In-situ electrochemical ATR-IR study on electrocatalytic nitrate reduction to ammonia on Cu

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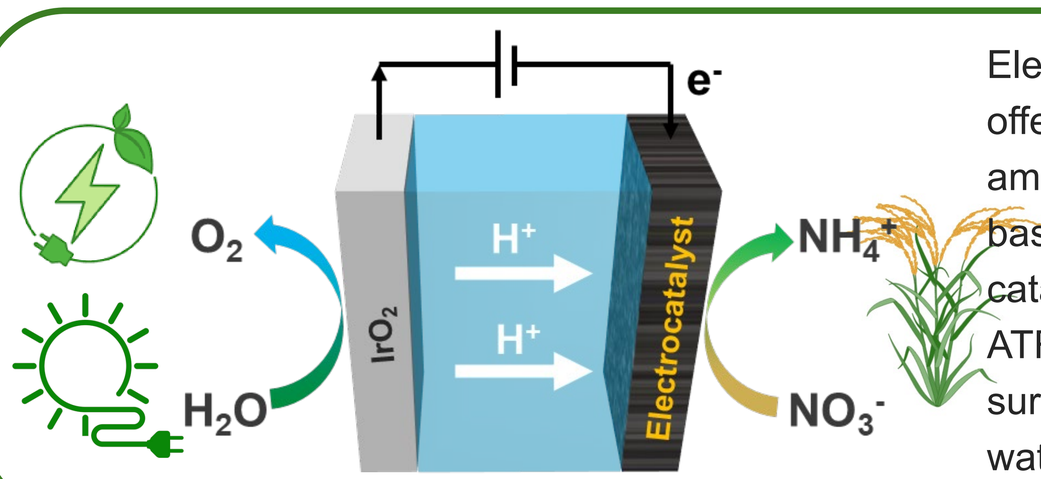
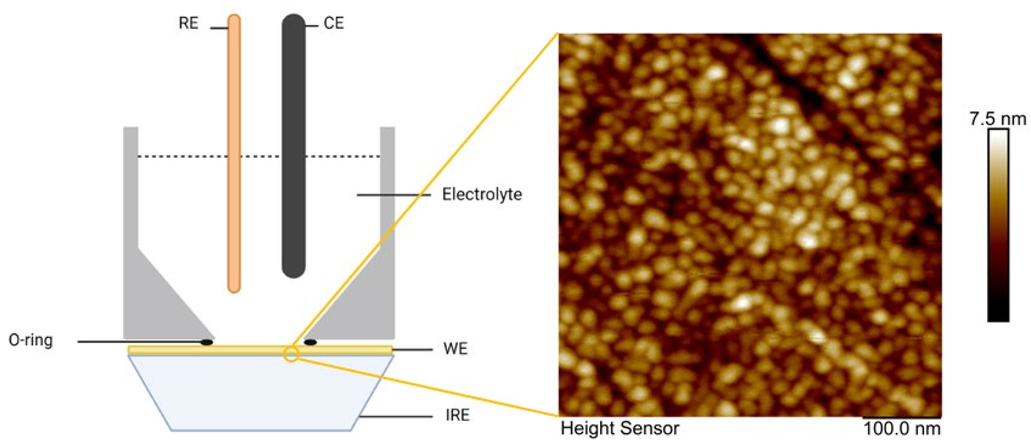


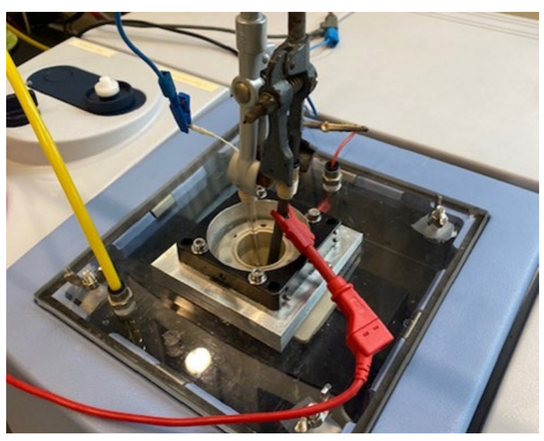
Electrochemical reduction of nitrate (NO_3^-) to ammonia (NH_3) offers a sustainable and decentralized approach for green ammonia (NH_3) production and wastewater treatment. Copper-based electrocatalysts exhibit a promising performance for this catalytic process. In this study, we used in-situ electrochemical ATR-IR spectroscopy to unveil the active intermediate on Cu surface for nitrate reduction to ammonia and study the role of water in this electrocatalysis process.

