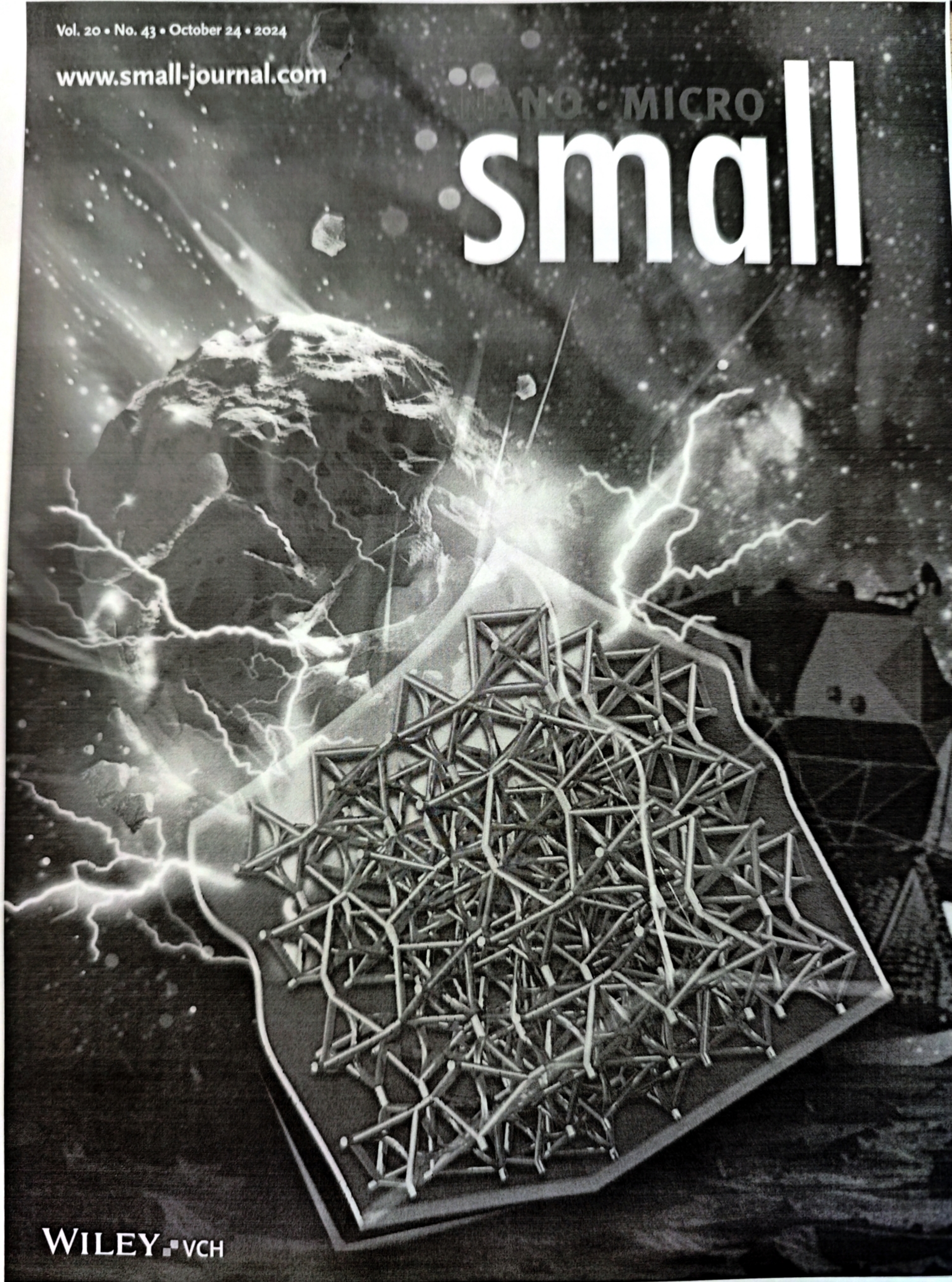


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Enrichment of Active Hydrogen at Amorphous CoO/Cu₂O Heterojunction Interfaces Enhances Electrocatalytic Nitrate Reduction to Ammonia

