学 位 論 文 内 容 の 要 約

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学 位 論 文 題 名

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 a greenhouse gas with a global warming potential nearly 300 times higher than CO_2 and is currently the dominant anthropogenic cause of stratospheric ozone depletion. Its atmospheric concentration continues to rise, driven by agricultural and industrial emissions, presenting an urgent environmental challenge. Although conventional thermal decomposition can convert N_2O into N_2, it requires high temperatures (≥ 250–500 °C) and often produces undesired NO_x byproducts. In contrast, the electrochemical N_2O reduction (e-N_2ORR) enables selective conversion of N_2O to N_2 at room temperature via a two-electron transfer pathway. However, the highest-performing catalysts reported to date typically rely on noble metals such as Pt or Pd, limiting cost-effective scalability.

This dissertation focuses on developing non-precious metal electrocatalysts capable of activating e-N_2ORR under mild conditions and elucidating their underlying catalytic mechanisms.

Through a set of coordinated experimental and theoretical studies, this thesis demonstrates the rational preparation of both molecular electrocatalysts and single-atom catalysts capable of activating N_2O under ambient electrochemical conditions. First, multinuclear copper complexes of 1,2,4-triazole are electrochemically converted into low-coordination copper clusters, which act as the true active centers for N_2O reduction. Second, in the case of the binuclear 3,5-diamino-1,2,4-triazole copper complex, the triazole ligands participate directly in the redox process, displaying non-innocent electron-donating behavior that facilitates N-O bond activation. Third, high-spin Fe-N_4 single-atom sites accelerate e-N_2ORR by creating a favorable electronic environment that strengthens N_2O binding and lowers the barrier for N-O bond dissociation. This study proposes design principles applicable to molecular and single-atom catalytic systems, providing transferable theoretical insights and

broadly applicable methodological guidance for the development of efficient N_2O electrocatalysts.

In **Chapter II**, a multinuclear copper complexes of 1,2,4-triazole supported on Ketjenblack EC-600JD (Cutrz/KB) was synthesized using a one-step solution method. The catalyst exhibited selective conversion of N_2O to N_2 with high Faradaic efficiency (FE), accompanied by a correspondingly high turnover frequency (TOF), demonstrating that the Cutrz/KB functions as an effective non-precious metal electrocatalyst under ambient conditions. To elucidate the mechanism, *in situ* X-ray absorption fine structure (*in situ* XAFS) and extended X-ray absorption fine structure (EXAFS) analyses were conducted. When the potential was shifted to more negative values, Cu(II) was reduced to Cu(0), which was evidenced by the low coordination number of the resulting Cu cluster and the loss of Cu-N scattering features. N_2O initially absorbs onto the surface of the Cu clusters, after which it undergoes electron transfer and is reduced to N_2 (**Figure 1**). The low-coordination nature of these clusters provides a higher density of accessible active sites and an electronic environment that promotes N_2O binding and subsequent N-O bond cleavage.

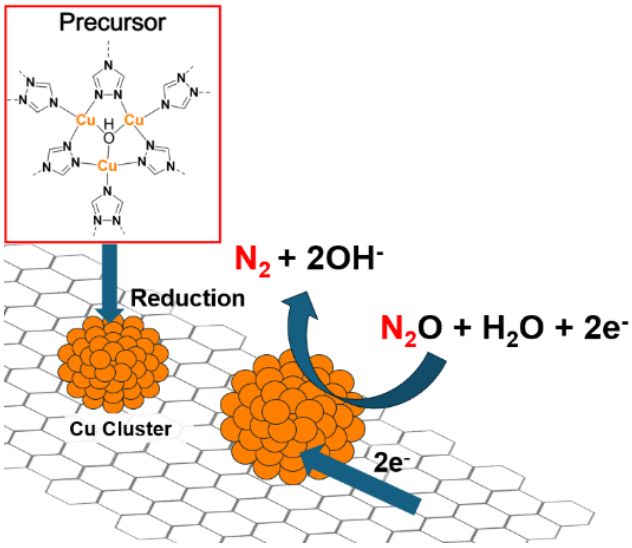

Figure 1. Reduction of copper complexes of 1,2,4-triazole precursor into Cu cluster for N_2O electroreduction

In **Chapter III**, a binuclear copper complex coordinated by 3,5-diamino-1,2,4-triazole loaded on Ketjenblack EC-600JD (CuHdatrz/KB) was investigated to highlight the role of ligand-induced electronic tuning in N_2O electroreduction. Compared with the triazole system in Chapter II, this diamino-functionalized ligand introduces a more electron-rich coordination environment, strengthening the electron-donation capacity of the ligand and allowing the copper centers to reversibly switch oxidation states during catalysis. Electrochemical evaluation showed that CuHdatrz/KB exhibits excellent selectivity with 100%

