

Electrocatalytic Nitrate Reduction on Oxide-Derived Silver with **Tunable Selectivity to Nitrite and Ammonia**

Hengzhou Liu, Jaeryul Park, Yifu Chen, Yang Qiu, Yan Cheng, Kartik Srivastava, Shuang Gu, Brent H. Shanks, Luke T. Roling,* and Wenzhen Li*



 NH_4^+ FE of 89%, indicating a tunable selectivity to the key nitrate reduction products (NO_2^- or NH_4^+) on OD-Ag. Density functional theory computations provided insights into the unique NO2⁻ 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 NO3⁻-containing agricultural wastewater, leading to 95+% of NO_3^- conversion to N_2 with minimal NO_X gases. In addition to the wastewater treatment process to N_2 and the electrochemical synthesis of NH_{3} , NO_2^- derived from electrocatalytic NO_3^- conversion can serve as a reactive platform for the distributed production of various nitrogen products.

KEYWORDS: density functional theory, electrocatalysis, heterogeneous catalysis, nitrate reduction, selectivity, wastewater treatment

INTRODUCTION

NH

Nitrate (NO_3^{-}) is a toxic chemical that is increasingly found in agricultural runoff and industrial wastes. Nitrate is directly responsible for the notorious eutrophication in natural waters as well as other environmental problems.¹ The waste nitrate also finds its way into drinking water, and the intake of excess nitrate has been linked to severe health issues,² specific cancers, and birth defects.³ A recent study showed that the existing nitrate pollution of drinking water in the United States might cause more than 12,500 cases of cancer each year,⁴ and wastewater treatment accounts for about 3-4% of the United States' electrical energy load.⁵

Currently, NO₃⁻ can be removed by biological denitrification,^{6,7} reverse osmosis,⁸ and ion exchange.⁹ The biological approach is inexpensive; however, the growth of bacteria requires additional purification. Both reverse osmosis and ion exchange are useful. However, the created concentrated nitrate-containing wastes required harsh reaction conditions (e.g., high pressure, specific pH, and H_2 feeding) and exhibited relatively low sensitivity toward NO3⁻ ions, which largely increased the energy and materials cost as well as induced additional pretreatment and postdisposal processes.

Driven by renewable electricity from wind and sunlight, electrocatalytic reduction reactions can convert NO₃⁻ to N₂ under mild conditions, which offers an attractive alternative to closing the loop of the global N cycle.^{10,11} However, achieving high selectivity toward the desirable N_2 has proven kinetically challenging,¹² especially via electrochemical conversions, in part because the N-N coupling reaction is rather difficult and competes with the facile kinetics to NH_4^+/NH_3 and H_2 [from the hydrogen evolution reaction (HER)].¹³⁻¹⁵ In particular, the NO_3^- -to- NO_2^- reaction, which regulated the $NO_3^$ reduction pathway and typically controlled the overall rate toward different N-species, was confirmed to be challenging to manipulate.^{16,17} Additionally, most reports on electrochemically produced N₂ (<30% selectivity) were based on nitrogen balance estimation (produced N_2 = reacted NO_3^- – produced

Received: April 2, 2021 **Revised:** May 30, 2021





Figure 1. Metal surfaces with a distinctive electrocatalytic preference between NO_3^- reduction and NO_2^- reduction. (a) Onset potential difference between NO_3^- reduction and NO_2^- reduction: " $E_{onset}(NO3RR) - E_{onset}(NO2RR)$ ", and the onset potential difference between NO_3^- reduction and HER: " $E_{onset}(NO3RR) - E_{onset}(HER)$ ". The detailed LSV curves to obtain onset potentials are shown in Figure S1a-p. The error bars represent the standard deviation from at least three independent measurements. (b,c) LSV curves of the Cu foil and the Ag foil in three different solutions: 0.1 M KCl (black curve), 0.1 M KCl with 0.1 M NO_3^- (red curve), and 0.1 M KCl with 0.1 M NO_2^- (blue curve). A scan rate of 5 mV s⁻¹ was used for LSV on all metal surfaces, and all electrolytes were adjusted to pH 4. The geometric area of all metal foils was 4 cm².

 NO_2^{-} and NH_4^{+}).^{12,13} This indirectly quantified N_2 failed to rule out the following possibilities: (1) experimental errors in the quantification of NO_3^{-} , NO_2^{-} , and NH_4^{+} , (2) possible NO_x (NO, NO₂, and N₂O) intermediates, and (3) imperfectly sealed reactors during sample collection and transformation, as 79% N₂ in the air may largely interfere with accurate N₂ quantification. Hence, establishing an accurate nitrogen and electron balance is necessary but still challenging for the Ncycle chemistry management, especially considering that a series of possible N-containing intermediates exist from the highest valence of N in NO_3^{-} to the lowest of N in NH_4^+ (e.g., NO_2 , NO_2^{-} , NO, N₂O, N₂, NH₂OH, NH₄⁺, and so forth.).

In addition to converting fixed N (e.g., NO_3^- or NO_2^-) to inert N₂ for denitrifying wastewater, recent studies have highlighted that the electrochemical transformation of $NO_3^$ into NH_4^+ (in particular from nitrate-rich waste streams) shows promise to mitigate the need for NH₃ production from the energy-intensive Haber–Bosch process.^{18–20} Electrochemical ammonia synthesis, particularly from NO_3^- conversion, not only helps address the environmental problems but also holds the potential to reduce energy consumption, as ammonia is an irreplaceable fertilizer and essential precursor for fuels and chemicals.²¹ Therefore, it is critical to acquire a deep understanding of nitrate reduction mechanisms and rationally design electrocatalysts or processes to carefully manipulate NO_3^- reduction pathways toward the desired products.

Herein, we discovered the unique selectivity and superior activity on an OD-Ag electrocatalyst for converting NO_3^- to NO_2^- . Up to 98% selectivity and 95% Faradaic efficiency (FE) of NO_2^- were achieved and well maintained in a wide potential window. Moreover, electrokinetics identified the selective conversion of NO_3^- to NO_2^- , and further reduction of NO_2^- to NH_4^+ can be well regulated by the cathodic potential. Benefiting from the superior NO_3^- -to- NO_2^- activity, 99% of NO_3^- can be converted to NH_4^+ with a FE of 89% when the applied potential exceeds an apparent gating potential via passing the theoretical charge (116 C) from NO_3^- to NH_4^+ .



Figure 2. NO3RR performance on OD-Ag at pH 4. (a) Photograph and SEM image of OD-Ag. (b) AFM image of OD-Ag. The inset graph shows the height profile of a 7 μ m section (the white line). (c) Linear sweep voltammetry of OD-Ag in three different solutions: 0.1 M KCl (black curve), 0.1 M KCl with 0.1 M NO₃⁻ (red curve), and 0.1 M KCl with 0.1 M NO₂⁻ (blue curve). The onset potentials for NO3RR, NO2RR, and HER are marked, leading to the " $E_{onset}(NO3RR) - E_{onset}(NO2RR)$ " = 440 mV, and " $E_{onset}(NO3RR) - E_{onset}(HER)$ " = 540 mV. The geometric area for OD-Ag was 4 cm². (d) Product selectivity and conversion of NO₃⁻ in 0.1 M KCl with 0.05 M NO₃⁻ (left columns) and 0.01 M NO₃⁻ (right columns) at different applied potentials on OD-Ag with 29 C applied charge. The error bars represent the standard deviation for at least three independent measurements. (e) 0.01 M NO₃⁻ at -1.30 V_{Ag/AgCl} on different electrodes. The geometric area of the electrode was 6 cm² for -1.00 and -1.10 V_{Ag/AgCl} with 0.01 M NO₃⁻, and 2 cm² for all other conditions. The methods of product detection are detailed in the Supporting Information, and their calibrations are shown in Figures S5 and S6.

