学 位 論 文 内 容 の 要 旨/Dissertation Abstract

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学 位 論 文 題 名/Title of Dissertation

Development of non-precious metal-based electrocatalysts for N_2O reduction under ambient conditions
（常温条件下におけるN_2O還元に向けた非貴金属系電極触媒の開発）

Nitrous oxide (N_2O) is the third most significant anthropogenic greenhouse gas after CO_2 and CH_4, with a global warming potential approximately 310 times higher than CO_2 and an atmospheric lifetime of ~114 years. Beyond its climate impact, N_2O is currently the dominant ozone-depleting substance in the stratosphere. Anthropogenic emissions from agriculture, fossil fuel combustion, and industrial processes continue to rise, leading to a steady annual increase of ~1 ppb in atmospheric N_2O concentration, which highlights the urgent need for efficient and sustainable removal strategies. Conventional thermal decomposition of N_2O requires temperatures exceeding 500°C, which is energy-intensive, poorly selective, and prone to generating secondary pollutants such as NO_x. Electrocatalysis, in contrast, offers an attractive pathway for N_2O reduction to N_2 under ambient conditions, using renewable electricity without additional chemical reductants. However, progress in this field remains nascent: while noble metals such as Pd display excellent activity and selectivity, their scarcity and high cost hinder large-scale deployment. Thus, the development of non-precious-metal-based electrocatalysts with high efficiency, selectivity, and durability remains an urgent challenge. While the discovery and rational design of such catalysts are demanding, molecular electrocatalysts inspired by nitrous oxide reductase, and the single-atom catalysts featuring near-theoretical atomic utilization, represent particularly promising strategies for advancing e-N_2ORR.

In this study, I systematically designed and investigated three categories of non-precious metal electrocatalysts for electrochemical N_2O reduction (e-N_2ORR): multinuclear copper complex of 1,2,4-Triazole (Cutrz), binuclear copper complex of 3,5-diamino-1,2,4-triazole (CuHdatrz), and atomically dispersed iron and nitrogen doped carbon catalysts (Fe-N-C). Their performances were comprehensively evaluated through a combination of electrochemical measurements, quantitative product analysis, advanced spectroscopic techniques, and density functional theory (DFT) calculations. By integrating experimental and theoretical approaches, this work aimed to elucidate the correlations between active-site structure and catalytic activity, thereby providing fundamental design principles and practical guidelines for the rational development of cost-effective, selective, and durable electrocatalysts for e-N_2ORR.

First, the multinuclear copper triazole complex supported on Ketjenblack (Cutrz/KB) was synthesized via a one-step method and applied to e-N_2ORR under alkaline conditions. Electrochemical testing demonstrated excellent catalytic performance: Cutrz/KB delivered a Faradaic efficiency (FE) of 100% toward N_2 at -0.2 V vs. RHE, and the turnover frequency (TOF) continuously increased with applied potential, reaching 267 h^{-1} at -0.6 V vs. RHE. To uncover the structural origin of this behavior, *in situ* and *ex situ* X-ray absorption spectroscopy (XAS) analyses were conducted. The results revealed a stepwise transformation pathway of Cu(II) → Cu(I) → Cu(0) during electrolysis. Extended X-ray absorption fine structure (EXAFS) fitting indicated that these clusters consist of approximately 309 atoms, of which about 162 are exposed surface copper atoms exhibiting an average coordination number of 7.2. Such under-coordinated surface sites are widely recognized as catalytically favorable motifs, providing optimized

binding strength for reaction intermediates and thereby accounting for the superior e-N_2ORR activity of Cutrz/KB. These findings confirm that the *in situ* generation of low-coordinated Cu clusters from multinuclear complexes is a strategy to design highly active and selective non-precious-metal electrocatalysts.

Second, I focused on a binuclear copper complex of 3,5-diamino-1,2,4-triazole supported on KB (CuHdatrz/KB), which mimic the structural features of the active site, so-called Cu_Z center, in nitrous oxide reductase. The CuHdatrz/KB catalyst displayed outstanding selectivity and activity, achieving the FE of 100% for N_2 at relatively mild potentials of -0.2 V and -0.3 V vs. RHE, while simultaneously suppressing hydrogen evolution. At more negative potentials, the TOF increased significantly, reaching as high as 656 h^{-1} at -0.6 V vs. RHE, which surpasses all previously reported molecular-based catalysts for e-N_2ORR. XAFS analyses revealed that the electrochemical reduction of Cu(II) to Cu(I) within the complex is accompanied by a distinct contraction of the Cu-Cu bond distance. Complementary DFT calculations further supported this mechanism, indicating that the reduction of Cu(II) to Cu(I) is associated with a reduced Cu-Cu bond length. This structural evolution strongly resembles the transformation of the natural Cu_Z center during enzymatic process. Collectively, these results demonstrate that the rational mimicry of structural and functional features of natural enzymes offers a powerful and feasible strategy for designing advanced non-precious molecular-based electrocatalysts for e-N_2ORR.

Third, I extended the investigation to atomically dispersed Fe catalysts embedded in nitrogen-doped carbon (Fe-N-C), aiming to explore single-atom strategies for e-N_2ORR. A series of Fe-N-C catalysts was synthesized by employing Hemin as the Fe precursor and Vulcan as the carbon support, followed by pyrolysis at different temperatures. Systematic electrochemical testing revealed a strong dependence of catalytic activity on pyrolysis temperature. Among the obtained samples, the catalyst prepared at 500 °C (FeNC_500) exhibited the most outstanding performance, achieving a TOF of 1579 h^{-1} at -0.6 V vs. RHE. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) confirmed that Fe was atomically dispersed in carbon framework, excluding the presence of Fe nanoparticles or clusters. XAS revealed that FeNC_500 undergoes a reversible transformation between Fe(III) and Fe(II) during electrocatalysis. Complementary X-ray emission spectroscopy (XES) identified the presence of a high-spin Fe state, which was directly correlated with the superior catalytic activity of FeNC_500. Importantly, the identification of this electronic configuration established a direct correlation between spin state and catalytic performance, with the high-spin Fe species being responsible for the superior activity. DFT calculations further demonstrated that the high-spin configuration significantly reduces the energy barrier for N-O bond cleavage, thereby enhancing catalytic efficiency. Collectively, these results provide critical mechanistic insights into the role of spin state in determining the activity of e-N_2ORR of single atom electrocatalyst.

This research establishes a foundation for further studies on bio-inspired and single atoms electrocatalysts for e-N_2ORR. Nevertheless, several critical challenges remain that must be addressed. The comparative study of Cutrz and CuHdatrz highlights the critical role of ligand properties in determining catalytic mechanisms. In Cutrz, the innocent 1,2,4-triazole ligand cannot buffer electron density, resulting in direct reduction of Cu(II) to metallic Cu(0) clusters. In contrast, CuHdatrz utilizes 3,5-diamino-1,2,4-triazole ligands that function as non-innocent ligands, acting as electron reservoirs to stabilize Cu(I) species and prevent over-reduction. This biomimetic design, inspired by nitrous oxide reductase, achieves superior activity and stability, underscoring the importance of ligand-assisted electronic tuning for molecular electrocatalysts. For the single-atom electrocatalyst Fe-N-C, although high-spin states have been identified as key contributors to superior activity, strategies for precisely controlling spin configuration and coordination structures during synthesis—particularly through tuning pyrolysis temperature—remain underdeveloped. Addressing these challenges will not only deepen the fundamental understanding of structure–function relationships, but also accelerate the development of next-generation electrocatalysts with higher activity and selectivity.