Supporting Information

A new catalyst based on the disposed red mud for the efficient electrochemical reduction of nitrate-to-ammonia

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Experimental Procedures

Material and chemicals

KNO$_3$ [≥ 99%, Aladdin], ethanol [99.8%, Aladdin], KH$_2$PO$_4$ [99.5%, Aladdin], K$_2$HPO$_4$ [99%, Aladdin], KOH [85%, Aladdin], NH$_4$Cl [99.999%, Aladdin], KNO$_2$ [97%, Aladdin], carbon cloth (CC) [W1S1009, CE-Tech Co., Ltd.], Ar gas [99.999%]. All chemicals were used as received without any purification.

Characterization

X-ray diffraction (XRD) was recorded with PANalytical X’Pert Pro MPD. X-ray photoelectron spectrums (XPS) were performed on ESCALAB 250Xi. Scanning electron microscopy (SEM) images were taken with a Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM) and corresponding energy-dispersive X-ray spectroscopy (EDS) images were obtained by the JEM-2100F transmission electron microscope with energy spectrometer. The concentration of NH$_3$/NH$_4^+$ analysis was detected on the ammonia nitrogen analyzer (AMTAX compact II type, HACH co.). The proton nuclear magnetic resonance (1H-NMR) was measured on Bruker AVANCE III 400 MHz system. The analysis of metal element content of red mud was detected on inductively coupled plasma optical emission spectrometer (ICP-OES, OPTIMA 8000DV), in which the samples were fully dissolved by mixed acid solution ($V$(HF): $V$(HNO$_3$): $V$(HCl) = 4:1:3). 77 K N$_2$ sorption isotherms were recorded on Quantachrome Autosorb-iQ-2 apparatu.

Preparation of the working electrode

Massive red muds were ground in an agate mortar and sieved through a 125-μm mesh. The obtained red mud powders were washed by pure water 24 h using a Soxhlet extractor to remove the water-soluble impurities. And then the red muds were dried in an oven at 60 °C.

5 mg red muds were dispersed in 1.2 mL of 1:1 v/v water/ethanol with 20 μL Nafion by one-hour sonication to form a homogeneous suspension. CC (1x1 cm$^2$) was clean by anhydrous alcohol and deionized water for 1 h through ultrasonication prior to red mud deposition. Then the red mud ink was dropped onto carbon cloth to yield a red mud loading of 0.8 mg cm$^{-2}$. As for the pure Fe$_2$O$_3$, the mass loading was reduced to 0.24 mg cm-2 to ensure the same Fe content on working electrode with RM one.

Electrochemical measurements

All electrochemical tests were performed on ZAHNER PP211 and CHI760 electrochemical workstations. The electrolyte solution was bubbled by Ar flow for at least 30 min prior to electrochemical experiments. The electrocatalysis test were performed in a gas-tight H-cells separated by proton exchange membrane (Nafion 211) at room temperature.
The proton exchange membranes were activated in dilute 5 wt% H$_2$SO$_4$ aqueous solution at 80 $^\circ$C for 0.5 h, and then washed by copious amounts of water and soaked in distilled water for at least 3 h. 15 mL of electrolyte was used in the cathodic chamber.

For the three-electrode system, an ultra-pure graphite rod and an Ag/AgCl electrode saturated KCl solution ($E(\text{Ag/AgCl}) = 0.197$ V) were employed as the counter electrode and the reference electrode, respectively. A red mud coated CC (1×1 cm$^2$) was the working electrode. All potentials in this work were expressed in the reference of RHE, which can be calculated by the Nernst equation:

$$E(\text{RHE}) = E(\text{experiment}) + 0.059\text{pH} + E(\text{Ag/AgCl})$$

where $E(\text{RHE})$ is the converted potential and $E(\text{experiment})$ is the measured potential.

For the three-electrode system, a nickel foam was used as anode and 1 M KOH aqueous solution as anodic electrolyte.

All linear sweep voltammetry (LSV) curves were tested with a scan rate of 10 mV s$^{-1}$ without iR compensation. The catalytic performance was evaluated under chronoamperometry mode for 0.5 h with magnetic stirring (900rpm).

Solar-driven NARR tests were powered by the ABET Sun 3000 solar simulator at different light intensities (0.04, 0.05, 0.06, 0.07, 0.08, 0.09 and 0.10 W cm$^{-2}$) for 30 mins.

