Electrocatalytic Reduction of Nitrate to Nitrite and Ammonia over Oxide-Derived Silver Electrodes

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The nitrogen cycle plays a key role biological, energy, environment, and industrial processes. Breaking natural nitrogen cycle is leading to accumulation of reactive nitrogen chemicals in water and atmosphere, therefore, better management of N-cycle has emerged as an urgent research need in energy and environmental science. Removing excessive nitrate (NO_3^-) from wastewater has increasingly become an important research topic in light of the growing concerns over the related environmental problems and health issues. In particular, catalytic/electrocatalytic approaches are attractive for NO_3^- removal, because NO_3^- from wastewater can be converted to N_2 and released back to the atmosphere using renewable H_2 or electricity, closing the loop of the global N cycle. However, achieving high product selectivity towards the desirable N_2 has proven challenging in the direct NO_3^--to-N_2 reaction. In this presentation, we will report our finding on unique and ultra-high electrochemical NO_3^--to-NO_2^-activity on an oxide-derived silver electrode (OD-Ag). Up to 98% selectivity and 95% faradaic efficiency of NO_2^- were observed and maintained under a wide potential window. Benefiting from overcoming the rate-determining barrier of NO_3^--to-NO_2^-during nitrate reduction, further reduction of accumulated NO_2^- to NH_4^+ can be well regulated by the cathodic potential on OD-Ag to achieve a faradaic efficiency of 89%. These indicated the potential controllable pathway to the key nitrate reduction products (NO_2^-or NH_4^+) on OD-Ag. DFT computations provided insights into the unique NO_2^-selectivity on Ag electrodes compared with Cu, showing the critical role of a proton-assisted mechanism. Based on the ultra-high NO_3^--to-NO_2^-activity on OD-Ag, we designed a novel electrocatalytic-catalytic combined process for denitrifying real-world NO_3^--containing agricultural wastewater, leading to 95+% of NO_3^- conversion to N_2 with minimal NO_x gases. Importantly, NO_2^- derived from nitrate may serve as a crucial reactive platform for distributed production of various nitrogen products, such as NO, NH_2OH, NH_3, and urea.