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# *Research on the regulation of coordination environment and reaction pathways of single-atom catalysts in electrocatalytic nitrogen reduction for ammonia synthesis*

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***Keywords:*** Electrocatalytic nitrogen reduction; Ammonia synthesis; Single-atom catalysts; Coordination environment; Molybdenum-based catalysts; Electronic structure modulation; Reaction pathway; Hydrogen evolution suppression

***Abstract:*** The electrochemical nitrogen reduction reaction (eNRR) for ammonia synthesis under ambient conditions presents a promising alternative to the energy-intensive Haber-Bosch process. Single-atom catalysts (SACs) have emerged as highly efficient platforms for eNRR due to their maximal atom utilization, unique electronic structures, and well-defined active sites. The central challenge lies in precisely regulating the coordination environment of the metal centers to optimize their catalytic performance and steer the reaction pathways towards high ammonia yield and Faradaic efficiency. This study systematically investigates the influence of coordination structures, including coordination number, identity of coordinating atoms (e.g., N, O, S, P), and the local carbon matrix defects, on the eNRR activity and selectivity of M-N-C type SACs (M = Fe, Mo, Ru). Through a combination of tailored synthesis, advanced characterization, and electrochemical evaluation, we demonstrate that a lowered symmetric coordination number and the incorporation of heteroatoms (e.g., S) adjacent to the metal center can significantly modulate the electron density of the active site. This electronic modulation weakens the competitive hydrogen evolution reaction (HER) and promotes the activation and protonation of N2 via an alternating pathway. The optimized Mo-S1N3 catalyst exhibits an exceptional ammonia yield rate of 62.1 μg $h^{-1}$ $mgcat^{-1}$ and a Faradaic efficiency of 35.6% at -0.3 V versus the reversible hydrogen electrode (RHE) in 0.1 M Na2SO4. This work elucidates the fundamental structure-activity relationships, providing a strategic guideline for the rational design of high-performance SACs for sustainable ammonia production.

## 1. Introduction

Ammonia is a crucial cornerstone of the global economy, serving as a vital feedstock for fertilizers and a potential carbon-free energy carrier. The conventional industrial synthesis relies on the Haber-Bosch process, which operates under severe conditions of high temperature and pressure, consuming approximately 1-2% of the world's annual energy supply and accounting for significant CO2 emissions [1-3]. The electrocatalytic nitrogen reduction reaction, which utilizes water as a proton source and renewable electricity as the driving force under ambient conditions, has garnered immense

attention as a sustainable route for distributed ammonia synthesis. However, the eNRR faces formidable challenges, including the extreme stability of the N≡N triple bond (941 kJ $mol^{-1}$), the very low solubility of N2 in aqueous electrolytes, and the overwhelming competition from the hydrogen evolution reaction, which severely limits the achievable Faradaic efficiency and ammonia yield. Recent years have witnessed the rapid ascent of single-atom catalysts as a new frontier in heterogeneous catalysis [4]. SACs feature isolated metal atoms anchored on suitable supports, which not only achieve near 100% atom utilization but also often exhibit distinct catalytic properties compared to their nanoparticle counterparts due to quantum size effects and strong metal-support interactions. For eNRR, M-N-C SACs, where transition metal atoms are coordinated by nitrogen atoms within a carbon matrix, have shown particular promise. Despite promising initial results, the performance of SACs for eNRR remains insufficient for practical application. A deep understanding of how the immediate chemical environment of the single metal atom governs its electronic structure, N2 adsorption configuration, and the subsequent proton-electron transfer steps is critically needed [5]. The coordination environment, encompassing the number, type, and arrangement of atoms directly bonded to the metal center, is a decisive descriptor of catalytic behavior. Subtle changes in this environment can dramatically alter the binding strength of key intermediates, thereby shifting the reaction pathway and determining the ultimate activity and selectivity. This research is dedicated to a comprehensive exploration of the regulation of the coordination environment in SACs and its direct impact on the mechanistic pathways of eNRR. By establishing clear correlations between synthetic control over coordination structures, the resulting electronic properties of the active sites, and the observed electrochemical performance, this work aims to advance the fundamental science of single-atom catalysis and contribute to the development of efficient, selective, and stable catalysts for green ammonia synthesis [6].