Density functional theory (DFT) computations provided insights into the unique NO2⁻selectivity on Ag electrodes compared with Cu, showing the critical role of a protonassisted mechanism. We further proposed a combined electrocatalytic-catalytic process by splitting the scientific challenge of electrochemical NO3-to-N2 conversion into two steps as follows: electrocatalytic NO₃⁻-to-NO₂⁻ step on oxidederived Ag (OD-Ag), with a subsequent catalytic NO₂⁻-to-N₂ step on a Pd catalyst using H₂ generated on-site by a PEMbased water electrolyzer. The combined process ultimately removed 95+% of NO3⁻ from real-world agricultural wastewater to N₂, leaving the residual N in the treated solutions with <3.5 ppm of NH₄⁺-N. Our entire combined process can be powered by renewable electricity and is an innovative strategy for facile conversion from NO3⁻ to N2, thus opening a new scenario for the N-cycle management toward an N-neutral future.

RESULTS AND DISCUSSION

Strong Electrocatalytic Preference for NO_3^- Reduction over NO_2^- Reduction on Ag. Owing to the higher reactivity of NO_2^- than the stable NO_3^- , it is generally easier to electrochemically reduce NO_2^- on most metal surfaces. Indeed, as observed in linear sweep voltammetry (LSV, Figure S1), 15 of 18 commonly used metal foils possessed a more negative onset potential for the NO_3^- reduction reaction (NO3RR) than for the NO_2^- reduction reaction (NO2RR),

rendering the onset potential difference [that is, " $E_{\text{onset}}(\text{NO3RR}) - E_{\text{onset}}(\text{NO2RR})$ "] negative, gradually from -160 to -10 mV on Ti, Pt, Zr, Fe, Ni, Pd, Au, V, Mo, Bi, Co, Zn, Sn, Al, and W, respectively (Figure 1a and Table S1). Note that the onset potential was consistently defined as the potential under which -0.75 mA cm⁻² was reached in LSV for NO3RR, NO2RR, and HER in this work. This selected current density represented the apparent occurrence of the corresponding reactions without interference from the electrode double-layer charging-discharging. A positive onset potential difference indicated more favorable NO3RR than NO2RR or HER. Clearly, those 15 metal surfaces prefer the NO2RR to the NO3RR under the same test conditions. No preference between NO3RR and NO2RR was observed on the Pb foil; the onset potential of the NO3RR was precisely the same as that of the NO2RR (–1.60 $V_{Ag/AgCl},\,V_{Ag/AgCl}$ V vs Ag/AgCl, hereinafter).

Interestingly, Cu and Ag are the only two metal surfaces that showed a distinctive preference for NO3RR over NO2RR, i.e., " $E_{onset}(NO3RR) - E_{onset}(NO2RR)$ " is positive. Specifically, the onset potentials of the NO3RR in LSV are very close to each other as follows: $-1.00 V_{Ag/AgCl}$ and $-0.94 V_{Ag/AgCl}$ on Ag and Cu, respectively (Figure 1b,c). Importantly, the onset potential of the NO2RR is far more negative on Ag than on Cu ($-1.41 V_{Ag/AgCl}$ vs $-0.99 V_{Ag/AgCl}$), substantiating the higher energy barrier of NO₂⁻ reduction on the Ag surface. Therefore, as shown in Figure 1b,c, blue region, the potential window



Figure 3. Kinetics and mechanism study of NO3RR on OD-Ag. (a) NO₃⁻ order dependence fitting in 0.1 M KCl with different concentrations of NO₃⁻ (pH = 4) at $-0.85 V_{Ag/AgCl}$ with the data obtained from LSV curves shown in Figure S17. (b) LSV of OD-Ag in 0.1 M KCl with 0.1 M NO₃⁻ at different ratios of D₂O/H₂O as the solvent. (c) FE and NO₃⁻ conversion in 0.1 M KCl with 0.1 M NO₃⁻ (pH = 4) at $-1.10 V_{Ag/AgCl}$ and $-1.35 V_{Ag/AgCl}$. The applied charges were 29 C (the theoretical charge for the NO₃⁻-to-NO₂⁻ reaction) and 116 C (the theoretical charge for the NO₃⁻-to-NH₄⁺ reaction) at $-1.10 V_{Ag/AgCl}$ and $-1.35 V_{Ag/AgCl}$ respectively. The top inset was the reaction pathway for NO3RR on OD-Ag. (d) Concentration of produced ¹⁴NH₄⁺ and ¹⁵NH₄⁺ in 0.1 M KCl containing 0.025 M ¹⁵NO₃⁻ and 0.025 M ¹⁴NO₂⁻ at potentials of -1.30 and $-1.50 V_{Ag/AgCl}$ respectively, with different applied charges. The isotopic product detection is detailed in the Supporting Information Experimental Section, and their calibrations are shown in Figure S7.

between NO3RR and NO2RR onsets is significantly wider on Ag than on Cu (410 vs 50 mV). In addition, Ag holds a 180 mV more negative onset potential for HER than Cu (-1.53 $V_{Ag/AgCl}$ vs. -1.35 $V_{Ag/AgCl}$), and the " E_{onset} (NO3RR) – E_{onset} (HER)" is 530 mV (Ag) versus 410 mV (Cu) (Figure 1b,c, blue + orange region). The strong preference for the NO3RR over the NO2RR and HER could be particularly beneficial for selectively converting NO₃⁻ to NO₂⁻, as the produced NO₂⁻ (from NO₃⁻ reduction) may be preserved as the final product on the electrode.

Highly Selective NO_3^- -to- NO_2^- Pathway with Enhanced Activity on OD-Ag. In order to significantly enhance NO3RR activity, OD-Ag electrocatalysts were directly prepared from the Ag foil by performing square-wave voltammetry and then conducting chronoamperometry (CA) under a constant negative potential.²² The color change of the Ag foil during the preparation is shown in Supporting Information Figure S2a and Movie S1. The chemical state change between AgO_x and Ag^0 during synthesis and the successful formation of OD-Ag was confirmed by X-ray diffraction (XRD) spectroscopy (Figure S2b) and X-ray photoelectron spectroscopy (XPS) (Figure S2c).²³ Scanning electron microscopy (SEM) imaging (Figure 2a) shows that OD-Ag has a rough surface with small particles (around 100 nm), in contrast to the smoother surface of the Ag foil (Figure

S3). Interestingly, optimized synthesis created a stepped and periodic wave-like morphology with ± 250 nm of surface depth, which was confirmed by atomic force microscopy (AFM) analysis (Figures 2b and S3a-d) and lower magnification SEM images (Figure S3e-f). The underpotential deposition (UPD) of Pb²⁴ (Figure S4) showed that OD-Ag has 27.1 cm² of electrochemical surface area (ECSA), or 13 times as much as the same geometric size of the Ag foil (2.1 cm²).

As shown in Figure 2c, compared with the Ag foil, the onset potentials (NO3RR, NO2RR, and HER) on OD-Ag are positively shifted by approximately 200 mV, with the wide onset potential window still being maintained. In particular, by comparing Figure 2c with Figure 1a, OD-Ag showed the widest potential difference between NO3RR and NO2RR (440 mV, blue region), as well as between NO3RR and HER (540 mV, blue + orange region), among the total 18 metals screened.

The superior NO_3^- -to- NO_2^- activity on OD-Ag was confirmed by comparing with the Ag foil and the commercial nano-Ag catalyst (i.e., Ag NPs/Ag: Ag nanoparticle-coated Ag foil). As can be seen from Figure S9b, throughout the potential range from -0.90 to -1.15 $V_{Ag/AgCl}$, OD-Ag delivers 5-10 times higher NO_3^- conversion than the Ag foil in the same electroreduction experiment with the electrolyte containing 0.1 M NO_3^- for 1 h. More importantly, ultra-high FE toward NO_2^- ranging from 95.4 to 91.3% and selectivity between 98.8 and 95.9% were obtained under the electrode potential from -0.90 V to -1.15 V_{Ag/AgCb} accordingly (Figure S9c). In addition, the intrinsic activity of NO3RR was largely enhanced on the in situ electrochemically fabricated OD-Ag, as confirmed by comparing OD-Ag with Ag NPs/Ag. As shown in Figure S10, under similar conditions (particle size, substrate, etc.), OD-Ag exhibits tripled area-specific activity (0.72 vs 0.26 mA cm_{Ag}⁻²) and over doubled NO₃⁻ conversion (19.6 vs 8.5%).

