng, *J. Am. Chem. Soc.* **2021**, *143*, 19992–20000; b) S. Liu, M. Wang, Y. He, Q. Cheng, H. Ji, Y. Huan, X. Shen, X. Zhou, T. Qian, C. Yan, *Adv. Mater.* **2023**, *35*, 2303703; c) D. Chen, S. Zhang, D. Yin, W. Li, X. Bu, Q. Quan, Z. Lai, W. Wang, Y. Meng, C. Liu, S. Yip, F.-R. Chen, C. Zhi, J. C. Ho, *Adv. Energy Mater.* **2023**, *13*, 2203201.
- [4] a) C. Chen, H. Jin, P. Wang, X. Sun, M. Jaroniec, Y. Zheng, S.-Z. Qiao, *Chem. Soc. Rev.* **2024**, *53*, 2022–2055; b) H.-L. Du, M. Chatti, R. Y. Hodgetts, P. V. Cherepanov, C. K. Nguyen, K. Matuszek, D. R. MacFarlane, A. N. Simonov, *Nature* **2022**, *609*, 722–727.
- [5] a) Z. Fang, P. Wu, Y. Qian, G. Yu, *Angew. Chem.* **2021**, *133*, 4321–4327; b) Y. Li, Y. Ji, Y. Zhao, J. Chen, S. Zheng, X. Sang, B. Yang, Z. Li, L. Lei, Z. Wen, X. Feng, Y. Hou, *Adv. Mater.* **2022**, *34*, 2202240.
- [6] a) L. Zhang, H. Zhou, X. Yang, S. Zhang, H. Zhang, X. Yang, X. Su, J. Zhang, Z. Lin, *Angew. Chem. Int. Ed.* **2023**, *62*, e202217473; b) Y. Kong, Y. Li, X. Sang, B. Yang, Z. Li, S. Zheng, Q. Zhang, S. Yao, X. Yang, L. Lei, S. Zhou, G. Wu, Y. Hou, *Adv. Mater.* **2022**, *34*, 2103548; c) L. Wen, K. Sun, X. Liu, W. Yang, L. Li, H. L. Jiang, *Adv. Mater.* **2023**, *35*, 2210669.
- [7] S. Qiang, F. Wu, J. Yu, Y. T. Liu, B. Ding, *Angew. Chem. Int. Ed.* **2023**, *62*, e202217265.
- [8] Y. Gu, B. Xi, W. Tian, H. Zhang, Q. Fu, S. Xiong, *Adv. Mater.* **2021**, *33*, 2100429.
- [9] a) B. H. Suryanto, K. Matuszek, J. Choi, R. Y. Hodgetts, H.-L. Du, J. M. Bakker, C. S. Kang, P. V. Cherepanov, A. N. Simonov, D. R. MacFarlane, *Science* **2021**, *372*, 1187–1191; b) S. Zhang, D. Chen, Y. Guo, R. Zhang,