Faradaic efficiency from -0.2 to -0.3 V vs. RHE, together with a high turnover frequency of up to 656 h^{-1} at -0.6 V vs. RHE. Notably, this TOF exceeds those reported for previously studied molecular electrocatalysts for N_2O reduction and approaching the value of nitrous oxide reductase (N_2OR). To uncover the structural origin of this enhanced activity, *in-situ* XAFS combined with EXAFS oscillation analysis was carried out. The results demonstrated that variations in the applied potential induce a reversible interconversion between Cu(I) and Cu(II) centers in CuHdatrz/KB, while the overall molecular framework remains intact. In addition, a shortening of the Cu-Cu distance was observed, indicating that the two copper sites become more electronically coupled under operating conditions. These findings imply that the 3,5-diamino-1,2,4-triazole ligand exhibits redox non-innocent behavior, actively participating in electron transfer rather than merely stabilizing the metal centers. Furthermore, under strongly alkaline conditions, the change in onset potential does not follow the Nernst equation. EXAFS oscillation analysis revealed that this originates from a deprotonation process occurring on the ligand. Density functional theory (DFT) calculations not only support that deprotonation takes place at the coordinated H_2O ligand, but also indicate that, at relatively low potentials, the reduction of Cu(II) to Cu(I) is accompanied by a contraction of the Cu-Cu distance. Such structural evolution closely resembles that observed for the native CuZ center in N_2OR, as well as for artificial CuZ center. The similarity in structural response suggests that the high activity of CuHdatrz/KB arises from its successful biomimicry of the CuZ catalytic active site. Collectively, Chapter III demonstrates that ligand redox non-innocence, rather than metal identity alone, is crucial for boosting N_2O electroreduction. The cooperative effect between copper centers and electron-donating triazole ligands offers a rational molecular-design strategy for constructing efficient non-precious N_2O electrocatalysts.

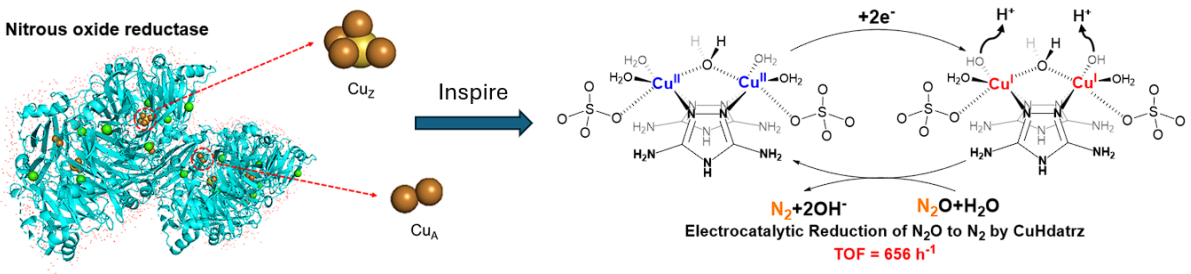

Figure 2. Biomimetic N_2O Reduction Inspired by N_2OR

In **Chapter IV**, a series of Fe-N-C single-atom electrocatalysts were prepared by pyrolyzing a hemin and Vulcan XC-72R at different temperatures. High-angle annular dark-field STEM confirmed that Fe is atomically dispersed as isolated Fe-

N_4 sites rather than forming metallic aggregates. Electrochemical evaluation showed that the catalytic activity strongly depends on the electronic structure tuned by thermal treatment. Spectroscopic analyses, including XAS and XES, identified a high-spin Fe-N_4 configuration as the active site, providing an electronic state that promotes N_2O adsorption and lowers the N-O bond-cleavage barrier. This finding underscores that spin modulation, beyond atomic dispersion alone, is key to enhancing N_2O reduction on Fe-N-C catalysts.

This work demonstrates that non-precious metals can effectively catalyze N_2O reduction at room temperature when their local electronic and coordination environments are precisely controlled. Copper-based systems supported on Ketjenblack EC-600JD reveal that catalytic activity can arise either from in situ-generated Cu clusters or redox-active ligands that mimic the electron-mediating function of the CuZ center in N_2OR. In contrast, Fe-N_4 single-atom catalysts show that spin state, rather than atomic dispersion alone, governs N_2O activation. These insights provide practical design guidelines for developing scalable, non-precious electrocatalysts for N_2O reduction.