At lower NO₃⁻ concentrations (0.05 and 0.01 M), as shown in Figure 2d, NO₂⁻ production still dominates on OD-Ag with the NO₃⁻-to-NO₂⁻ selectivity, all being higher than 87.3% in the potential range from -1.00 to -1.30 V_{Ag/AgCb} by applying the exact amount of theoretical charge (i.e., 29 C) required to completely reduce 0.01 M NO₃⁻ to NO₂⁻. More negative potentials resulted in a gradual increase in NH₄⁺ generation, while the charge consumption by HER remained insignificant for all the tested conditions (FE: <10%, Figure S11). The high NO₃⁻-to-NO₂⁻ selectivity on OD-Ag was maintained in a wide potential window even with low NO₃⁻ concentrations, indicating a robust and well-regulated transformation.

We also compared OD-Ag with the widely used Cu foil at $-1.30 V_{Ag/AgCl}$ under the same experimental conditions. With 0.01 M NO₃⁻, it was found that OD-Ag outperformed Cu in both NO₃⁻ conversion (65.3 vs 39.0%) and NO₃⁻-to-NO₂⁻ selectivity (87.3 vs 48.5%, Figure 2e). Their performance difference was further validated by tests under different NO₃⁻ concentrations and strongly negative potential of $-1.50 V_{Ag/AgCl}$ (Figure S12). Control experiments (Figure S13) by replacing KNO₃ with K¹⁵NO₃ have confirmed that the N source of produced NH₄⁺ was derived from NO3RR, and the quantification of NO₂⁻ was accurate as the approached selectivity measured by different analysis methods (liquid chromatography and colorimetry). The exceptionally high NO3RR selectivity to NO₂⁻ on OD-Ag also outperforms many other reported Cu-based catalysts.^{25–28}

As expected, the observed potential $(-1.30 V_{Ag/AgCl})$ of losing dominance (>90% selectivity) for NO_3^- -to- NO_2^- is fairly consistent with the potential $(-1.25 V_{Ag/AgCl})$ that triggers the NO_2^- -to- NH_4^+ reaction at the same concentration of 0.01 M NO_2^- solution (Figure S14). Interestingly, a detectable level of NH₂OH showed up under relatively more negative potentials in NO3RR (Figure 2c). In addition, more NH₂OH was generated from direct NO2RR (selectivity up to 5.6%, Figure S14). Such results are in concert with the recognition that NH₂OH is a reaction intermediate to NH_4^+ for the reduction of NO_3^- and $NO_2^{-29,30}$

In addition to the high NO_3^- -to- NO_2^- activity, OD-Ag appeared highly durable and robust under testing conditions. As evidenced by XPS and XRD spectra (Figure S15a-b), the chemical state of Ag in OD-Ag was unchanged after the electrochemical measurements. Neither structural change nor Ag leaching was detected (Figure S15c-d). Moreover, no apparent loss of selectivity and FE of NO_2^- was observed for four consecutive 1 h measurements (Figure S15e).

Mechanism and Kinetics of NO3RR on OD-Ag. To obtain more mechanistic insights into the electrokinetics for NO_3^- -to- NO_2^- , the reaction order with respect to the NO_3^- concentration was analyzed by fitting the partial current density for NO_3^- -to- NO_2^- against the NO_3^- concentration in a log-log scale. Under -0.85 $V_{Ag/AgCl}$ (i.e., 60 mV more negative than the onset potential), ~100% FE of NO_3^- to NO_2^- has been verified on OD-Ag in all the tested NO_3^-

concentrations (0.010-0.100 M, adjusted to pH 4 for each case), allowing the LSV currents (Figure S16) of NO₃⁻ reduction to be used as the partial currents for NO₃⁻-to- NO_2^{-} . Note that the same reference electrode (Ag/AgCl) was used in all NO₃⁻ concentrations to ensure accurate potential control, thanks to its pH insensitive nature.³¹ As shown in Figure 3a, a slope of 0.87 is obtained in the concentration range from 0.010 to 0.075 M, strongly suggesting the firstorder dependence of the NO₃⁻-to-NO₂⁻ reaction on the NO₃⁻ concentration. A concentration of 0.100 M NO₃⁻ does not follow the fitting, mainly due to the saturated active sites in NO₃⁻ adsorption. The Tafel curves showed a slope of 120 mV dec⁻¹ (Figure S17), which corresponds to an empirical transfer coefficient $\left[\alpha = 2.303 \text{RT/F} \times \text{dlog}(j)/\text{dE}\right]$ of 0.48. This suggested the first-electron transfer involved in the RDS of the NO₃⁻-to-NO₂⁻ reaction on OD-Ag.³² Further, in the temperature range of 20-71 °C, a moderate apparent activation energy was obtained (15.8 kJ mol⁻¹, under $-1.10 V_{Ag/AgCl}$) Figure S18).

In particular, the NO3RR pathway can be well regulated by the cathodic potential applied on OD-Ag. As shown in Figures 3c and S19, by applying the theoretical charge (29 C) in converting 0.01 \dot{M} NO₃⁻ to NO₂⁻ at -1.10 V_{Ag/AgCl}, the reaction kinetics (or the current density) was gradually decreased to zero during the consumption of NO_3^{-} , in which the NO_3^- conversion attained 92.8% with an observed NO_2^- FE of 87.2%. Extending the reaction time or applying excess charges under the same potential cannot overcome the activation obstacle for further reducing the accumulated NO₂⁻ to NH4⁺ or triggering HER on OD-Ag. In sharp contrast, by applying a potential $(-1.35 V_{Ag/AgCl})$ more negative than the onset potential of NO2RR, 99.0% of NO3⁻ can be converted with an NH₄⁺ FE of 88.8% via passing 116 C charge (the theoretical charge for the NO_3^- -to- NH_4^+ reaction). The performance of the FE to NH4+ in the present work is competitive with or better than the state-of-the-art NO3RR electrocatalysts reported recently (detailed comparison in Table S2).

The high FE to NH_4^+ benefited from the ultra-high activity of NO_3^- -to- NO_2^- on OD-Ag because it has been confirmed to regulate the overall NO3RR pathway.^{16,17} The above results further indicated that a "gating potential" (or the potential starting to trigger the NO_2^- -to- NH_4^+ route) exists in the NO3RR pathway; exceeding the gating potentials, further reduction of accumulated NO_2^- to NH_4^+ would have rapid kinetics and with HER still much suppressed. Furthermore, a series reduction pathway of NO_2^- -to- NH_2OH -to- NH_4^+ was proposed in this work (Figure 3c top inset), based on the observation of the minor NH_2OH and major NH_4^+ products during NO2RR (Figure S19) and the transformation of NH_2OH into NH_4^+ with a lower onset potential and facile kinetics (Figure S20).

Because two protons are involved in the NO₃⁻-to-NO₂⁻ reaction, the H/D kinetic isotope effect (KIE) was studied by comparing the LSV in different solvents as follows: pure H₂O, pure D₂O, and two ratios of mixtures on OD-Ag in a 0.1 M NO₃⁻-containing electrolyte. As shown in Figure 3b, a prominent isotopic effect is observed with a KIE value of 1.33 under -0.85 V_{Ag/AgCl} (not a mass-transport-limited potential). Such an observation implies that protons participated in the RDS of the NO₃⁻-to-NO₂⁻ reaction, in agreement with the proton-assisted mechanism identified by DFT computations discussed in the next section.

¹⁴N/¹⁵N isotopic experiments were designed and conducted to probe the NO₃⁻ reduction kinetics and pathways on OD-Ag. Specifically, an equal concentration (0.025 M) of ¹⁵NO₃⁻ and ¹⁴NO₂⁻ was used in the solution medium, and two characteristic strongly negative electrode potentials (-1.30 and -1.50 V_{Ag/AgCl}) were investigated, under which considerable levels of NH₄⁺ were generated. Enabled by the simultaneous detection of both isotopically labeled ¹⁴NH₄⁺ and ¹⁵NH₄⁺ by NMR spectroscopy (Figure 3d), the kinetics of the following three separate reactions can be revealed: ¹⁵NO₃⁻ to ¹⁵NO₂⁻ (reaction 1, k_1 as the apparent rate constant), ¹⁴NO₂⁻ to ¹⁴NH₄⁺ (reaction 2, k_2), and ¹⁵NO₃⁻ to ¹⁵NH₄⁺ (reaction 3, k_3). The detailed kinetic model derivation, data collection, and kinetic regressions analysis are shown in Supporting Information, Note 1 and Figure S21.