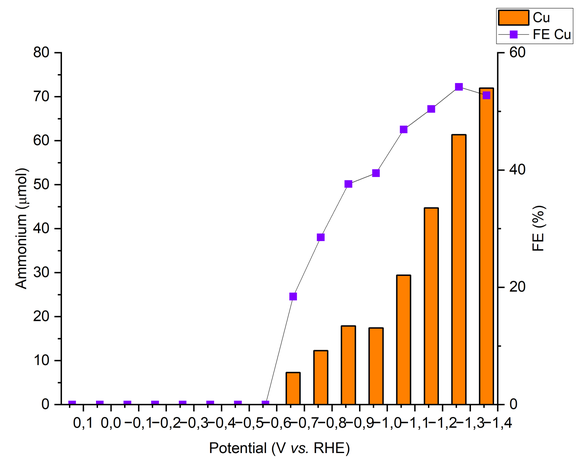
Experimental method



The experiments were conducted in three-electrode cell with a germanium crystal .Ag/AgCl was used as reference electrode (RE) and graphite rod was used as the counter electrode (CE). 30 nm Cu was prepared by magnetron sputtering as working electrode (WE).

Electrocatalytic NO3RR performance





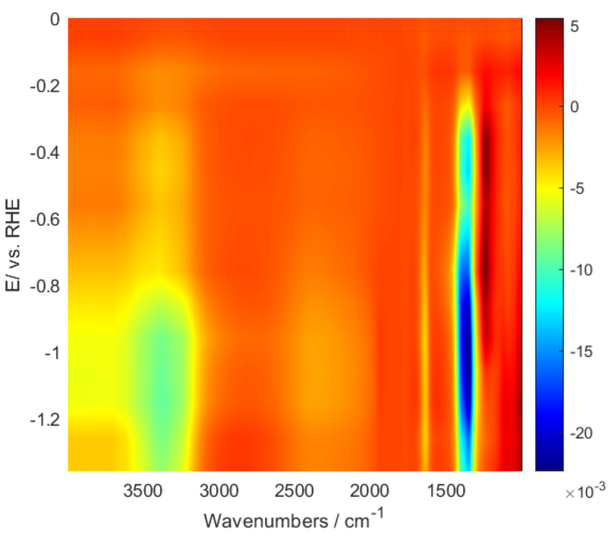
Pre-treatment: cyclic Voltammetry from -0.3 to -0.9 V vs Ag/AgCl