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The reduction of nitrate into valuable ammonia via electrocatalysis offers a green and sustainable synthetic pathway for ammonia. The electrocatalytic nitrate reduction reaction (NO₃RR) encompasses two crucial reaction steps: nitrate deoxygenation and nitrite hydrogenation. Notably, the nitrite hydrogenation reaction is regarded as the rate-determining step of the process. Herein, the amorphous CoO support introduced for the construction of the a-CoO/Cu₂O tandem catalyst provides sufficient active hydrogen and synergistically catalyzes the NO₃RR. The a-CoO/Cu₂O catalyst showed excellent performance with a maximum NH₃ Faradaic efficiency of 95.72% and a maximum yield rate of 0.96 mmol h⁻¹ mg_{cat}⁻¹ at -0.4 V. In the flow cell, the maximum NH₃ yield rate of 12.14 mmol h⁻¹ mg_{cat}⁻¹ is achieved at -800 mA. The high NO₃RR activity of a-CoO/Cu₂O is attributed to the synergistic cascade effect of amorphous CoO and Cu₂O at the heterojunction interface, where Cu₂O serves as the adsorption site for NO₃⁻, while the accelerated active hydrogen generation of amorphous CoO promotes the nitrite hydrogenation reaction. This work provides a strategy for designing multi-site cascade catalysts centered on amorphous structures to achieve efficient NO₃RR.

emissions.^[2] As a result, there is an urgent need to develop an alternative, low-energy synthesis method to replace the conventional process.^[3] Furthermore, the accumulation of NO₃⁻ pollutants in groundwater and industrial wastewater poses a significant threat to ecological balance and human health.^[4] The technology of synthesizing NH₃ from pollutant NO₃⁻ as a raw material and renewable electrical energy as a driving force has garnered widespread attention.^[5] However, the electrocatalytic nitrate reduction reaction (NO₃RR) process is a complex proton-coupled electron transfer process with slow reaction kinetics and numerous by-products. The NO₃RR process involves two key reaction steps: nitrate deoxygenation and nitrite hydrogenation. Among them, the nitrite hydrogenation reaction is considered to be the rate-limiting step of the process. Therefore, effective catalytic materials need to be developed to promote intermediate hydrogenation to enhance NO₃RR performance.^[6]

1. Introduction

NH₃ is a crucial component in the chemical industry, playing a vital role in global food production and economic growth.^[1] However, the current Haber-Bosch process for industrial NH₃ synthesis is both energy-intensive and produces high levels of carbon

Cu-based catalysts are efficient electrocatalysts for NO₃RR due to their low cost and easy availability, favorable NO₃⁻ adsorption activity, and inhibition of hydrogen. However, pure Cu catalysts suffer from weak hydrogenation ability and strong adsorption of intermediate NO₂⁻, leading to rapid catalyst deactivation and accumulation of NO₂⁻, ultimately resulting in low Faradaic efficiency (FE).^[7] To address the above limitations, the introduction of hetero-elements or heterostructures has been adopted to adjust the electronic structure of Cu, optimize the intermediate adsorption energy, and design active and functional group elements to construct tandem catalysis.^[8] For instance, He et al.^[9] utilized the concept of tandem catalysts by employing Cu-Co binary sulfide as synergistic active sites. In this system, NO₂⁻ intermediates are preferentially formed on the Cu basal phase and subsequently cleaved to the nearby Co basal phase to selectively catalyze the NO₂⁻ reduction to NH₃, realizing a cascade NO₃⁻ to NH₃ conversion. Similarly, Fang et al.^[10] mimicked the bifunctional nature of Cu-type NO₂⁻ reductase and prepared CuCo bimetallic catalysts, which efficiently remove NO₂⁻. In their strategy, Cu promotes NO_x⁻ adsorption and attachment, while Co acts as a proton-giving center to promote NO₃⁻ hydrogenation to NH₃ via adsorbed "H species.

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