As shown in Figure S21, k_2 (0.0064 min⁻¹) is approximately a quarter of k_1 (0.0273 min⁻¹) under -1.30 V_{Ag/AgCl}, while k_3 (0.0007 min⁻¹) is negligible. Under -1.50 V_{Ag/AgCl}, both k_2 and k_3 grew much more prominently than k_1 . k_2 and k_3 increased by 4 times and 8 times, respectively, from -1.30 to -1.50 V_{Ag/AgCl}. As such, k_2 (0.0255 min⁻¹) and k_3 (0.0056 min⁻¹) attained about 81 and 18% of k_1 , respectively. These calculated kinetic constants agreed well with the product selectivity observed from CA tests.

More interestingly, k_3 is non-negligible under strongly negative potentials, indicating a NO₃⁻-to-NH₄⁺ reaction pathway that potentially "bypasses" the desorption of the reaction intermediate NO₂^{*} to produce NO₂⁻ ions in the bulk solution,^{33,34} and instead directly forms the NH₄⁺ product. This experimentally detected direct NO₃⁻-to-NH₄⁺ reaction pathway is consistent with the DFT calculation prediction noted by the recent work on a Cu-based catalyst.³⁵

In addition, very low FE toward NO_x gas products was detected from both NO3RR and NO2RR (N₂O \leq 0.19%, NO/NO₂ \leq 0.007%). Noted that these low amounts of NO_x are detectable and can be accurately quantified, with the details shown in Supporting Information, Table S3. These results excluded the possible side reactions to yield intermediate NO_x products and also justified the reasonability of our kinetic model.

DFT Computations of the NO3RR Mechanism. Firstprinciples DFT calculations^{36,37} employing a simple electrochemical model³⁸ were performed to obtain a fundamental understanding of the experimental observations. As detailed in the computational methods, the adsorption of NO₃⁻ to form NO₃^{*} was calculated according to previous work;³⁹ this adsorption is potential dependent to account for the transfer of the electron upon adsorption. Two mechanisms were considered for the reduction of NO3 to NO2, as the details leading to N-O bond scission have not been fully elucidated. In the first ("direct dissociation") pathway, an N-O bond in NO_3^* is broken by the catalyst surface to form adsorbed NO_2^* and O*. This does not involve the direct transfer of a protonelectron pair, so the calculated energetics are independent of the potential. Due to anticipated difficulties with performing this on a weak-binding metal such as Ag, a second ("hydrogen assisted") pathway was considered in which a proton-electron pair is transferred to NO3, forming HNO3; this subsequently dissociates to form NO^{*}₂ and OH*. The dissociation of HNO^{*}₃ has very low barriers and is unaffected by the potential. The O*/OH* formed by these two pathways are subsequently reduced to water.

We evaluated the detailed energetics of these two mechanisms for the reduction of NO_3^* and NO_2^* on Ag(111), Cu(111), and Pd(111). We additionally performed calculations on Ag(211), which we selected as a simple approximation for OD-Ag due to the wave-like, amorphous structure exposing an increased fraction of undercoordinated sites.^{40,41} Although we do not have direct experimental evidence of the undercoordinated sites on OD-Ag, due to the challenge of performing HRTEM on a bulk foil-based material, we note that its largely enhanced ECSA implies a lower average degree of atomic coordination. Further, the nature of the synthesis (high-frequency electrochemical oxidation-reduction treatment) is anticipated to leave a rough, undercoordinated surface. Direct comparisons are made here between Ag(211) and Cu(111); Ag(111) and Pd(111) data are presented in Table S4. We note that detailed activation energies were not calculated for all N-O bond breaking steps on Ag(111) and Pd(111), as we focused our analysis on understanding the interesting selectivity differences between OD-Ag and the Cu foil.

The calculated reaction energetics at 0.00 $V_{\rm RHE}$ (-0.43 $V_{\rm Ag/AgCl}$) on Ag(211) are presented in Figure 4a. These results show that the direct dissociation of NO₃^{*} on Ag(211) is highly activated (1.14 eV). Notably, the H-assisted pathway occurring by first forming adsorbed HNO₃^{*} is substantially more favorable than forming the transition state for direct dissociation (TS1a), even under mild reducing potentials (0.46 eV at 0.00 $V_{\rm RHE}$), and the dissociation of HNO₃^{*} (TS1b) is spontaneous (activation free energy of 0.00 eV). This illustrates a key advantage of the H-assisted mechanism over direct dissociation; the favorability of HNO₃^{*} formation increases as the potential becomes more negative, decreasing the effective barrier to N–O bond breaking.

Our results show that a similar mechanism holds for the second reduction of adsorbed NO_2^* : direct dissociation on Ag(211) also has a high activation energy (1.64 eV), but the formation of HNO_2^* (0.46 eV at 0.00 V_{RHE}) enables a lowerenergy dissociation (0.10 eV). The dissociation of HNO_2^* therefore has a slightly higher energy barrier than HNO_3^* dissociation on Ag(211).

We compared the Ag(211) results with those obtained on Cu(111) (Figure 4b) and found that Cu(111) has more favorable activation energy barriers for direct dissociation of NO₃^{*} (0.45 eV) and NO₂^{*} (0.50 eV) than does Ag(211) (1.14 and 1.64 eV, respectively). This suggests some feasibility of direct dissociation on Cu(111), though rates will be relatively slow due to these larger barriers. The H-assisted pathways at 0.00 V_{RHE} on Cu(111) have effective barriers comparable in magnitude to the corresponding direct dissociations of both NO₃⁻ and NO₂⁻, though the H-assisted pathways again become more favorable and dominate at more negative potentials. A detailed comparison of the reaction energetics between Ag(211) and Cu(111) is presented in Figure S22 to emphasize the difference of energetics between the metal surfaces for each mechanism.

The energetics on both surfaces at $-0.90 \text{ V}_{Ag/AgCl}$ are also presented in Figure 4, after adjusting the computational reference potential from RHE to Ag/AgCl (KCl saturated, $E^0 =$ 0.197 V vs. SHE) in a pH 4 electrolyte ($E_{RHE} = -0.467 \text{ V}$ under this condition; see the Supporting Information Experimental Section for details). This figure clearly shows the favorability of the H-assisted mechanisms on both Ag(211) and Cu(111) at more reducing potentials. We calculate that



Figure 4. Energy diagrams of the considered NO_3^- reduction pathways on (a) Ag(211) and (b) Cu(111) at $-0.43 V_{Ag/AgCl}$ (0.00 V_{RHE}) and $-0.90 V_{Ag/AgCl}$ ($-0.47 V_{RHE}$). Shared states are shown in black. Transition states (TSs) are labeled for (H)NO₃^{*} dissociation (TS1) and (H)NO₂^{*} dissociation (TS2). The most stable adsorption geometries of NO₃^{*} and NO₂^{*} + OH^{*} on Ag(211) and Cu(111) are shown in the diagrams, with atom colors: Ag (gray), Cu (brown), H (white), N (blue), and O (red).

the energetics of HNO₃^{*} formation are energetically favorable (i.e., $\Delta G < 0$ for all elementary steps) at potentials more negative than $-0.90~V_{Ag/AgCl}$ on Ag(211) and $-0.94~V_{Ag/AgCl}$ on Cu(111). These values correspond well, considering the approximate nature of our surface models, to the experimentally observed onset potentials for NO3RR at roughly -0.79 V and -0.94 V on OD-Ag and the Cu foil, respectively, offering an explanation for the strong reducing potentials required for experimental activity. Because all the electrochemical steps have favorable energetics (i.e., $\Delta G < 0$) under potentials more negative than these onset potentials, HNO3 dissociation (which is not an electrochemical step) becomes rate determining along the preferred H-assisted pathway to form NO₂⁻. Further, we note that the activation enthalpy of this potential independent step (Table S7) on Ag(211) (0.12) eV, 11.6 kJ mol⁻¹) is consistent with the experimental apparent activation energy discussed above for OD-Ag (15.8 kJ mol⁻¹ at $-1.10~V_{Ag/AgCl}).$ These computational results indeed suggest that the electrochemically active site is likely to be relatively undercoordinated in nature, due to the consistency of our model and experimental results.