The $\text{FE}_{\text{NH}_3}$, $r_{\text{NH}_3}$, $\text{EE}_{\text{NH}_3}$, $\text{EE}_{\text{Solar-to-NH}_3}$ were calculated according to the following equations:

$$\text{FE}_{\text{NH}_3} (%) = 8 \times F \times c(\text{NH}_3) \times V / Q \times 100%$$

$$r_{\text{NH}_3} \text{ (mmol cm}^{-2}\text{ h}^{-1}) = c(\text{NH}_3) \times V / (A \times t)$$

$$\text{EE}_{\text{NH}_3} (%) = c(\text{NH}_3) \times V \times \Delta H_m / (U \times I \times t)$$

$$\text{EE}_{\text{Solar-to-NH}_3} (%) = c(\text{NH}_3) \times V \times \Delta H_m / (L \times A_{\text{PVC}})$$

where $F$ is the Faradaic efficiency, 96485 C mol$^{-1}$; $c(\text{NH}_3)$ is the concentration of NH$_3$; $V$ is the volume of cathodic electrolyte, 15 mL; $Q$ is the integrated charge during NARR test; $A$ is the electrode surface area, 1 cm$^2$; $t$ is the electrolysis time, 1800 s; $\Delta H_m$ is calculated according to the overall reaction of KNO$_3$ + 2H$_2$O $\rightarrow$ NH$_3$(g) + KOH+ 2O$_2$(g), 595.5 kJ mol$^{-1}$; $U$ is the total cell voltage; $I$ is the electrolysis current; $L$ is the light intensity of sun simulator; $A_{\text{PVC}}$ is the area of the photovoltaic cell, 210 cm$^2$.

For the long-term recycle test, electrolysis under −0.73 V (vs. RHE) lasting 4 hours for each cycle was performed by chronoamperometry with the electrolyte containing 1.0 M PBS and 1.0 M KNO$_3$. After finishing electrolysis of each cycle, we replaced the electrolyte with a refresh one while the same working electrode is maintained for the next cycle.

**Ammonia detection and quantification**
1 mL sample solution was diluted into 10 mL prior to NH₃ detecting. The concentration of NH₃ was determined according to colorimetric methods by an ammonia nitrogen analyzer (HACH AMTAX compact II type). The calibration curve between concentration of NH$_3$/NH$_4^+$ and absorbance was shown as follows:

![Calibration Curve for NH₃](image)

\[ y = 8.40x + 0.0224 \]
\[ R^2 = 0.9995 \]

**Nitrite detection and quantification.**

1 mL sample solution was diluted into 10 mL prior to NO$_2^-$ detecting. 0.4 mL sulfanilic acid solution (4 g/L sulfanilic acid in 20% HCl) was mixed with 10 mL nitrite-containing sample. After standing for 5 mins, 0.2 mL N-(1-naphthyl)-ethylenediamine dihydrochloride solution (2 g/L) was added and the mixture was further stand for 15 mins. Finally, the solution was detected at 550 nm. The calibration curve between concentration of NO$_2^-$ and absorbance was shown as follow:

![Calibration Curve for NO₂⁻](image)

\[ y = 8.26x + 0.207 \]
\[ R^2 = 0.9997 \]

**Explanation on the FE$_{NH3}$ evolutions upon nitrate concentrations and electrolysis times**

The insight of FE$_{NH3}$ evolutions upon nitrate concentrations and electrolysis time are probably related to the evolution of reactants and products in the electrolyte solution. Notably, the electrolysis cell is a closed system, leading
all concentrations of reactants, products and by-products changes along the electrolysis time. And the reaction pathway of NARR on the catalyst surface could likely be a stepwise hydrogenation process: $\text{NO}_3^- + \text{H}_2\text{O} \rightarrow \text{NO}_x\text{H}_y \rightarrow \text{NH}_3$. Meanwhile, there is a competing side reaction potentially: $\text{H}_2\text{O} \rightarrow \text{H}_2$. And the surface coverage ($\theta$) of $\text{NO}_3^- (\theta_{\text{NO}_3^-})$, $\text{H}_2\text{O} (\theta_{\text{H}_2\text{O}})$ and $\text{NH}_3 (\theta_{\text{NH}_3})$ are respectively related to concentrations of reactants and products based on their adsorption equilibriums thermodynamically.

Initially only $\text{NO}_3^-$ and $\text{H}_2\text{O}$ exist on the catalyst surface, in favor for its transformation toward the intermediate $\text{NO}_x\text{H}_y$. And the formation of $\text{NH}_3$ is naturally accelerated upon the increase of $\theta$ of $\text{NO}_x\text{H}_y (\theta_{\text{NO}_x\text{H}_y})$. As the reaction proceeds and the $\text{NH}_3$ concentration increases, the forward of the reaction toward $\text{NH}_3$ is gradually balanced by the backward one and responds a drop in $\text{FE}_{\text{NH}_3}$ consequently. Therefore, the highest $\text{FE}_{\text{NH}_3}$ is achieves at the first 30 mins and declines along reaction time prolonging in Fig. S9. By the way, this is also the reason that $\text{FE}_{\text{NH}_3}$ per cycle in the long-term recycling test is lower than 92.8%.

