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## Electrochemical reduction of nitrate to hydroxylamine on gold electrode†

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In this study, we explore the efficacy of gold (Au) as a selective electrocatalyst for the reduction of nitrate to hydroxylamine, a valuable nitrogen-based chemical, while also evaluating the by-product formation of ammonia. We systematically optimized various experimental parameters including nitrate concentration, pH, and applied potential. We found that at an applied potential of  $-0.7$  V vs. RHE in  $0.1$  M  $\text{HNO}_3$ , Au achieves a  $230.1 \pm 19$   $\mu\text{mol NH}_2\text{OH h}^{-1} \text{cm}^{-2}$  yield, with a  $34.2 \pm 2.8\%$  faradaic efficiency. This study underscores the potential of Au as an efficient and selective electrocatalyst for generating value-added nitrogen products through an electrochemical pathway.

Nitrogen, an element essential to all life, manifests in numerous forms, from its stable diatomic gas in the atmosphere to a myriad of nitrogen-containing molecules such as ammonia, nitrate, and organic compounds. Human activities, from industrial manufacturing to agriculture, transform these nitrogen states in ways that significantly impact the global nitrogen cycle. Such transformations—either as unintended byproducts in chemical and combustion processes or through deliberate production of fertilizers and chemicals—distort natural pathways.<sup>1,2</sup> Nitrate, the most oxidized form of nitrogen, is a well known pollutant in water bodies, which in excess threatens the biodiversity of ecosystems and has proven to have negative

health effects.<sup>3,4</sup> Additionally, excesses are eventually removed by natural denitrification processes, performed by microbial organisms. Due to poor selectivity, this also leads to the production of significant amounts of nitrous oxide ( $\text{N}_2\text{O}$ ), a potent greenhouse gas.<sup>5</sup> Converting waste nitrates into valuable chemicals represents a key aspect of sustainable development and poses a significant challenge that engages engineering and research communities worldwide.

The electrochemical reduction of nitrate ( $\text{NO}_3\text{RR}$ ) is gaining prominence as a method that is not only energy-efficient in producing valuable products but also environmentally beneficial for treating water pollution.<sup>4</sup> This process can yield a variety of nitrogen products with different oxidation states; however, research has predominantly focused on producing ammonia,<sup>6</sup> often overlooking the potential for selective reduction to hydroxylamine ( $\text{NH}_2\text{OH}$ ). Hydroxylamine deserves further investigation due to its critical role as a precursor in the synthesis of  $\epsilon$ -caprolactam for Nylon-6 production, which consumes more than 95% of the world's estimated production of 800 000 tons per year.<sup>7,8</sup> Additionally, the potential of  $\text{NH}_2\text{OH}$  as a renewable energy carrier amplifies its significance.<sup>9,10</sup> Traditional methods for producing  $\text{NH}_2\text{OH}$ , such as the Raschig process and catalytic hydrogenation of nitric oxide, face challenges including the use of toxic reagents such as  $\text{SO}_2$  or  $\text{NO}$ , harsh conditions, complex processes, low conversion rates and environmental hazards.<sup>11</sup> Selective electrochemical  $\text{NO}_3\text{RR}$  to  $\text{NH}_2\text{OH}$  conversion presents a greener, more sustainable, cost-effective, and operationally simpler alternative. Concentrating on electrochemical routes, especially for the selective production of hydroxylamine, could drastically lower the carbon footprint as well as environmental impact of the synthesis of this key industrial chemical. This underscores the importance of targeted research into optimizing  $\text{NO}_3\text{RR}$  selectivity and efficiency. Recent studies have identified mercury as an effective electrode material for the electrochemical  $\text{NO}_3\text{RR}$  to  $\text{NH}_2\text{OH}$ .<sup>12</sup> However, its utility is considerably restricted due to toxicity concerns and the challenges of handling it in its liquid form. Compared to standard  $\text{NO}_3\text{RR}$  reactions performed in

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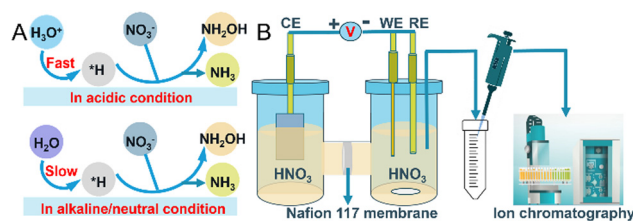