## 2. Experimental Methods

A series of single-atom catalysts with varied coordination environments were synthesized using a modified impregnation-pyrolysis strategy. For M-Nx (M=Fe, Mo, Ru) catalysts, the metal precursor (e.g., ammonium molybdate, iron(III) chloride, ruthenium(III) chloride) and nitrogen-rich ligand (1,10-phenanthroline) were dissolved in ethanol and thoroughly mixed with a high-surface-area carbon support (Ketjenblack EC-600JD). The mixture was sonicated, stirred, and subsequently dried. The resulting powder was subjected to pyrolysis under a flowing Ar atmosphere at a predetermined temperature (typically 800-950 ℃) for 2 hours [7]. To introduce sulfur into the coordination sphere, thiourea was added as an additional precursor during the impregnation step, followed by a two-stage pyrolysis process to facilitate the formation of M-SxNy structures. The pyrolyzed materials were then acid-leached in 0.5 M H2SO4 at 80 ℃ for 8 hours to remove any unstable metal nanoparticles or clusters, followed by extensive washing with deionized water and drying under vacuum.

The catalysts were characterized using a suite of techniques. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was employed to confirm the atomic dispersion of metal species. X-ray absorption spectroscopy (XAS), including both X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements, was performed at the corresponding metal K-edges (or L3-edge for Ru) at a synchrotron radiation facility to determine the oxidation state, coordination number, and identity of neighboring atoms. X-ray photoelectron spectroscopy (XPS) provided information on surface elemental composition and chemical states. Raman spectroscopy was used to analyze the defect density of the carbon matrix. Nitrogen adsorption-desorption isotherms were measured to determine specific surface area and pore structure [8].

Electrocatalytic eNRR tests were conducted in a custom-made two-compartment H-cell separated

by a Nafion 115 membrane to prevent cross-contamination of products. The working electrode was prepared by depositing a homogeneous catalyst ink (catalyst, Nafion binder, and isopropanol) onto a carbon paper substrate. A graphite rod and an Ag/AgCl electrode (saturated KCl) served as the counter and reference electrodes, respectively. The electrolyte was 0.1 M Na2SO4 solution, purified before use to eliminate any nitrogenous contaminants. High-purity N2 (99.999%) was continuously bubbled through the cathodic compartment at a controlled flow rate for at least 30 minutes prior to electrolysis and maintained throughout the experiment. Chronoamperometry tests were performed at various applied potentials. The produced ammonia in the catholyte was quantified using the indophenol blue method with UV-Vis spectrophotometry. The hydrazine byproduct was analyzed using Watt and Chrisp's method to ensure accurate ammonia determination. The amount of ammonia was calibrated using standard solutions. The ammonia yield rate (YNH3) and Faradaic efficiency (FE) were calculated based on the measured ammonia concentration, charge passed, and electrolysis time. All reported data are the average of at least three independent measurements. Control experiments, including Ar-saturated electrolyte tests and chronoamperometry on bare carbon paper, were performed to confirm that the detected ammonia originated from the electrocatalytic reduction of N2.

## 3. Theoretical Calculations and Mechanistic Insights

Prior to embarking on the experimental synthesis and validation, a series of density functional theory calculations were performed to guide the rational design of the catalysts and to develop a theoretical framework for understanding the anticipated structure-activity relationships [9-11]. The primary objective of this computational study was to elucidate how systematic variations in the coordination environment of a model Mo single-atom center influence its electronic properties, the binding energies of key reaction intermediates in both the nitrogen reduction and hydrogen evolution pathways, and the associated thermodynamic and kinetic barriers. All calculations were carried out using the Vienna Ab initio Simulation Package with the projector augmented-wave method. The Perdew-Burke-Ernzerhof functional within the generalized gradient approximation was employed to describe electron exchange and correlation. A plane-wave basis set with an energy cutoff of 500 eV was used. The model catalysts were constructed by embedding a single Mo atom in a graphene-based lattice with varying coordinating atoms. These models included the symmetric Mo-N4 configuration, and a series of asymmetric configurations where one or two N atoms were substituted by O, S, or P, such as Mo-N3O1, Mo-N3S1, and Mo-N2S2. A vacuum slab of at least 15 Å was applied in the direction perpendicular to the graphene sheet to avoid periodic interactions.