Effect on concentration can be explained by a similar mechanism. The concentration of $\text{NO}_3^-$ determines $\theta$ of $\text{NO}_3^-$ ($\theta_{\text{NO}_3^-}$) on the catalyst surface, also involving $\text{H}_2\text{O} (\theta_{\text{H}_2\text{O}})$ in the electrolyte. The raising $\text{NO}_3^-$ concentration increases $\theta_{\text{NO}_3^-}$, while naturally decreases $\theta_{\text{H}_2\text{O}}$. A relatively low $\theta_{\text{NO}_3^-}$ likely inhibits NARR by some side reactions (such as HER). Conversely, a decreased $\theta_{\text{H}_2\text{O}}$ (available activated hydrogen) further likely resulted in the incomplete hydrogenation of $\text{NO}_3^-$. Therefore, the increase of nitrate concentration results in the drop of $\text{FE}_{\text{NH}_3}$. A 1.0 M in nitrate concentration here is just around the critical point and provides an optimal ratio of $\theta_{\text{NO}_3^-}/\theta_{\text{H}_2\text{O}}$, as thus a highest $\text{FE}_{\text{NH}_3}$.

The motivation of the initial water washing operation for RM sample

The RM contains a number of contaminants. We removed water soluble part, such as residual alkali, mainly because of the NARR tests in aqueous solution, where the water-soluble contaminations might be dissolved by the electrolyte solution to impact NARR tests regarding likely effects on the surface structures of RM samples and the NARR pathway and performance. With these concerns, we performed the water-washing procedure to remove the water-soluble contaminants on the RM surface prior to be as NARR catalysts.

Involvement of different components in RM for NARR

Among different metal oxides species in RM, $\text{Fe}_2\text{O}_3$ severs as the major active species as NARR catalysis while Ti atoms intergrown in $\text{Fe}_2\text{O}_3$ lattices synergistically help to promote its NARR activity and the $\text{NH}_3$ selectivity. While, $\text{Al}_x\text{Si}_y\text{O}_z$ species (such as AIOOH in RM, Cancrinite and Katoite) serve as porous matrixes to support catalysts, increasing active surface area.
The reason of suppressing the HER

(1) As we known, the acidic media can promote the HER process for most of HER catalysts, those catalysts can merely perform outstandingly in the neutral condition. Thus, the neutral pH environment in this study helps the suppression of its HER activity to some extent.

(2) As for the presence of nitrate, on the one hand, the competitive adsorption of *NO$_3$ reduces the similar *H adsorption and its surface coverage, consequently decreasing the tendency from *H toward H$_2$. Moreover, the proton transfer energy can be decreased by switching the reaction pathway from HER to NARR, resulting in selective reaction toward NARR (*J. Mater. Chem. A, 2022, DOI: 10.1039/D2TA04707A*).
Fig. S1 HRTEM image of RM. For image filtering, the selected local regions were firstly performed a Fast Fourier Transform (FFT) followed by an inverse FFT using the Gatan Digital Micrographic. And then the lattice spacing was directly measured by the line profile tool and calculated by averaging the results over at least three periods.

Fig. S2 HRTEM image of RM.
Fig. S3 SEM image of RM.

Fig. S4 High resolution Fe2p XPS profile for RM.

Fig. S5 Compositions of RM based on ICP-OES.
**Fig. S6** (a) 77 K N₂ sorption isotherms of RM and (b) the corresponding pore diameter distribution.

