

Squeezing Water Molecular Network with Kosmotropic Chemistry to Enhance Nitrogen-to-Ammonia Electrofixation

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Significance and Relevance

The electrochemical nitrogen reduction reaction (NRR) is promising for green ammonia production due to its mild operation conditions but still facing challenges like low solubility and inertness of nitrogen (N_2) and the competing hydrogenation process between hydrogen evolution reaction (HER) and NRR. By squeezing the water molecular network at the point-of-catalysis, our work offers a unique perspective to chemically enhance electrochemical NRR and modulate catalytic pathways. We envision advancements in both functional surface chemistry and efficient electrocatalytic materials are jointly critical to accelerate progress towards green ammonia production in sustainable energy and chemical applications.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis; Multiscale modeling and advanced simulation aspects

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Ammonia plays a crucial role in modern civilization as a nitrogen precursor, but current ammonia production relies mainly on the harsh Haber-Bosch process (200 atm, 500°C) [1,2]. To enable sustainable urbanization and industrialization, immense research efforts have thus focused on developing greener nitrogen fixation methods for ammonia production [3-5]. The electrochemical NRR is promising for green ammonia production due to its use of milder proton sources (e.g., water), ambient operation conditions, and facile integration with renewable electrical energy [6-8]. However, achieving efficient NRR remains a formidable challenge due to the high stability of the N≡N triple bond. Additionally, the electrochemical HER competes strongly with NRR because the twoelectron HER process is kinetically favored over the six-electron NRR [9,10]. Herein, we enhance electrochemical NRR by functionalizing electrocatalyst surfaces with hydrophilic molecules that impart unique kosmotropic chemistry to control water molecules near the catalytic sites. This kosmotropic chemistry strengthens water-water intermolecular hydrogen bonding to expel N₂ molecules from the water network, thereby facilitating their approach towards and interaction with the electrocatalytic sites for promoting NRR. Our work's novelty thus lies in regulating the local water microenvironment to promote NRR, distinct from conventional hydrophobic surface modifications that deter water molecules from the electrocatalyst.

Materials and Methods

We begin by synthesizing nanoporous gold bowls (NPGB) catalysts through a two-step, seed-mediated method. This process involves the initial synthesis of AgCl nanocube as sacrificial template with poly(vinyl pyrrolidone) (PVP) serving as surfactant, followed by growth of NPGBs onto the AgCl templates and subsequent chemical etching of AgCl template. The as-synthesized NPGBs exhibit a gyri-like morphology, comprising bowl-like structures with uniformly interdigitated ligaments. We subsequently functionalize the NPGB surfaces with five different para-substituted aromatic thiols to impart kosmotropic or chaotropic surface chemistries, leveraging the strong affinity of thiol moieties with gold. We confirm the successful modification of NPGB with these thiol molecules through XPS and SERS characterizations.



Results and Discussion

Based on our NPGBs electrocatalyst, we demonstrate that kosmotropic chemistry is crucial for boosting NRR among the five surface chemistries investigated. Notably, our best-performing kosmotropic electrocatalyst (BTP-modified NPGBs) achieves superior NH_3 yield rate and Faradaic efficiency, with over 16-fold and 20-fold improvements compared to chaotropic counterparts, respectively. These enhancements can be infinitely superior considering that the most chaotropic NPGB yields no ammonia. Mechanistic investigations reveal that kosmotropic molecules strengthen hydrogen bonding among water molecules, creating a tightly bound water molecular network that readily expels N_2 reactants from the water matrix. This phenomenon is crucial for promoting catalyst- N_2 interactions and kinetically boosting NRR while suppressing HER.



Figure 1. (A) Schematic of the electrochemical cell for NRR using various surface-modified NPGBs as the electrocatalysts. (B) Linear sweep voltammograms (LSV) recorded from BTP-modified NPGBs under N₂ or Ar bubbling. Insert, a magnified LSV plot between 0 and -0.7 V. (C) Electrochemical NH₃ yield rate and (D) corresponding Faradaic efficiency of various thiol-modified NPGBs at -0.3 V vs RHE.

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