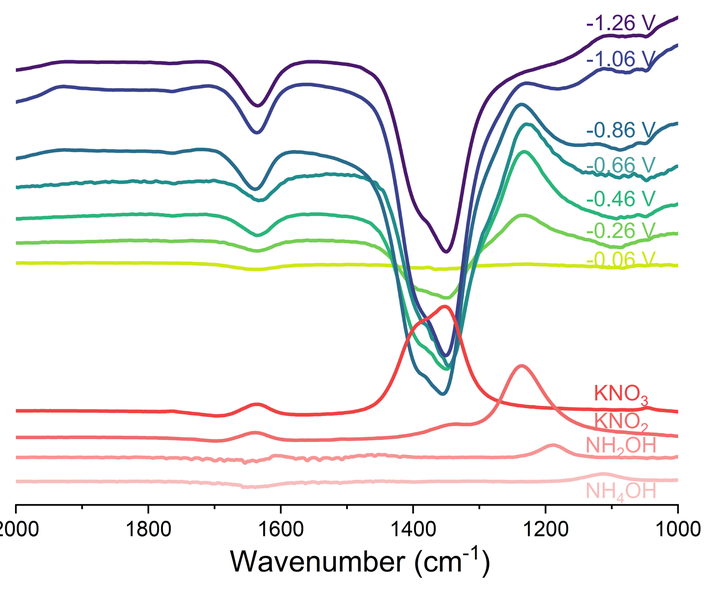
Electrolyte solution: 1M KNO_3

Measurement: Chronoamperometry (CA) at different voltage for 600s

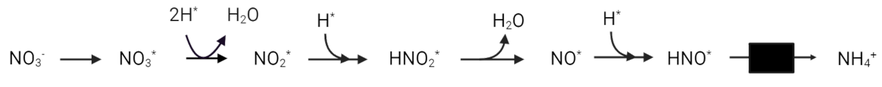
Product analysis: ammonium ions were detected by ion chromatography

ATR-SEIRAS measurements



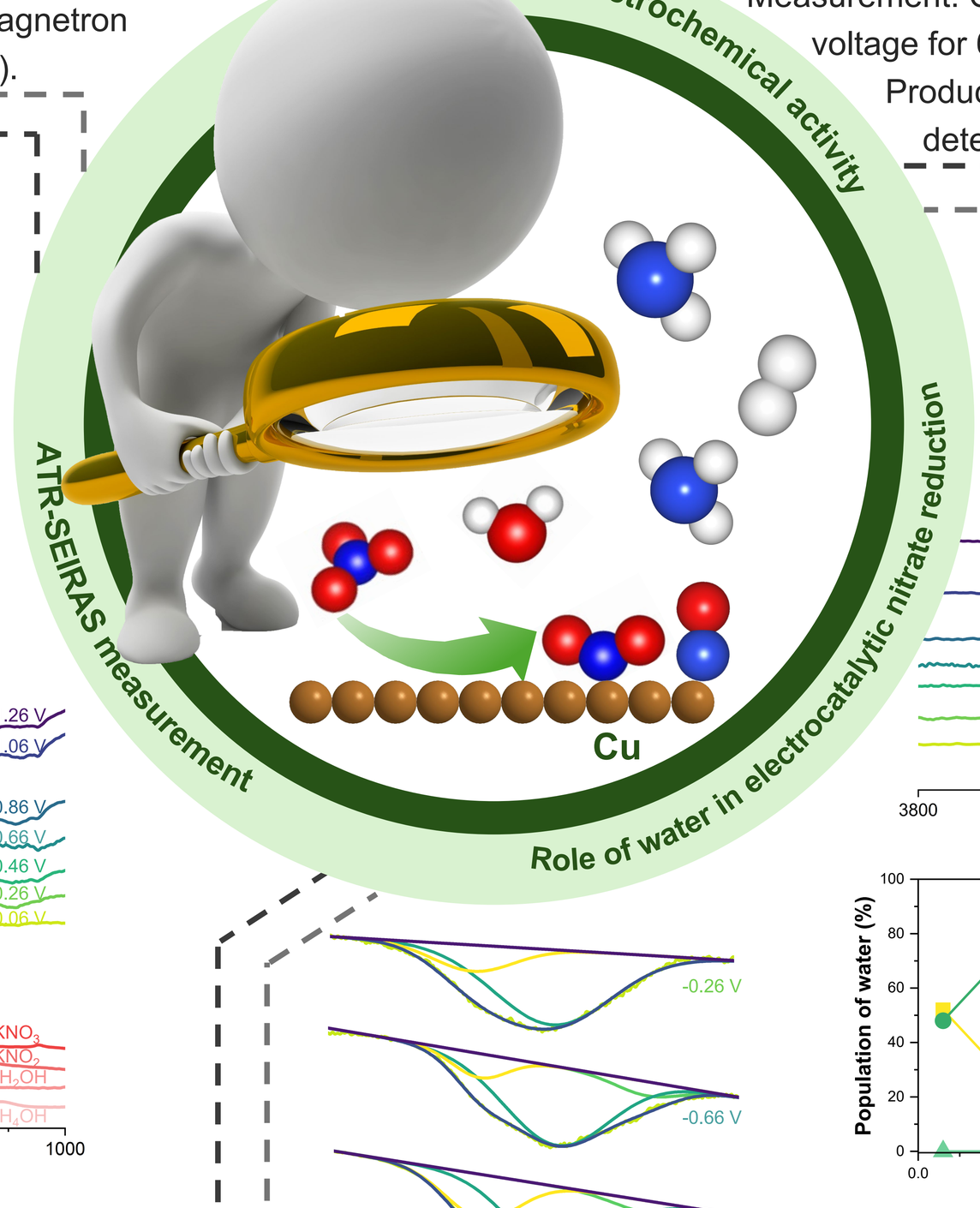


Possible pathway:

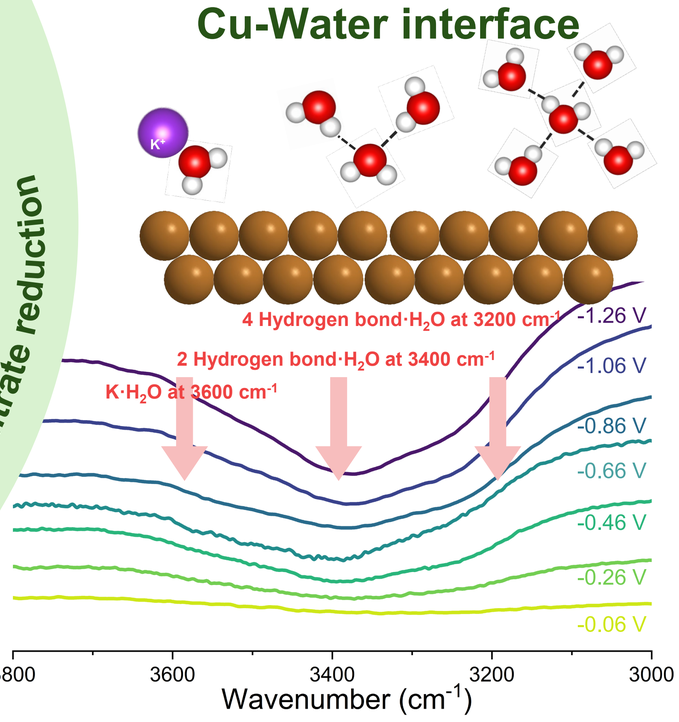


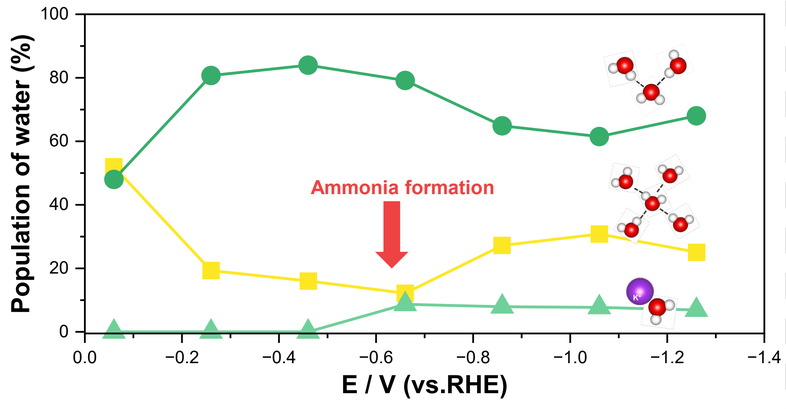
Rate determining step:

1. At lower voltage (<1V vs. RHE), nitrite (NO_2*) is accumulated on the surface, further hydrogenation is limited by the adsorption of hydrogen (H*);
2. At higher voltage is the formation of NO_2*.



Cu-Water interface





$K{\cdot}H_2O$ can be discovered at -0.66 V vs. RHE which is a weakly boned water, this can help:

1. Enhance the dissociation capacity of H_2O;
2. Triggers the generation of more H* and promote nitrate reduction.

References:

1. *Nature.* 2021, 600, 81–85.
2. *Angew. Chem. Int. Ed.* 2025, 64, e202413033.
3. *J. Am. Chem. Soc.* 2024, 146, 8928−8938.
4. *Nat Catal.* 2022, 5, 900–911.

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