Fig. 1 (A) Pathways for surface adsorbed hydrogen,  $^*H$ , generation under acidic or neutral/alkaline conditions; (B) schematic representation of the experimental approach used for the  $NO_3RR$ , including the H-cell configuration and ion chromatography for product analysis.

neutral conditions, which use nitrate salts and lead to the generation of stoichiometric alkali metal hydroxide byproducts, exploring the reaction in acidic nitrate conditions becomes interesting.<sup>13–15</sup> The increased acidity, compared to alkaline and neutral conditions, provides ample protons for sustained  $NO_3^-$  hydrogenation reactions, resulting in an enhanced conversion rate of  $NO_3^-$  and more energy-efficient  $NH_2OH$  and  $NH_3$  generation (Fig. 1A).<sup>15</sup> The hydrogen evolution reaction (HER) inevitably competes with  $NO_3RR$  in acidic media. Such conditions necessitate careful electrode material selection to mitigate corrosion. Among noble metal-based electrodes, palladium generally favors  $NH_3$  production,<sup>16</sup> while platinum is known for its efficacy in the hydrogen evolution reaction. Given these considerations, gold emerges as a particularly suitable material, noted for its durability and exceptional resistance to corrosion, even in strongly acidic conditions. This prompted our investigation into the capabilities of Au as an electrode for  $NO_3RR$ , particularly focusing on its selectivity for  $NH_2OH$  production. We rigorously tested the effects of applied potential,  $NO_3^-$  concentration, and the pH of the electrolyte on the selectivity and electrochemical activity of Au towards  $NH_2OH$ . Our experiments revealed a significant peak faradaic efficiency (FE) of  $34.2 \pm 2.8\%$  for  $NH_2OH$  at an applied potential of  $-0.7$  V *versus* RHE in a 0.1 M  $HNO_3$  solution. Notably, the  $NO_3^-$  concentration was found to have a profound impact on both the yield and selectivity towards  $NH_2OH$ , with yields diminishing from  $230.1 \pm 19 \mu\text{mol h}^{-1} \text{cm}^{-2}$  in 0.1 M  $NO_3^-$  to zero at 1 M  $KNO_3$ . Furthermore, the optimum yield of  $NH_2OH$ ,  $333 \mu\text{mol h}^{-1} \text{cm}^{-2}$ , was achieved at a pH of 0.3 in  $H_2SO_4$  with a 0.1 M  $NO_3^-$  concentration. These findings underline the potential of Au electrodes to serve as both an efficient and selective catalyst for the electrochemical reduction of  $NO_3^-$  to  $NH_2OH$ , offering an environmentally friendly alternative to conventional production methods and mitigating associated environmental impacts.

The nitrate reduction is a complicated multi-electron, multi-proton transfer process. The electroreduction of  $NO_3^-$  to  $NH_2OH$  involves the transfer of eight protons and six electrons. Conversely, the production of  $NH_3$  from  $NO_3^-$  requires ten protons and eight electrons for electroreduction. Consequently, the HER inevitably emerges as a competing reaction for  $NO_3RR$  in acidic media. The reactions in this work are summarized in eqn (1)–(3), where  $E^0$  is relative to the standard hydrogen electrode (SHE):

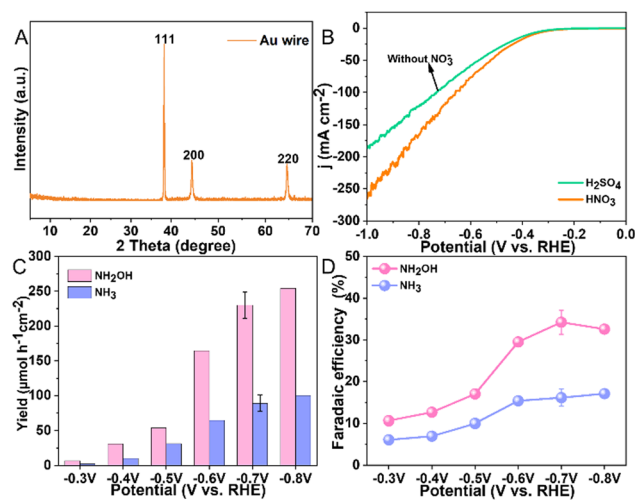
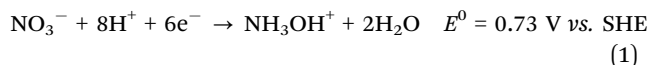
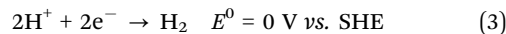
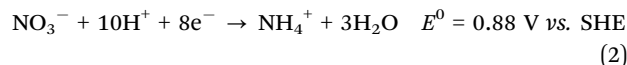