Our DFT calculations also provide insights into the reasons for the high NO₃⁻-to-NO₂⁻ selectivity observed on OD-Ag that was not prominent on the Cu foil, which relates to the relative energies of dissociating NO₃^{*} and NO₂^{*} through the respective H-assisted pathways. The free energy of forming the HNO^{*}₂ transition state (TS2b) relative to NO^{*}₂ is 0.10 eV more difficult than forming the HNO₃^{*} transition state (TS1b) from NO $_3^*$ on Ag(211). In contrast, forming TS2b is only 0.08 eV more difficult than forming TS1b from the respective states on Cu(111). This facilitates the relative dissociation rate of HNO_2^* on Cu(111) and prevents NO_2^- from being the dominant product. More significantly, NO_2^* is also bound 0.05 eV more weakly on Ag(211) than on Cu(111) (Table S5–S6). Together, these suggest fundamental reasons for the ability of OD-Ag to desorb NO_2^- relative to the Cu foil, which instead further reduces NO_2^* to NH_4^+ . Though the differences in energetics are small, we note that 0.06 eV represents roughly an order of magnitude difference in rate constants at room temperature. Overall, the decomposition of NO3 has more favorable kinetics than that of NO2; this agrees with the experimental findings of a higher apparent rate constant k_1 compared to k_2 on OD-Ag.

The remaining electrochemical steps to form NH₃ were calculated to be energetically favorable after the dissociation of HNO^{*} to form NO^{*}; in fact, a pathway exists such that all the steps are more favorable than the corresponding NO3RR and NO2RR electrochemical steps (Figures S23-S24). This is in agreement with our expectation that N-O bond breaking in NO₃^{*} is rate determining, and the experimental observation that NO₂⁻ and NH₄⁺ are nearly exclusively the only products formed. Additional factors may influence the relative reduction activities on the considered surfaces. First, the relatively strong adsorption of NO3* on Ag(211) (0.11 eV stronger than Cu(111), see Tables S5-6) increases its coverage and the reaction rate; NO₃⁻ adsorption has previously been reported to limit the NO₃⁻-to-NO₂⁻ reaction.^{42,43} Second, hydrogen competes for surface sites with NO_3* and decreases its coverage. 10,42 The free energy of atomic hydrogen on all surfaces was more negative than that on Ag(211), suggesting another reason for the favorable NO₃⁻ reduction properties on OD-Ag relative to Cu(111), Pd(111), and Ag(111). We also note the relatively strong adsorption of O* and OH* on Cu(111), which hinders the ability to recover free sites through proton-electron addition, reducing the observed activity and onset potential.¹⁰ We note that the precise value of the gating potential to NH₄⁺ was not quantitatively identified in the theoretical study, likely due to the simple nature of the model (Ag(211), and other assumptions noted below). Still, the energetics detailed above offer crucial insights into the reduction onset potential and relative performance of OD-Ag and the Cu foil, most notably due to the energies required to form TS1b and TS2b in the respective systems.

It is additionally meaningful to compare energetics on Ag(211) with those on Ag(111) to understand the intrinsic structure sensitivity on Ag and the relatively low activity of the Ag foil (see Tables S4–S5 and S7). The calculated activation energies of N–O bond dissociation via the H-assisted pathway are very similar [0.12 eV on Ag(211) and 0.13 eV on Ag(111)]; we highlight two possible explanations that surface coverage effects dominate the relative activities of these surfaces, rather than N–O dissociation kinetics. First, the calculated adsorption free energies of NO^{*}₃ were -0.27 eV on Ag(211) and +0.10 eV on Ag(111) at -0.90 V_{Ag/AgCL}

pubs.acs.org/acscatalysis



Figure 5. Nitrate removal by the combined electrocatalytic—catalytic process. Three solution media were tested as follows: 0.1 M KCl, simulated waste stream from ion-exchange columns, and real-world agricultural wastewater (collected from Des Moines Water Works, Iowa), all of which were enriched with 0.01 M NO₃⁻ (i.e., 140 ppm-N). (a) System components of the two-step combined process: electrochemical NO₃⁻-to-NO₂⁻ reaction, NO₂⁻-to-N₂ reaction, and a PEM-based water electrolyzer to produce H₂ for NO₂⁻ reduction in the batch reactor. CO₂ was fed during the test to maintain a constant pH.⁹ (b) Online GC to detect products from the catalytic reduction of 0.5 M NO₂⁻ during different experimental periods. The retention time of N₂ was at around 4.7 min. (c) Product selectivity of catalytic reduction of 0.5 M NO₂⁻ for 2 h. The details were shown in the Supporting Information Experimental Section. (d) Voltage profile of the PEM electrolyzer at 1.4 A, and the NO₂⁻ concentration before and after the reaction. At *t* = 10–25 min, the gas outlet of the sealed cathode water tank was connected to the cell for NO₂⁻ reduction. (e) NO₃⁻ conversion on OD-Ag at $-1.00 V_{Ag/AgCI}$ in the first step (left part) and NO₂⁻ conversion on Pd/C by H₂ in the second step (right part). The error bars represent the standard deviation for at least three independent measurements. (f) Compositions of N-containing compounds in the wastewater after the first (electrocatalytic) step and second (catalytic) step of the treatment. The detailed experimental results and some other test conditions are summarized in Table S11.

demonstrating the relative difficulty of nitrate uptake on Ag(111). Second, H* adsorbs 0.06 eV more strongly on Ag(111) than on Ag(211); as discussed above, the strong adsorption of H* can reduce the availability of active sites for NO₃^{*} adsorption and dissociation.

Other factors not considered here influence the quantitative agreement between modeling and experiments and should be considered in future studies. Potential-dependent activation energy barriers for electrochemical steps were neglected similar to previous work;^{44,45} although we calculate that this is reasonable at the strong reducing conditions used in this study (see Supporting Information, Note 2), these barriers will be more relevant at lower overpotentials desirable in future-designed catalysts.⁴⁶ Briefly, other limitations involve the inclusion of solvent effects on energies of intermediates and transition states⁴⁷ and surface coverage effects.⁴⁸ Our computational insights are nevertheless in good agreement with our experimental results showing superior electrocatalytic performance on OD-Ag for NO₃⁻-to-NO₂⁻ reduction relative to Cu(111), Pd(111), and Ag(111).

Combined Electrocatalytic–Catalytic Process for NO_3^- Removal from Agricultural Waste Streams. Apart from recycling NO_3^- into NH_4^+ as a useful chemical, it is desirable in other circumstances (e.g., drinking water processing) to return the fixed nitrogen to the atmosphere in the form of inert N_2 as the final step of closing the nitrogen

cycle. However, the direct one-step electrocatalytic NO_3^{-} -to- N_2 reaction has proved challenging and kinetically unfavorable.^{12,13} Herein, built on the discovered exceptionally high NO_3^{-} -to- NO_2^{-} selectivity (up to 98%) and conversion (>95%) on OD-Ag, we propose a combined electrocatalytic–catalytic process for NO_3^{-} removal from agricultural waste streams by coupling the electrocatalytic NO_3^{-} -to- NO_2^{-} step on OD-Ag with the subsequent catalytic NO_3^{-} -to- NO_2^{-} step on a Pd catalyst using H₂ that is generated on-site by a PEM-based water electrolyzer (Figures 5a and S25).

Pd is one of the most active metals to efficiently catalyze the reduction of NO₂⁻ by H₂ at room temperature and ambient pressure,^{49,50} particularly showing much more facile kinetics and favorable N_2 selectivity than the direct reduction of NO_3^{-} . The development of a catalyst for NO_2^- reduction is not in the scope of this work, and we only employed a commercial low-Pd loading carbon-supported Pd catalyst (5 wt % Pd/C) here as a proof of concept. Concentrated NO_2^- solution (0.5 M) was bubbled by H₂ for 2 h in order to increase gas product intensity that can be accurately quantified. Highly selectively produced N₂ and minimized NO_x gases through catalytic reaction were confirmed by different analysis methods. On-line gas chromatography (GC) confirmed 93.4% selectivity was toward N_2 (Figure 5b,c), and the selectivity toward NH_4^+ , NO, and N₂O were all <0.5% (Figure S26a and Table S9) based on colorimetry and off-line GC methods. The detailed product quantification and analyses are shown in the Supporting Information. In light of the possible adsorption of NH_4^+ or NO_2^- on the porous carbon support,⁵¹ control experiments elucidated a negligible adsorption effect and the importance of CO_2 buffering in our catalytic system (Figure S27).