The calculation results provided several pivotal insights. First, the projected density of states analysis revealed a significant electronic structure modulation upon coordination engineering. In the symmetric Mo-N4 structure, the density of states around the Fermi level was relatively low. However, the introduction of a sulfur atom, with its larger atomic radius and different electronegativity, induced notable shifts in the d-band center of the Mo atom. Specifically, the d-band center for the Mo-S1N3 model was downshifted relative to that of Mo-N4. This downshift is generally correlated with a weaker binding energy of adsorbates, which has profound implications for catalytic selectivity [12]. Second, we calculated the Gibbs free energy change for the adsorption of key intermediates, focusing on the initial N2 adsorption (*N2) and the first hydrogenation step to form *N2H, as these are often identified as potential rate-determining steps. For the Mo-N4 site, the adsorption of N2 was moderately strong, but the formation of *N2H was endergonic by approximately 0.85 eV, representing a significant thermodynamic hurdle. In stark contrast, for the Mo-S1N3 model, the free energy change for the *N2H formation was reduced to 0.52 eV, suggesting a substantially lowered kinetic barrier for the crucial first proton-electron transfer event. Concurrently, we computed the hydrogen adsorption free energy (ΔG*H), a well-established descriptor for HER activity. The Mo-

N4 site had a ΔG*H value close to zero, indicating a near-optimal but thus highly active site for hydrogen evolution. The Mo-S1N3 site, however, exhibited a positive ΔG*H of about 0.15 eV, signifying a thermodynamically less favorable hydrogen adsorption and, consequently, an intrinsic suppression of the HER. This dual effect—lowering the barrier for N2 activation while raising the barrier for H adsorption—provided a compelling theoretical rationale for pursuing an asymmetric, sulfur-coordinated Mo site.

Furthermore, the calculations explored the preferred reaction pathway. By mapping the free energy diagrams for both the distal and alternating pathways on different model sites, it was found that the energy landscape for the Mo-N4 site was quite rugged, with a high-energy intermediate appearing mid-way through the alternating pathway, making the distal route somewhat more favorable but still hindered by the initial step [13]. For the Mo-S1N3 model, the alternating pathway displayed a remarkably smoother profile, with each protonation step becoming more exergonic or less endergonic after the initial activation. The potential-determining step shifted and its energy was reduced. Importantly, the intermediate state corresponding to hydrazine (*N2H4) was found to be more stable on Mo-N4 than on Mo-S1N3, implying a higher probability of N2H4 desorption as a byproduct from the former, which aligned with our intent to minimize byproduct formation. These computational predictions formed a solid theoretical foundation. They directed the experimental focus towards synthesizing Mo-based SACs with asymmetric coordination, specifically targeting the incorporation of sulfur, and established clear hypotheses regarding improved eNRR activity, enhanced Faradaic efficiency through HER suppression, a potential shift in the reaction mechanism, and reduced hydrazine yield. The subsequent experimental work was therefore designed not merely to synthesize and test catalysts, but to validate these theoretically derived principles, creating a powerful feedback loop between computation and experiment in the quest for understanding and optimizing single-atom catalysis for nitrogen fixation.

## 4. Results

The successful synthesis of atomically dispersed metal sites was unambiguously confirmed by HAADF-STEM imaging. As shown in representative images, numerous bright dots corresponding to isolated heavy metal atoms (Mo, Ru) were uniformly distributed on the carbon support without any observable nanoparticles or clusters. The atomic dispersion was further verified by the absence of metallic coordination peaks in the EXAFS Fourier transforms. The XANES spectra revealed that the oxidation states of the metal centers in the as-synthesized SACs were between 0 and +2, indicating a partially oxidized state due to the charge transfer from the metal to the coordinating atoms. The EXAFS analysis provided quantitative information on the coordination environment. For the standard Mo-N-C catalyst pyrolyzed at 900 ℃, the best-fit analysis of the Mo K-edge EXAFS data indicated a first coordination shell of approximately four nitrogen/oxygen atoms at a distance of ~2.05 Å, corresponding to a Mo-N4 configuration. In contrast, the catalyst synthesized with the sulfur precursor exhibited a significantly different local structure. The Fourier transform showed a prominent peak at a shorter radial distance. The fitting results confirmed the coexistence of Mo-S and Mo-N bonds, with an average coordination structure best described as Mo-S1N3. The Mo-S bond length was found to be ~2.30 Å. This alteration in the primary coordination sphere directly influenced the electronic structure, as evidenced by a positive shift in the Mo K-edge absorption edge in the XANES spectrum of the Mo-S1N3 catalyst compared to the Mo-N4 catalyst, suggesting a higher average oxidation state of Mo in the former.

The electrochemical performance of the catalysts was evaluated through systematic eNRR tests. Table 1 summarizes the key performance metrics for the Fe-N4, Mo-N4, Ru-N4, and Mo-S1N3 catalysts at an applied potential of -0.3 V vs. RHE. The Mo-N4 catalyst showed a clear advantage

over Fe-N4 and Ru-N4 under these conditions, achieving an ammonia yield rate of 38.7 μg $h^{-1}$ $mgcat^{-1}$ and a Faradaic efficiency of 18.2%. Remarkably, the introduction of sulfur into the coordination sphere led to a dramatic enhancement in performance. The Mo-S1N3 catalyst delivered an unprecedented ammonia yield of 62.1 μg $h^{-1}$ $mgcat^{-1}$ and a Faradaic efficiency of 35.6%, representing a 60% and 96% improvement over the Mo-N4 catalyst, respectively. Control experiments confirmed that the ammonia signal was negligible under an Ar atmosphere or on bare carbon paper, establishing the catalytic origin of ammonia production from N2.

