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# Operando XAFS Study of $Cu_2O$ Microcrystal Transformation during Electrocatalytic Nitrate Reduction Reaction to Ammonia

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## 1 Introduction

The electrochemical nitrate reduction reaction ($NO_3RR$) offers a sustainable route for $NH_3$ synthesis under ambient conditions while simultaneously mitigating $NO_3^-$ pollution. Among the various catalysts investigated, Cu and Cu-based oxides exhibit excellent $NO_3RR$ to $NH_3$ performance, achieving high Faradaic efficiencies (72–99%) and substantial ammonia production rates. Operando X-ray absorption spectroscopy (XAS) is a powerful technique for monitoring catalyst structural evolution under reaction conditions. In particular, XANES provides information on the electronic state of the catalyst, whereas EXAFS reveals the local coordination environment and bond distances.

In this study, operando Cu K-edge XAS measurements were performed on $Cu_2O$ microcrystals (~1 μm) electrodeposited on carbon fibers without binders. The objective was to elucidate the relationship between the structural transformation of oxide-derived Cu species and their activity and selectivity for $NO_3RR$ over a wide potential range.[1]

## 2 Experiment

Cu K-edge XAS measurement was carried out at BL-9A of the Photon Factory, KEK. Monochromatic X-rays were obtained using a Si(111) double-crystal monochromator. XAS spectra were collected in transmission mode using ionization chambers and recorded in quick-scan mode.

$Cu_2O$ microcrystals were electrodeposited on a carbon fiber substrate.[2] The resulting $Cu_2O$/C electrode (loading: 2 mg $cm^{-2}$) was used as the working electrode (1 $cm^2$) in a custom-built H-type electrochemical cell. An Hg/HgO electrode and a Pt wire served as the reference and counter electrodes, respectively. The cathode and anode compartments, each containing 20 mL of electrolyte, were separated by an anion-exchange membrane.

Chronoamperometric measurements were conducted between +0.6 to −0.7 $V_{RHE}$ with 0.1 V intervals. Each potential was maintained for 600 s. XAS acquisition began 30 s after application of the bias, and seven spectra were recorded at each potential.

## 3 Results and Discussion

Operando quick-XAS measurements were conducted on the $Cu_2O$/C electrode during $NO_3RR$ in 100 mM $NaNO_3$ (pH 13). The XANES and EXAFS analyses revealed the gradual reduction of $Cu_2O$ to metallic Cu during electrolysis (Figure 1). This structural transformation occurred over several tens of minutes and was accompanied by enhanced $NH_3$ production. In contrast, in a nitrate-free electrolyte, $Cu_2O$ was reduced much more rapidly, reaching complete reduction within a few minutes at more positive potentials. This observation suggests that adsorbed nitrate species partially passivate the $Cu_2O$ surface and retard its reduction during $NO_3RR$. The fully reduced catalyst preferentially produced $NO_2^-$ at relatively mild cathodic potential and $NH_3$ at more negative potentials. These findings demonstrate that the dynamic structural evolution of $Cu_2O$ significantly influences $NO_3RR$ performance and provide valuable insights into the design of Cu-based electrocatalysts for selective electrochemical hydrogenation reactions.

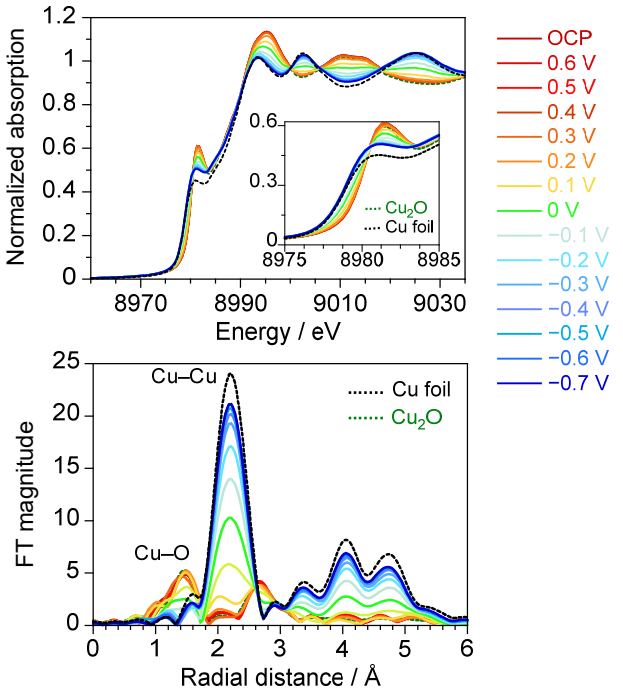


Fig. 1: Operando Cu K-edge quick-XAS spectra of the $Cu_2O$/C electrode during $NO_3RR$ in 0.1 M $NaNO_3$ under potential-step from +0.6 to −0.7 $V_{RHE}$: (a) XANES spectra, (b) Fourier-transformed EXAFS spectra.

## References

[1] R. M. Surya, S. P. Singh, K. Beppu, F. Amano, *ChemSusChem*, **18**(23), e202501785 (2025).
[2] R. M. Surya, S. P. Singh, T. Okazaki, K. Beppu, F. Amano, *Artificial Photosynthesis*, **1**(2), 97–105 (2025).

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