The kinetics of the catalytic reaction for NO₂⁻-to-N₂ using H₂ was examined on Pd/C in 0.01 M NO₂⁻, and a pseudofirst-order behavior was observed with a very high coefficient of determination ($R^2 = 0.99$, Figure S26b), leading to the Pdnormalized and surface Pd-normalized rate constants of 3.06 and 27.96 L g_{Pd}⁻¹ min⁻¹, respectively. In fact, it took only 5 min for Pd/C to remove >99% of 0.01 M NO₂⁻. No apparent drop in catalytic performance was observed in three consecutive operations on Pd/C (Figure S26c).

To examine the robust NO_3^- removal capability, the combined electrocatalytic-catalytic process was tested to treat three solution media as follows: 0.1 M KCl, a simulated waste stream from ion-exchange columns,⁵² and real-world agricultural wastewater (collected from Des Moines Water Works, Iowa), all of which were enriched to contain 0.01 M NO_3^{-} (i.e., 140 ppm-N). LSV showed no significant difference in the three solution media (Figure S28). After the combined process for water treatment, 95+% of NO3- was converted with <3.5 ppm of NH4⁺-N and <5.9 ppm of NO3⁻-N remained, and no NO₂⁻-N was detected in any of the treated solutions (Figure 5b). Detailed experimental results and other tested reaction conditions are summarized in Table S10. The combined denitrification process in this work presents one of the lowest undesirable selectivity toward NH₄⁺ and one of the highest desirable selectivities toward N2 among other reported catalytic/electrocatalytic processes, as shown in Table S11. In particular, the combined process presented in our work outperformed a conventional two-step electrochemical NO3-to- N_2 route (electrocatalytic reduction of NO_3^- -to- NH_4^+ coupled with the oxidation of NH_4^+ -to- N_2)^{13,53} from an electron efficiency aspect, as the valence of N is first lowered from the initial +5 (in NO_3^-) to -3 (in NH_3) and then is raised back to 0 (in N_2).

In addition, we have experimentally demonstrated that H_2 generated on-site by a PEM-based water electrolyzer can completely replace the H_2 feed from the pressurized cylinder (Figures 5d and S29), avoiding the use of commercial H_2 which not only relies heavily upon the reforming of fossil fuels for production⁵⁴ but also requires costly infrastructure for storage and transportation.⁵⁵

Considering that the pH of wastewater from different sources may vary,⁵⁶ we examined the electrocatalytic performance of OD-Ag in the pH range of 4.0-13.0 and observed a zeroth-order dependence on H⁺ concentration (Figure S30-31). Besides, as from both the LSV and 1 h CA or chronopotentiometry (CP) measurements (Figure S31-32), the potential-regulated ultra-high FE of NO₂⁻ was preserved in a broad range of pH on OD-Ag. In addition, the excellent electrocatalytic NO3-to-NO2 activity on OD-Ag in the Htype cell is transferable to a flow reactor for its continuous conversion (Figure S33). Based on the flow demonstration, a simple technoeconomic analysis was conducted on the electrocatalytic-catalytic combined process driven by renewable electricity (Supporting Information, Note 4). The estimated capital cost for removing NO3--containing wastewater to N_2 was \$0.066 per m³ in our combined process, which is competitive with or outperforms other treatment methods (Table S12).⁵⁷ To sum up, our tandem wastewater treatment

process is operable in a wide pH range, resistible to interferences from different possible impurities (cations, anions, and microbes) in real wastewater, and shows promising economic feasibility.

We note that NO₂⁻ is a more toxic species than NO₃⁻ in drinking water; however, NO₂⁻ could be utilized as an intermediate product, as long as NO₂⁻ can be quickly and completely converted to safe end products.^{58,59} As demonstrated in Figure 5, 100% of NO₂⁻ conversion is readily attained for all wastewater media, while the conversion of NO₃⁻ on the same commercial Pd/C catalyst is negligible (<1%, Figure S27c-d). In addition to the wastewater treatment to N₂, NO₂⁻ derived from nitrate may serve as a crucial reactive platform for the distributed production of various nitrogen products, such as NO₆⁶⁰ NH₂OH, NH₃,^{61,62} and urea,⁶³ particularly using high concentrations of NO₃⁻ from nuclear power plants⁶⁴ or slaughterhouses.⁶⁵

CONCLUSIONS

In this work, we discovered the unique and ultra-high NO_3^{-1} to- NO_2^- activity on OD-Ag, with up to 98% selectivity and 95% FE were achieved and well maintained in a wide potential window. Electrokinetics has identified the reduction of NO₃⁻ to NO_2^- or further reduction of NO_2^- to NH_4^+ as well regulated by the cathodic potential on OD-Ag. DFT computations provided mechanistic insights into the ultrahigh NO₃⁻-to-NO₂⁻ selectivity observed on OD-Ag, which was not prominent on Cu. Built on the efficient pathway, we have demonstrated a novel combined process for NO₃⁻ removal by coupling the electrocatalytic NO₃⁻-to-NO₂⁻ step on OD-Ag with the subsequent catalytic NO₂⁻-to-N₂ step on a Pd catalyst using H₂ generated on-site by a PEM-based water electrolyzer, resulting in 95+% of NO3⁻ removal from the 0.01 M NO3⁻ containing real-world agriculture wastewater. Moreover, different N-containing intermediates (NO₂, NO₂, NO, N₂O, N₂, NH₂OH, and NH₄⁺) have been analyzed and quantified via different online or offline methods in our work, with accurate nitrogen balances (~95%) being established for both electrocatalytic and catalytic processes. Powered by inexpensive renewable electricity, the directional reduction of NO₃⁻ might unlock the potential to denitrify agricultural wastewater toward utterly harmless N2 or economically valuable NH3. The produced NO₂⁻ may also be utilized as a reactive platform species for the distributed manufacturing of various nitrogenbased products in need.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c01525.

Experimental details; LSV curves of metal foil electrodes; characterization of the Ag foil during the preparation of OD-Ag and the surface morphology of OD-Ag; measurement of ECSA for the Ag electrodes; UV-vis, HPLC, and 1H NMR calibrations; NO3RR measurement and its experimental setup; comparison of OD-Ag and Ag NPs/Ag; FE of NO3RR on OD-Ag; product selectivity and NO_3^- conversion of NO3RR on OD-Ag and the Cu foil; comparison of different quantification methods; stability measurements on OD-Ag for NO3RR; LSV curves of OD-Ag; Tafel plot; electrochemical reduction of NH₂OH on OD-Ag; summary of onset potentials, state-of-the-art NO3RR electrocatalysts, experimental results of the combined denitrification process, reported electrocatalytic or catalytic systems, and reported cost for wastewater treatment of nitrate; content of gaseous and NO and N₂O products; calculated zero-point energy corrections, entropies, free energies, and activation energies; most stable adsorption configurations of NO₃*, HNO₃*, and NO₂*; technoeconomic analysis estimation; isotopic experiment and kinetic modeling; potential-dependent activation energy of electrochemical steps; pH effect study for NO3RR on OD-Ag; and characterization data (PDF)

Preparation of oxide-derived Ag (MP4)

AUTHOR INFORMATION

Corresponding Authors

- Luke T. Roling Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa 50011, United States; orcid.org/0000-0001-9742-2573; Email: roling@iastate.edu
- Wenzhen Li Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa 50011, United States; orcid.org/0000-0002-1020-5187; Email: wzli@iastate.edu

Authors

- Hengzhou Liu Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa 50011, United States
- Jaeryul Park Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa 50011, United States
- Yifu Chen Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa 50011, United States
- Yang Qiu Institute for Integrated Catalysis, Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington 99352, United States
- Yan Cheng Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa 50011, United States
- Kartik Srivastava Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa 50011, United States
- **Shuang Gu** Department of Mechanical Engineering, Wichita State University, Wichita, Kansas 67260, United States
- Brent H. Shanks Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa 50011, United States; o orcid.org/0000-0002-1805-415X

Complete contact information is available at: https://pubs.acs.org/10.1021/acscatal.1c01525

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported in part by the NSF through the Future Manufacturing program (ChE 2036944). We thank Drs. Dapeng Jing, Curtis L. Mosher, Warren E. Straszheim, and Patrick A. Johnston for their assistance with XPS, AFM, SEM, and ICP-OES measurements, and Jeff Mitchell from Des

Moines Water Works for supplying agricultural wastewater. We also acknowledge Dr. Myeongseong Lee and Dr. Jacek A. Koziel for their GC test for N_2O quantification. W. Li is grateful to his Bailey Research Career Development Award and his Richard Seagrave Professorship. L. T. Roling recognizes support from the Michael and Denise Mack Fellowship. Computations were partially supported by the HPC@ISU equipment at Iowa State University, some of which was purchased through funding provided by the NSF under MRI grant number 1726447.