Fig. 2 Characterization and performance of a Au electrode in electrochemical  $NO_3RR$ : (A) XRD pattern, (B) comparative LSV curves for the Au wire electrode measured in 0.1 M  $HNO_3$  and 0.1 M  $H_2SO_4$ , (C) influence of applied potential on the  $NO_3RR$  yield rates of  $NH_2OH$  and  $NH_3$ , and (D) faradaic efficiency integrated over 1 hour in 0.1 M  $HNO_3$ .



The morphology of the Au wire (diam. 0.5 mm, 99.999% pure) electrode was analyzed using scanning electron microscopy, revealing an irregular surface texture as illustrated in Fig. S1, (ESI<sup>†</sup>). Compositional analysis through energy-dispersive X-ray spectroscopy confirmed that this electrode solely exists of Au, with the detailed spectrum shown in Fig. S2, (ESI<sup>†</sup>). To ascertain the crystallinity of the electrode, X-ray diffraction was employed, with the results displayed in Fig. 2A. The recorded XRD pattern clearly exhibits the characteristic peaks of pure gold at  $38.2^\circ$ ,  $44.4^\circ$ , and  $65.58^\circ$ . These peaks correspond to the (111), (200), and (220) crystallographic planes of Au, respectively. These results are in agreement with standard data (JCPDS 04-0784), confirming the purity of the Au wire.

We commenced our study by evaluating the electrocatalytic behavior of the Au electrode in 0.1 M  $HNO_3$  and  $H_2SO_4$  solutions, respectively, employing linear sweep voltammetry (LSV) for this characterization. This approach allowed us to assess the electrode's activity across a range of potentials from 0 V to  $-1$  V *vs.* RHE (Fig. 2B). A notable increase in current density was observed beyond  $-0.3$  V *vs.* RHE in 0.1 M  $HNO_3$ , peaking at  $-266 \text{ mA cm}^{-2}$  at  $-1$  V *vs.* RHE. The elevated current density in  $HNO_3$ , compared to that in  $H_2SO_4$  (without  $NO_3^-$ ), underscores the Au electrode's specific activity towards  $NO_3^-$  reduction. Subsequent, our focus shifted to identifying the reaction products produced in an H-shaped three-electrode quartz cell, which was partitioned by a Nafion 117 membrane and contained 0.1 M  $HNO_3$  as the electrolyte (Fig. 1B). The products of the  $NO_3RR$  were monitored using ion chromatography (IC), which revealed only the presence of  $NH_3$  and  $NH_2OH$  (Fig. S3, ESI<sup>†</sup>). Subsequent experiments aimed to determine the impact of various applied potentials on the



production rates and selectivity of these identified products. By experimenting with potentials ranging from  $-0.3$  V vs. RHE (Fig. S4, ESI<sup>†</sup>), we observed that the yield of  $\text{NH}_2\text{OH}$  increased with more negative potentials, increasing from  $6.7 \mu\text{mol h}^{-1} \text{cm}^{-2}$  at  $-0.3$  V vs. RHE to  $254.3 \mu\text{mol h}^{-1} \text{cm}^{-2}$  at  $-0.8$  V vs. RHE (Fig. 2C). Additionally, the FE for  $\text{NH}_2\text{OH}$  production demonstrated a progressive increase from 10.6% at  $-0.3$  V vs. RHE, peaking at  $34.2 \pm 2.8\%$  at  $-0.7$  V vs. RHE, and then slightly declining to 32.6% at  $-0.8$  V vs. RHE (Fig. 2D), possibly due to the enhanced competition from the HER at these more negative potentials. The yield and FE of  $\text{H}_2$  were determined to be  $482.7 \pm 40.3 \mu\text{mol h}^{-1} \text{cm}^{-2}$  and  $27.1 \pm 0.9\%$  at  $-0.7$  V vs. RHE, respectively (Fig. S5, ESI<sup>†</sup>). The  $\text{NH}_3$  yield measured from UV-vis method ( $81 \pm 10.1 \mu\text{mol h}^{-1} \text{cm}^{-2}$ ) was close to IC method ( $89 \pm 11.9 \mu\text{mol h}^{-1} \text{cm}^{-2}$ ) at  $-0.7$  V vs. RHE, indicative of the reliability of the determined experimental data (Fig. S6, ESI<sup>†</sup>). Notably, throughout these experiments, the yields and FE for  $\text{NH}_3$  were consistently lower than those for  $\text{NH}_2\text{OH}$ , highlighting a pronounced selectivity towards  $\text{NH}_2\text{OH}$  production.