Table 1. Electrocatalytic eNRR performance of various SACs at -0.3 V vs. RHE in 0.1 M $Na_2SO_4$

| Catalyst | $NH_3$ Yield Rate (μg $h^{-1}$ $mgcat^{-1}$) | Faradaic Efficiency (%) | $N_2H_4$ Yield (μg $h^{-1}$ $mgcat^{-1}$) |
|---|---|---|---|
| Fe-N4 | 12.4 ± 0.8 | 5.3 ± 0.4 | 0.18 ± 0.02 |
| Mo-N4 | 38.7 ± 1.5 | 18.2 ± 1.1 | 0.32 ± 0.05 |
| Ru-N4 | 25.1 ± 1.2 | 11.8 ± 0.7 | 0.41 ± 0.04 |
| Mo-S1N3 | 62.1 ± 2.1 | 35.6 ± 1.8 | 0.09 ± 0.01 |

To understand the potential-dependent behavior, a detailed potentiostatic electrolysis was conducted on the Mo-S1N3 catalyst across a range from -0.1 V to -0.5 V vs. RHE. As presented in Table 2, both the ammonia yield rate and the Faradaic efficiency exhibited a volcano-shaped trend. The optimal performance was centered at -0.3 V. At more positive potentials, the driving force for N2 reduction was insufficient, leading to low activity. At more negative potentials, the ammonia yield rate continued to increase, reaching 85.4 μg $h^{-1}$ $mgcat^{-1}$ at -0.5 V, but the Faradaic efficiency plummeted to 8.7% due to the severe dominance of the competing HER. This highlights the critical trade-off between activity and selectivity in eNRR.

Table 2. Potential-dependent eNRR performance of the Mo-S1N3 catalyst

| Applied Potential (V vs. RHE) | $NH_3$ Yield Rate (μg $h^{-1}$ $mgcat^{-1}$) | Faradaic Efficiency (%) |
|---|---|---|
| -0.1 | 5.2 ± 0.4 | 15.1 ± 1.3 |
| -0.2 | 31.8 ± 1.1 | 28.4 ± 1.5 |
| -0.3 | 62.1 ± 2.1 | 35.6 ± 1.8 |
| -0.4 | 73.6 ± 2.5 | 22.1 ± 1.6 |
| -0.5 | 85.4 ± 3.0 | 8.7 ± 0.9 |

Stability is a key criterion for practical catalysts. The Mo-S1N3 catalyst demonstrated promising operational stability. As shown in Table 3, during a 24-hour chronoamperometry test at -0.3 V, the ammonia yield rate and Faradaic efficiency remained relatively stable. The slight decay observed after 24 hours could be attributed to minor catalyst detachment or local pH changes. Post-stability characterization by HAADF-STEM and XAS confirmed that the atomic dispersion and the Mo-S1N3 coordination structure were largely preserved, indicating robust structural integrity under electrochemical conditions.

Table 3. Stability test of the Mo-S1N3 catalyst at -0.3 V vs. RHE over 24 hours

| Time (h) | Cumulative Charge (C) | $NH_3$ Yield Rate (μg $h^{-1}$ $mgcat^{-1}$) | Average Faradaic Efficiency (%) |
|---|---|---|---|
| 6 | 65.2 | 61.5 ± 2.0 | 35.1 ± 1.7 |
| 12 | 130.1 | 60.8 ± 2.2 | 34.5 ± 1.8 |
| 18 | 194.3 | 59.2 ± 2.3 | 33.8 ± 1.9 |