REFERENCES

(1) Council, N. R. Clean Coastal Waters: Understanding and Reducing the Effects of Nutrient Pollution; The National Academies Press: Washington, DC, 2000; p 428.

(2) Ward, M. H.; DeKok, T. M.; Levallois, P.; Brender, J.; Gulis, G.; Nolan, B. T.; VanDerslice, J. Workgroup Report: Drinking-Water Nitrate and Health-Recent Findings and Research Needs. *Environ. Health Perspect.* **2005**, *113*, 1607–1614.

(3) Ward, M.; Jones, R.; Brender, J.; de Kok, T.; Weyer, P.; Nolan, B.; Villanueva, C.; van Breda, S. Drinking Water Nitrate and Human Health: An Updated Review. *Int. Res. J. Publ. Environ. Health* **2018**, *15*, 1557.

(4) Temkin, A.; Evans, S.; Manidis, T.; Campbell, C.; Naidenko, O. V. Exposure-based assessment and economic valuation of adverse birth outcomes and cancer risk due to nitrate in United States drinking water. *Environ. Res.* **2019**, *176*, 108442.

(5) Gude, V. G. Wastewater treatment in microbial fuel cells - an overview. J. Clean. Prod. 2016, 122, 287–307.

(6) Park, J. Y.; Yoo, Y. J. Biological nitrate removal in industrial wastewater treatment: which electron donor we can choose. *Appl. Microbiol. Biotechnol.* **2009**, *82*, 415–429.

(7) Ghafari, S.; Hasan, M.; Aroua, M. K. Bio-electrochemical removal of nitrate from water and wastewater-A review. *Bioresour. Technol.* **2008**, *99*, 3965–3974.

(8) Schoeman, J. J.; Steyn, A. Nitrate removal with reverse osmosis in a rural area in South Africa. *Desalination* **2003**, *155*, 15–26.

(9) Samatya, S.; Kabay, N.; Yüksel, Ü.; Arda, M.; Yüksel, M. Removal of nitrate from aqueous solution by nitrate selective ion exchange resins. *React. Funct. Polym.* **2006**, *66*, 1206–1214.

(10) Martínez, J.; Ortiz, A.; Ortiz, I. State-of-the-art and perspectives of the catalytic and electrocatalytic reduction of aqueous nitrates. *Appl. Catal., B* **2017**, *207*, 42–59.

(11) Duca, M.; Koper, M. T. Powering denitrification: the perspectives of electrocatalytic nitrate reduction. *Energy Environ. Sci.* **2012**, *5*, 9726–9742.

(12) Fajardo, A. S.; Westerhoff, P.; Sanchez-Sanchez, C. M.; Garcia-Segura, S. Earth-abundant elements a sustainable solution for electrocatalytic reduction of nitrate. *Appl. Catal., B* **2021**, *281*, 119465. (13) Garcia-Segura, S.; Lanzarini-Lopes, M.; Hristovski, K.; Westerhoff, P. Electrocatalytic reduction of nitrate: Fundamentals to full scale water treatment applications. *Appl. Catal. B* **2019**, *226*

full-scale water treatment applications. *Appl. Catal., B* 2018, 236, 546–568. (14) Canfield, D. E.; Glazer, A. N.; Falkowski, P. G. The evolution

and future of Earth's nitrogen cycle. Science 2010, 330, 192–196.

(15) Rosca, V.; Duca, M.; de Groot, M. T.; Koper, M. T. Nitrogen cycle electrocatalysis. *Chem. Rev.* **2009**, *109*, 2209–2244.

(16) Wang, Z.; Richards, D.; Singh, N. Recent discoveries in the reaction mechanism of heterogeneous electrocatalytic nitrate reduction. *Catal. Sci. Technol.* **2021**, *11*, 705–725.

(17) Siriwatcharapiboon, W.; Kwon, Y.; Yang, J.; Chantry, R.; Li, Z.; Horswell, S.; Koper, M. Promotion effects of Sn on the electrocatalytic reduction of nitrate at Rh nanoparticles. *ChemElectroChem* **2014**, *1*, 172–179.

(18) Van Langevelde, P. H.; Katsounaros, I.; Koper, M. T. Electrocatalytic nitrate reduction for sustainable ammonia production. *Joule* **2021**, *5*, 290–294.

(19) Zeng, Y.; Priest, C.; Wang, G.; Wu, G. Restoring the Nitrogen Cycle by Electrochemical Reduction of Nitrate: Progress and Prospects. *Small Methods* **2020**, *4*, 2000672.

(20) Hao, D.; Chen, Z.; Figiela, M.; Stepniak, I.; Wei, W.; Ni, B.-J. Emerging alternative for artificial ammonia synthesis through catalytic nitrate reduction. *J. Mater. Sci. Technol.* **2020**, *77*, 163–168.

(21) Chen, G.-F.; Yuan, Y.; Jiang, H.; Ren, S.-Y.; Ding, L.-X.; Ma, L.; Wu, T.; Lu, J.; Wang, H. Electrochemical reduction of nitrate to ammonia via direct eight-electron transfer using a copper-molecular solid catalyst. *Nat. Energy* **2020**, *5*, 605-613.

(22) Ma, M.; Trześniewski, B. J.; Xie, J.; Smith, W. A. Selective and efficient reduction of carbon dioxide to carbon monoxide on oxidederived nanostructured silver electrocatalysts. *Angew. Chem.* **2016**, *128*, 9900–9904.

(23) Murray, B.; Li, Q.; Newberg, J.; Menke, E.; Hemminger, J.; Penner, R. Shape-and size-selective electrochemical synthesis of dispersed silver (I) oxide colloids. *Nano Lett.* **2005**, *5*, 2319–2324.

(24) Kim, C.; Jeon, H. S.; Eom, T.; Jee, M. S.; Kim, H.; Friend, C. M.; Min, B. K.; Hwang, Y. J. Achieving Selective and Efficient Electrocatalytic Activity for CO₂ Reduction Using Immobilized Silver Nanoparticles. J. Am. Chem. Soc. **2015**, 137, 13844–13850.

(25) Wang, Y.; Xu, A.; Wang, Z.; Huang, L.; Li, J.; Li, F.; Wicks, J.; Luo, M.; Nam, D.-H.; Tan, C.-S. Enhanced Nitrate-to-Ammonia Activity on Copper–Nickel Alloys via Tuning of Intermediate Adsorption. J. Am. Chem. Soc. **2020**, 142, 5702–5708.

(26) Reyter, D.; Bélanger, D.; Roué, L. Study of the electroreduction of nitrate on copper in alkaline solution. *Electrochim. Acta* **2008**, *53*, 5977–5984.

(27) Yoshioka, T.; Iwase, K.; Nakanishi, S.; Hashimoto, K.; Kamiya, K. Electrocatalytic reduction of nitrate to nitrous oxide by a coppermodified covalent triazine framework. *J. Phys. Chem. C* **2016**, *120*, 15729–15734.

(28) Pérez-Gallent, E.; Figueiredo, M. C.; Katsounaros, I.; Koper, M. T. M. Electrocatalytic reduction of Nitrate on Copper single crystals in acidic and alkaline solutions. *Electrochim. Acta* **2017**, *227*, 77–84.

(29) Wang, Y.; Zhou, W.; Jia, R.; Yu, Y.; Zhang, B. Unveiling the activity origin of a copper-based electrocatalyst for selective nitrate reduction to ammonia. *Angew. Chem., Int. Ed.* **2020**, *59*, 5350–5354.