To examine the effect of nitrate concentration on product selectivity while maintaining a constant pH of 1, experiments were conducted at an applied potential of  $-0.7$  V vs. RHE using 0.1 M  $\text{HNO}_3$  as the electrolyte and varying concentrations of  $\text{KNO}_3$ ; for the most dilute nitrate solution, a 0.05 M  $\text{KNO}_3$  solution was used with its pH adjusted to 1 using  $\text{H}_2\text{SO}_4$  (Fig. S7, ESI<sup>†</sup>). Fig. 3 illustrated the trends in product yield and FE with nitrate concentration at pH 1, demonstrating that the highest yield and FE of  $\text{NH}_2\text{OH}$  were achieved at a nitrate concentration of 0.1 M. At a reduced nitrate concentration of 0.05 M, the diminished adsorption of nitrate anions on the Au surface, likely slowed the  $\text{NO}_3\text{RR}$  reaction. Also at increased nitrate concentrations, a marked decline in  $\text{NH}_2\text{OH}$  yield and FE were observed. Note that, the detected hydroxylamine concentration consistently decreases over time, likely due to its oxidation by  $\text{HNO}_2$  in acidic medium ( $\text{NH}_2\text{OH} + \text{HNO}_2 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$ ). This was confirmed by a control experiment where  $\text{KNO}_2$  was added to a 0.1 M  $\text{HNO}_3$  solution containing  $\text{NH}_2\text{OH}$ . As shown in Fig. S8, (ESI<sup>†</sup>), there was a sharp drop in  $\text{NH}_2\text{OH}$  concentration following the addition. The reduced yields for both  $\text{NH}_2\text{OH}$  and  $\text{NH}_3$  at higher nitrate concentrations are likely due to additional nitrate adsorbates obstructing the Au surface. It is assumed that adsorbed hydrogen or water is necessary for nitrate to undergo  $\text{NH}_3$  conversion. Further analysis involved measuring the pH of the electrolyte solution post-reaction (Table S1, ESI<sup>†</sup>). Clearly, higher starting nitrate concentrations resulted in increased pH levels. Specifically, the pH increments post-reaction were ordered as follows: 0.1 M (pH = 1.30) < 0.3 M (pH = 1.73) < 0.5 M (pH = 1.96) < 0.7 M (pH = 2.20) < 1 M (pH = 2.74). The increased pH was attributed to the consumption of eight protons to produce  $\text{NH}_3\text{OH}^+$  and ten protons to produce  $\text{NH}_4^+$ , respectively.

To investigate the effect of pH on the selectivity and yield of electrocatalytic  $\text{NO}_3\text{RR}$  over the Au electrode, we modulated the electrolyte's pH, adjusted  $\text{H}_2\text{SO}_4$  while keeping 0.1 M  $\text{KNO}_3$  constant, and applied a potential of  $-0.7$  V vs. RHE for 1 hour (Fig. S9, ESI<sup>†</sup>). Fig. 4A and B and Fig. S10 (ESI<sup>†</sup>) illustrated that the selectivity and yield of  $\text{NH}_2\text{OH}$  and  $\text{NH}_3$  significantly