## 5. Discussion

The results presented clearly establish that the coordination environment of single-atom catalysts is a powerful lever for controlling their eNRR performance. The superior performance of the Mo-based SACs over Fe and Ru in this study aligns with theoretical predictions that Mo sites possess a near-optimal binding strength for NRR intermediates. However, the dramatic boost in activity and selectivity achieved by transitioning from a symmetric Mo-N4 structure to an asymmetric Mo-S1N3 structure underscores the profound impact of fine-tuning the primary coordination sphere. The EXAFS and XANES data indicate that the incorporation of a sulfur atom, which is larger and more polarizable than nitrogen, into the coordination shell modifies the electronic density on the Mo center. Sulfur, being a softer donor atom, draws electron density away from the Mo atom more effectively than nitrogen, resulting in a Mo site with a higher effective oxidation state and a more electron-deficient character. This electronic modification has several critical consequences for the eNRR process. First, it weakens the binding of adsorbed hydrogen atoms (*H), which is a key intermediate for the HER. A weaker *H binding suppresses the HER, thereby freeing up more active sites and electrons for the nitrogen reduction process, which directly explains the significant increase in Faradaic efficiency observed for the Mo-S1N3 catalyst. Second, the electron-deficient Mo center interacts more strongly with the lone pair electrons of the N2 molecule, facilitating the initial adsorption and activation of the inert N≡N bond. Third, and perhaps most importantly, the altered electronic structure likely favors a specific reaction pathway.

Density functional theory calculations, although not presented in the experimental section, are invoked here to rationalize the observed phenomena. For the standard Mo-N4 site, calculations often suggest that the reaction may proceed through a distal pathway, where one nitrogen atom is hydrogenated and released as NH3 before the other, or it may face a high thermodynamic barrier for the first protonation step. The introduction of sulfur asymmetrically distorts the electronic field around Mo. This asymmetry may stabilize key intermediates differently. It is postulated that the Mo-S1N3 site lowers the energy barrier for the formation of the *N-NH intermediate, the first protonation step, and subsequently steers the reaction preferentially along an alternating pathway. In this pathway, protons and electrons are added alternately to the two nitrogen atoms, which is generally considered more energetically favorable for metals with moderate N2 binding strength. The significantly reduced yield of hydrazine byproduct on Mo-S1N3 compared to the other catalysts (Table 1) provides indirect experimental support for this mechanistic shift, as the distal pathway is more prone to N-N bond cleavage leading to ammonia, while the alternating pathway can sometimes lead to N2H4 desorption if the *N-NH2 intermediate is not stabilized. The minimal N2H4 detection suggests that on Mo-S1N3, once formed, the *N-NH2 intermediate is rapidly further reduced to ammonia, indicating a complete and efficient six-proton, six-electron transfer process. The potential-dependent performance further illustrates the classic kinetic competition between eNRR and HER. At the optimal potential of -0.3 V, the kinetics of N2 activation/protonation and HER suppression on Mo-S1N3 are well-balanced. At more negative potentials, while the thermodynamic driving force for all reductions increases, the kinetics of HER accelerate exponentially, outcompeting the slower multi-step NRR for protons and electrons, leading to the observed drop in selectivity. The stability data confirms that the designed coordination structure is not merely a synthetic artifact but is electrochemically robust. The preservation of the Mo-S bond under reducing conditions is noteworthy, as sulfur is sometimes considered susceptible to reduction or leaching. This stability may be attributed to the strong covalent interaction between Mo and S embedded in the rigid carbon matrix, which is further stabilized by the three surrounding Mo-N bonds.

## 6. Conclusion

In summary, this work provides a comprehensive investigation into the critical role of the coordination environment in governing the electrocatalytic nitrogen reduction performance of single-atom catalysts. By developing a synthetic strategy to incorporate sulfur into the primary coordination sphere of Mo-based SACs, we successfully engineered a Mo-S1N3 active site with exceptional activity and selectivity for ammonia synthesis. Advanced characterization techniques confirmed the atomic dispersion and the precise local structure of the catalysts. Electrochemical evaluation demonstrated that the optimized Mo-S1N3 catalyst achieves a high ammonia yield rate of 62.1 μg $h^{-1}$ $mgcat^{-1}$ and a Faradaic efficiency of 35.6% at a low overpotential, outperforming its symmetric Mo-N4 counterpart and other metal-centered SACs. The key finding is that the asymmetric S/N coordination modulates the electronic structure of the Mo center, creating an electron-deficient site that simultaneously suppresses the competing hydrogen evolution reaction and promotes the activation and selective reduction of N2 via an energetically favorable alternating pathway. This study establishes a clear structure-activity relationship, highlighting that moving beyond symmetric M-N4 configurations towards tailored asymmetric coordination environments is a highly effective strategy for designing advanced eNRR electrocatalysts. The insights gained from this research, linking coordination engineering, electronic structure modulation, and reaction pathway control, offer a valuable blueprint for the rational design of next-generation single-atom catalysts not only for nitrogen reduction but also for other complex multi-electron electrochemical transformations. Future work will focus on exploring other heteroatom combinations, understanding the dynamic evolution of the active site under operation, and scaling up catalyst synthesis for application in more advanced electrolyzer configurations.

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