RESEARCH ARTICLE

- Y. Zhao, Z. Huang, J. Fan, J. C. Ho, C. Zhi, *Mater. Today* **2023**, *66*, 17–25.
- [10] Y.-C. Hao, Y. Guo, L.-W. Chen, M. Shu, X.-Y. Wang, T.-A. Bu, W.-Y. Gao, N. Zhang, X. Su, X. Feng, J.-W. Zhou, B. Wang, C.-W. Hu, A.-X. Yin, R. Si, Y.-W. Zhang, C.-H. Yan, *Nat. Catal.* **2019**, *2*, 448–456.
- [11] a) L. Shi, S. Bi, Y. Qi, R. He, K. Ren, L. Zheng, J. Wang, G. Ning, J. Ye, *ACS Catal.* **2022**, *12*, 7655–7663; b) Z. Qi, Y. Zhou, R. Guan, Y. Fu, J. B. Baek, *Adv. Mater.* **2023**, *35*, 2210575; c) X. Li, W. Xu, L. Q. Le, S. Chen, L. Song, T. S. Choksi, X. Wang, *Chem Catal.* **2023**, *3*, 100724.
- [12] a) X. Lin, Y. Wang, X. Chang, S. Zhen, Z. J. Zhao, J. Gong, *Angew. Chem.* **2023**, *135*, e202300122; b) Y. Ni, L. Lin, Y. Shang, L. Luo, L. Wang, Y. Lu, Y. Li, Z. Yan, K. Zhang, F. Cheng, J. Chen, *Angew. Chem. Int. Ed.* **2021**, *60*, 16937–16941.
- [13] a) Y. Fang, Y. Fan, K. Xie, W. Ge, Y. Zhu, Z. Qi, Z. Song, H. Jiang, C. Li, *Angew. Chem. Int. Ed.* **2023**, *62*, e202304413; b) T. Wang, Z. Tian, Z. You, Z. Li, H. Cheng, W. Li, Y. Yang, Y. Zhou, Q. Zhong, Y. Lai, *Energy Storage Mater.* **2022**, *45*, 24–32.
- [14] a) C. Xiao, L. Cheng, Y. Zhu, G. Wang, L. Chen, Y. Wang, R. Chen, Y. Li, C. Li, *Angew. Chem. Int. Ed.* **2022**, *61*, e202206544; b) Y. Zhang, L. Jiao, W. Yang, C. Xie, H. L. Jiang, *Angew. Chem. Int. Ed.* **2021**, *60*, 7607–7611.
- [15] a) K. Fan, J. Li, Y. Xu, C. Fu, Y. Chen, C. Zhang, G. Zhang, J. Ma, T. Zhai, C. Wang, *J. Am. Chem. Soc.* **2023**, *145*, 12682–12690; b) Q. Q. Sun, T. Sun, J. Y. Du, K. Li, H. M. Xie, G. Huang, X. B. Zhang, *Adv. Mater.* **2023**, *35*, 2301088; c) Y. Chen, M. Tang, Y. Wu, X. Su, X. Li, S. Xu, S. Zhuo, J. Ma, D. Yuan, C. Wang, W. Hu, *Angew. Chem. Int. Ed.* **2019**, *58*, 14731–14739; d) J. Gu, H. Fan, C. Li, J. Caro, H. Meng, *Angew. Chem.* **2019**, *131*, 5351–5355.
- [16] Z. Song, L. Miao, H. Duan, L. Ruhlmann, Y. Lv, D. Zhu, L. Li, L. Gan, M. Liu, *Angew. Chem.* **2022**, *134*, e202208821.
- [17] N. Cao, Z. Chen, K. Zang, J. Xu, J. Zhong, J. Luo, X. Xu, G. Zheng, *Nat. Commun.* **2019**, *10*, 2877.
- [18] X. Zhu, H. Huang, H. Zhang, Y. Zhang, P. Shi, K. Qu, S.-B. Cheng, A.-L. Wang, Q. Lu, *ACS Appl. Mater. Interfaces* **2022**, *14*, 32176–32182.
- [19] H. Zhang, F. Wan, X. Li, X. Chen, S. Xiong, B. Xi, *Adv. Funct. Mater.* **2023**, *33*, 2306340.
- [20] a) R. Zhang, Y. Guo, S. Zhang, D. Chen, Y. Zhao, Z. Huang, L. Ma, P. Li, Q. Yang, G. Liang, C. Zhi, *Adv. Energy Mater.* **2022**, *12*, 2103872; b) X. Li, S. Tang, S. Dou, H. J. Fan, T. S. Choksi, X. Wang, *Adv. Mater.* **2022**, *34*, 2104891.
- [21] S. Zhang, D. Chen, P. Chen, R. Zhang, Y. Hou, Y. Guo, P. Li, X. Liang, T. Xing, J. Chen, Y. Zhao, Z. Huang, D. Lei, C. Zhi, *Adv. Mater.* **2024**, *36*, 2310776.
- [22] J. Chen, Q. Ma, M. Li, D. Chao, L. Huang, W. Wu, Y. Fang, S. Dong, *Nat. Commun.* **2021**, *12*, 3375.
- [23] Y. Guo, J. Gu, R. Zhang, S. Zhang, Z. Li, Y. Zhao, Z. Huang, J. Fan, Z. Chen, C. Zhi, *Adv. Energy Mater.* **2021**, *11*, 2101699.
- [24] a) S. Zhu, X. Qin, F. Xiao, S. Yang, Y. Xu, Z. Tan, J. Li, J. Yan, Q. Chen, M. Chen, M. Shao, *Nat. Catal.* **2021**, *4*, 711–718; b) J.-Y. Fang, Q.-Z. Zheng, Y.-Y. Lou, K.-M. Zhao, S.-N. Hu, G. Li, O. Akdim, X.-Y. Huang, S.-G. Sun, *Nat. Commun.* **2022**, *13*, 7899; c) Y. Yao, S. Zhu, H. Wang, H. Li, M. Shao, *J. Am. Chem. Soc.* **2018**, *140*, 1496–1501.
- [25] D. Yao, C. Tang, L. Li, B. Xia, A. Vasileff, H. Jin, Y. Zhang, S. Z. Qiao, *Adv. Energy Mater.* **2020**, *10*, 2001289.

Entry for the Table of Contents



The Ni-single-atom molecular catalyst with asymmetric O/N coordination forms hydrogen bonds with H₂O to regulate proton transfer, simultaneously achieving superior NH₃ yield rate and Faradaic efficiency, and modulating the leverage relationship between activity and selectivity in nitrogen reduction reaction.