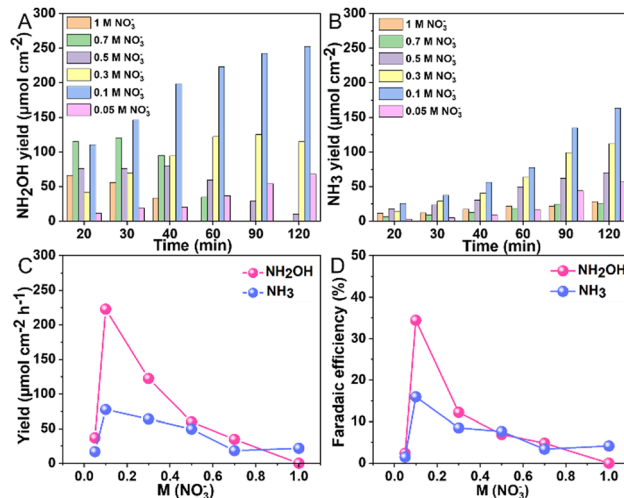


Fig. 3 Variation in  $\text{NH}_2\text{OH}$  (A) and  $\text{NH}_3$  (B) yield rates across different nitrate concentrations at pH 1; performance assessed at an applied potential of  $-0.7$  V vs. RHE over a 2-hour reaction time; (C) yield rates and (D) faradaic efficiency of  $\text{NH}_2\text{OH}$  and  $\text{NH}_3$  across different nitrate concentrations at pH 1 with an applied potential of  $-0.7$  V vs. RHE for a duration of 1 hour.

depended on the acidity of the solution, particularly at pH values below 0.5. The yield of  $\text{NH}_2\text{OH}$  notably increased from  $63.5 \mu\text{mol h}^{-1} \text{cm}^{-2}$  at pH 2 to  $333.1 \mu\text{mol h}^{-1} \text{cm}^{-2}$  at pH 0.3, but then decreased to  $146.6 \mu\text{mol h}^{-1} \text{cm}^{-2}$  at pH 0. Meanwhile, the yield of  $\text{NH}_3$  consistently rose at lower electrolyte pH levels, with a significant uptick observed within the pH range of 0 to 0.5, culminating in a yield of  $792.5 \mu\text{mol h}^{-1} \text{cm}^{-2}$  at pH 0. These data highlight the substantial impact of acidity on the

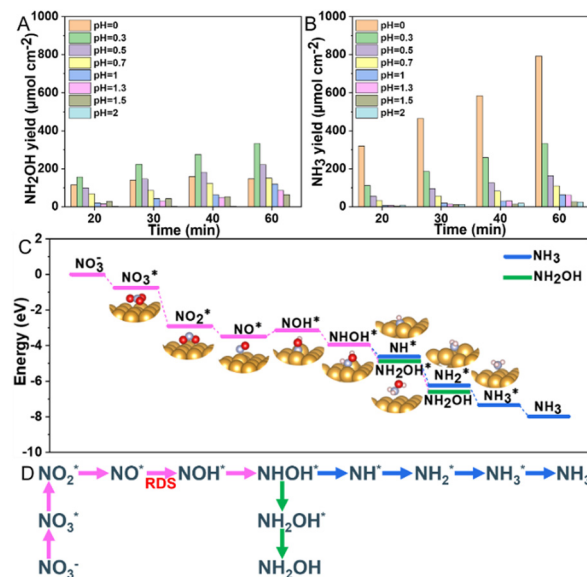


Fig. 4 Yield rates of  $\text{NH}_2\text{OH}$  (A) and  $\text{NH}_3$  (B) across various pH levels, assessed in a solution of 0.1 M  $\text{KNO}_3$  with  $\text{H}_2\text{SO}_4$  adjusting the pH, at an applied potential of  $-0.7$  V vs. RHE for a period of 1 hour; (C) the Gibbs free energy diagram for  $\text{NO}_3\text{RR}$  on Au wire; (D) the possible  $\text{NO}_3\text{RR}$  pathway on the Au electrode.





performance and selectivity of the Au electrode in the reduction of nitrate. At more acidic conditions, there is an increased proton availability facilitating the reaction outlined in eqn (1) and (2) for  $\text{NH}_2\text{OH}$  and  $\text{NH}_3$  production. However, this also favors the competing HER.