(30) Shen, J.; Birdja, Y. Y.; Koper, M. T. Electrocatalytic nitrate reduction by a cobalt protoporphyrin immobilized on a pyrolytic graphite electrode. *Langmuir* **2015**, *31*, 8495–8501.

(31) Eliaz, N.; Gileadi, E. Physical Electrochemistry: Fundamentals, Techniques, and Applications; John Wiley & Sons, 2019.

(32) Bard, A. J.; Faulkner, L. R. Fundamentals and applications. *Electrochem. Methods* **2001**, *2*, 580–632.

(33) Dima, G.; De Vooys, A.; Koper, M. Electrocatalytic reduction of nitrate at low concentration on coinage and transition-metal electrodes in acid solutions. *J. Electroanal. Chem.* **2003**, *554*, 15–23.

(34) Dima, G.; Beltramo, G.; Koper, M. Nitrate reduction on singlecrystal platinum electrodes. *Electrochim. Acta* **2005**, *50*, 4318–4326.

(35) Chen, G.-F.; Yuan, Y.; Jiang, H.; Ren, S.-Y.; Ding, L.-X.; Ma, L.; Wu, T.; Lu, J.; Wang, H. Electrochemical reduction of nitrate to ammonia via direct eight-electron transfer using a copper-molecular solid catalyst. *Nat. Energy* **2020**, *5*, 605–613.

(36) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev.* B: Condens. Matter Mater. Phys. **1996**, 54, 11169.

(37) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.

(38) Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jonsson, H. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J. Phys. Chem. B* **2004**, *108*, 17886–17892.

(39) Calle-Vallejo, F.; Huang, M.; Henry, J. B.; Koper, M. T.; Bandarenka, A. S. Theoretical design and experimental implementation of Ag/Au electrodes for the electrochemical reduction of nitrate. *Phys. Chem. Chem. Phys.* **2013**, *15*, 3196–3202. (40) Pander, J. E., III; Ren, D.; Huang, Y.; Loo, N. W. X.; Hong, S. H. L.; Yeo, B. S. Understanding the Heterogeneous Electrocatalytic Reduction of Carbon Dioxide on Oxide-Derived Catalysts. *Chem-ElectroChem* **2018**, *5*, 219–237.

(41) Back, S.; Yeom, M. S.; Jung, Y. Active sites of Au and Ag nanoparticle catalysts for CO_2 electroreduction to CO. ACS Catal. **2015**, 5, 5089–5096.

(42) de Groot, M. T.; Koper, M. T. M. The influence of nitrate concentration and acidity on the electrocatalytic reduction of nitrate on platinum. *J. Electroanal. Chem.* **2004**, *562*, 81–94.

(43) Petrii, O. A.; Safonova, T. Y. Electroreduction of nitrate and nitrite anions on platinum metals: A model process for elucidating the nature of the passivation by hydrogen adsorption. *J. Electroanal. Chem.* **1992**, 331, 897–912.

(44) Koper, M. T. M. Thermodynamic theory of multi-electron transfer reactions: Implications for electrocatalysis. *J. Electroanal. Chem.* **2011**, *660*, 254–260.

(45) Roling, L. T.; Herron, J. A.; Budiman, W.; Ferrin, P.; Mavrikakis, M. Dimethyl ether electro-oxidation on platinum surfaces. *Nano Energy* **2016**, *29*, 428–438.

(46) Akhade, S. A.; Bernstein, N. J.; Esopi, M. R.; Regula, M. J.; Janik, M. J. A simple method to approximate electrode potentialdependent activation energies using density functional theory. *Catal. Today* **2017**, *288*, 63–73.

(47) Xie, T.; Bodenschatz, C. J.; Getman, R. B. Insights into the roles of water on the aqueous phase reforming of glycerol. *React. Chem. Eng.* **2019**, *4*, 383–392.

(48) Bai, Y.; Mavrikakis, M. Mechanistic Study of Nitric Oxide Reduction by Hydrogen on Pt(100) (I): A DFT Analysis of the Reaction Network. J. Phys. Chem. B 2018, 122, 432–443.

(49) Hörold, S.; Vorlop, K.-D.; Tacke, T.; Sell, M. Development of catalysts for a selective nitrate and nitrite removal from drinking water. *Catal. Today* **1993**, *17*, 21–30.

(50) Shuai, D.; Choe, J. K.; Shapley, J. R.; Werth, C. J. Enhanced Activity and Selectivity of Carbon Nanofiber Supported Pd Catalysts for Nitrite Reduction. *Environ. Sci. Technol.* **2012**, *46*, 2847–2855.

(51) Toebes, M. L.; Van Dillen, J. A.; de Jong, K. P. Synthesis of supported palladium catalysts. *J. Mol. Catal. A: Chem.* **2001**, *173*, 75–98.

(52) Paidar, M.; Roušar, I.; Bouzek, K. Electrochemical removal of nitrate ions in waste solutions after regeneration of ion exchange columns. *J. Appl. Electrochem.* **1999**, *29*, 611–617.

(53) Liu, Z.; Dong, S.; Zou, D.; Ding, J.; Yu, A.; Zhang, J.; Shan, C.; Gao, G.; Pan, B. Electrochemically mediated nitrate reduction on nanoconfined zerovalent iron: Properties and mechanism. *Water Res.* **2020**, *173*, 115596.

(54) Feedstock, E. W. Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup, and Oxygen Separation Equipment; National Renewable Energy Laboratory, 2006.

(55) Van der Zwaan, B. C. C.; Schoots, K.; Rivera-Tinoco, R.; Verbong, G. P. J. The cost of pipelining climate change mitigation: An overview of the economics of CH_4 , CO_2 and H_2 transportation. *Appl. Energy* **2011**, *88*, 3821–3831.

(56) Glass, C.; Silverstein, J. Denitrification of high-nitrate, high-salinity wastewater. *Water Res.* **1999**, 33, 223–229.

(57) Seidel, C.; et al. An assessment of the state of nitrate treatment alternatives. Final Report of the American Water Works Association; In Inorganic Contaminant Research & Inorganic Water Quality Joint Project Committees, 2011; pp 118–121.

(58) Cammack, R.; Joannou, C.; Cui, X.-Y.; Martinez, C. T.; Maraj, S. R.; Hughes, M. N. Nitrite and nitrosyl compounds in food preservation. *Biochim. Biophys. Acta* **1999**, *1411*, 475–488.

(59) Carocho, M.; Morales, P.; Ferreira, I. C. Natural food additives: Quo vadis? *Trends Food Sci. Technol.* **2015**, *45*, 284–295.

(60) Park, J.; Jin, K.; Sahasrabudhe, A.; Chiang, P.-H.; Maalouf, J. H.; Koehler, F.; Rosenfeld, D.; Rao, S.; Tanaka, T.; Khudiyev, T. In situ electrochemical generation of nitric oxide for neuronal modulation. *Nat. Nanotechnol.* **2020**, *15*, 690–697.

(61) Li, H.; Yan, C.; Guo, H.; Shin, K.; Humphrey, S. M.; Werth, C. J.; Henkelman, G. Cu_xIr_{1-x} Nanoalloy Catalysts Achieve Near 100% Selectivity for Aqueous Nitrite Reduction to NH₃. *ACS Catal.* **2020**, *10*, 7915–7921.

(62) Clark, C. A.; Reddy, C. P.; Xu, H.; Heck, K. N.; Luo, G.; Senftle, T. P.; Wong, M. S. Mechanistic Insights into pH-controlled nitrite reduction to ammonia and hydrazine over rhodium. *ACS Catal.* **2019**, *10*, 494–509.

(63) Feng, Y.; Yang, H.; Zhang, Y.; Huang, X.; Li, L.; Cheng, T.; Shao, Q. Te-Doped Pd Nanocrystal for Electrochemical Urea Production by Efficiently Coupling Carbon Dioxide Reduction with Nitrite Reduction. *Nano Lett.* **2020**, *20*, 8282–8289.

(64) Katsounaros, I.; Dortsiou, M.; Kyriacou, G. Electrochemical reduction of nitrate and nitrite in simulated liquid nuclear wastes. *J. Hazard. Mater.* **2009**, *171*, 323–327.

(65) Three Quarters of U.S. Meat Processing Plants that Discharge into Waterways Violated Their Permits, 2016–2018, October 11, 2018.