To evaluate the stability of the Au wire, five consecutive cycles were performed in 0.1 M  $\text{HNO}_3$  at  $-0.7$  V vs. RHE, with each cycle lasting 1 hour. The consistent  $\text{NH}_2\text{OH}$  yield rate and FE observed indicate the favorable stability of the Au electrode under these conditions (Fig. S11, ESI<sup>†</sup>). SEM analysis of the Au wire after reaction showed preserved surface microstructure, with no apparent damage observed (Fig. S12, ESI<sup>†</sup>). Furthermore, also the XRD patterns remained unchanged (Fig. S13, ESI<sup>†</sup>). The current response results from LSV remained similar except for a slight increase (Fig. S14, ESI<sup>†</sup>), which may be attributed to the improved activation of the catalyst. Elemental analysis *via* inductively coupled plasma mass spectrometry (ICP-MS) analysis evidenced that there was no detectable  $\text{Au}^{3+}$  leaching in the electrolyte after reaction (Table S2, ESI<sup>†</sup>). These results demonstrated that Au wire serves as a robust catalyst under acidic conditions for the  $\text{NO}_3\text{RR}$  conversion to  $\text{NH}_2\text{OH}$  and  $\text{NH}_3$ .

To elucidate the mechanism of nitrate reduction on Au wire, density functional theory (DFT) calculations on Au (111) facet were performed. Fig. 4C details these simulations, which begins with the spontaneous adsorption of nitrate onto the Au electrode surface, marked by a favorable Gibbs free energy change of  $-0.75$  eV. The reduction sequence involves adsorbed nitrate ( $\text{NO}_3^*$ ) being reduced to adsorbed nitrite ( $\text{NO}_2^*$ ) which is then converted to  $\text{NO}^*$ . The subsequent step involves the reduction of this adsorbed nitric oxide to hydroxylamine oxime ( $\text{NOH}^*$ ), identified as the rate-determining step (RDS) in this pathway, requiring an energy of 0.35 eV.  $\text{NOH}^*$  is then further reduced to  $\text{NHOH}^*$ ,  $\text{NH}_2\text{OH}^*$  and finally  $\text{NH}_2\text{OH}$  desorbs. Conversely, the formation of  $\text{NH}_3$  from  $\text{NHOH}^*$  involves multiple steps beginning with  $\text{NHOH}^*$  first converting to  $\text{NH}^*$ , followed by  $\text{NH}_2^*$ , then to  $\text{NH}_3^*$  before  $\text{NH}_3^*$  desorbs to produce  $\text{NH}_3$  (Fig. 4D and Fig. S15, ESI<sup>†</sup>). The lower Gibbs free energies of the formation and the desorption of  $\text{NH}_2\text{OH}^*$  indicate it occurs spontaneously, inherently favoring the formation of  $\text{NH}_2\text{OH}$  (Table S3, ESI<sup>†</sup>). The relatively simplicity of the  $\text{NH}_2\text{OH}$  pathway, compared to the multi-step process required for  $\text{NH}_3$  formation, predominantly drives the selective formation of  $\text{NH}_2\text{OH}$ . The energy barrier of the RDS from Au (0.35 eV) is lower than that of other reported catalysts, such as Ni (0.37 eV),<sup>17</sup> Rh (0.39 eV),<sup>17</sup> Pd (0.72 eV),<sup>17</sup> PdFe (0.74 eV),<sup>18</sup> Cu/Cu<sub>2</sub>O (0.84 eV)<sup>19</sup> and  $\text{Fe}_3\text{C}-\text{Cu}_3$  (1.28 eV)<sup>20</sup> (Table S4, ESI<sup>†</sup>).

In summary, this study establishes Au as a highly effective electrocatalyst for the selective  $\text{NO}_3^-$  reduction to  $\text{NH}_2\text{OH}$ . Through meticulous experimentation involving electrolyte composition, nitrate concentration, pH and applied potential, we achieved an  $\text{NH}_2\text{OH}$  yield of  $230.1 \pm 19 \mu\text{mol h}^{-1} \text{cm}^{-2}$  under optimal conditions. This performance is notably exceeding the yields commonly reported in the literature and achieves a faradaic efficiency of  $34.2 \pm 2.8\%$  at  $-0.7$  V vs. RHE, setting a

new benchmark in electrochemical nitrate reduction. This study provides an understanding of the electrolyte engineering of nitrate solutions and may motivate further studies into gold or other materials to selectively generate  $\text{NH}_2\text{OH}$  and other products from waste nitrates.

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## Data availability

The data supporting this article have been included as part of ESI<sup>†</sup>.

## Conflicts of interest

There are no conflicts to declare.

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