**Fig. S7** CV curves for RM in 1 M PBS with and without KNO₃. Notably, a dramatic increase on current response is observed in the presence of nitrate. However, both oxidation and reduction peaks also can be observed in the absence of nitrate, demonstrating those peaks are not associated with nitrate. Associating with previous reports (*Sci. Rep.*, 2021, 11, 5185), it seemed to be related to an electrode surface process and not to charge transfer processes with nitrate. These peaks can be associated to ferric reduction and iron oxidation, as marked in the Figure.
Selectivities of NH$_3$ and NO$_2^-$ during NARR. Notably, the current closed electrolysis system maintains the changing concentrations of all species in its reaction operation. Regarding the NO$_2^-$ as the incomplete hydrogenation product in the NARR process, the chemical equilibrium on the electrode surface can be simplified as \( \text{**NO}_3 \rightleftharpoons \text{**NO}_2 \rightleftharpoons \text{**NH}_3 \). The initial coverages of \( \text{**NO}_2 \) and \( \text{**NH}_3 \) are 0, and it exhibits the intrinsic catalytic activity and a higher NH$_3$ selectivity at the initial 30 mins, which is reasonably set as the reaction time for the evaluation of the catalyst activity. The further prolonged until 2 h starts the gradual \( \text{**NH}_3 \) accumulation likely increases the suppression of the \( \text{**NO}_2 \) to \( \text{**NH}_3 \) conversion, affording an increased selectivity toward NO$_2^-$. Similarly, the increased coverage of \( \text{**NO}_2 \) will accelerate the NH$_3$ production, leading a gradually increased NH$_3$ selectivity after 2 h. This mechanism consequently determines the drop and later recovered NH$_3$ selectivity.
**Fig. S10** XRD patterns before and after NARR.

**Fig. S11** Fe2p XPS profiles before and after NARR.
Fig. S12 HRTEM image of the RM sample after NARR test.

Fig. S13 XRD pattern for pure Fe$_2$O$_3$ sample.
**Fig. S14** SEM image for pure $\text{Fe}_2\text{O}_3$ sample.

**Fig. S15** CV test in non-faradaic range with different scan rates for RM.

**Fig. S16** CV test in non-faradaic range with different scan rates for pure $\text{Fe}_2\text{O}_3$ sample.

**Fig. S17** ECSA fittings of RM and pure $\text{Fe}_2\text{O}_3$. 
Fig. S18 (a) 77 K N₂ sorption isotherms of Fe₂O₃ and (b) the corresponding pore diameter distribution. From the isotherms it can be clearly observed that the surface area of Fe₂O₃ is smaller than RM, and the pore diameter distribution reveals only a small amount of mesopores with ca. 5.6 nm, consisting well with the ECSA results (Fig. S17).

Fig. S19 Comparison of charge at different potentials between RM and pure Fe₂O₃.
**Fig. S20** EIS fitting results of (a) RM and (b) Fe$_2$O$_3$. Notably, the solution resistance ($R_s$), actually including the electrode resistance, of RM is slightly larger than Fe$_2$O$_3$. Considering to the same electrolyte solution, this is possibly due to the higher resistance of RM as the presence of its original Al$_x$Si$_y$O species.

**Fig. S21** Comparison of $r_{\text{NH}_3}$ at different potentials between RM and pure Fe$_2$O$_3$.

**Fig. S22** Gibbs free energy diagram based on the DFT calculation for Fe$_2$O$_3$ and Ti-doped Fe$_2$O$_3$. Reaction pathway: * →
*NO₃ → *NO₂ → *ON → *ONH → *ONH₂ → *ONH₃ → *O → *OH → *.

It can be found that the last step, the step of “*ON + H⁺ + e⁻ → *ONH”, undergoes the highest Gibbs free energy (ΔG) change of +2.076 eV for Fe₂O₃. While the highest ΔG step is merely +0.529 eV for the Ti-doped Fe₂O₃. Therefore, results reveal that the dopant Ti atoms can insightfully drop the reaction barrier and thus enhance the NARR performance toward the increase of the NH₃ selectivity.

The overall electrocatalytic NARR process “NO₃⁻ + 9H⁺ + 8e⁻ → NH₃ + 3H₂O” can be described as nine elementary steps:

<table>
<thead>
<tr>
<th>Step 1: * + NO₃⁻ → *NO₃ + e⁻</th>
<th>Step 2: *NO₃ + 2H⁺ + 2e⁻ → *NO₂ + H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 3: *NO₂ + 2H⁺ + 2e⁻ → *ON + H₂O</td>
<td>Step 4: *ON + H⁺ + e⁻ → *ONH</td>
</tr>
<tr>
<td>Step 5: *ONH + H⁺ + e⁻ → *ONH₂</td>
<td>Step 6: *ONH₂ + H⁺ + e⁻ → *ONH₃</td>
</tr>
<tr>
<td>Step 7: *ONH₃ → *O + NH₃</td>
<td>Step 8: *O + H⁺ + e⁻ → *OH</td>
</tr>
<tr>
<td>Step 9: *OH → * + H₂O</td>
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</tbody>
</table>

To avoid calculating the energy of charged NO₃⁻ directly, gaseous HNO₃ is chosen as a reference (Adv. Funct. Mater. 2021, 31, 2008533; ACS Catal. 2022, 12, 8698–8706). As a result, the NO₃⁻ adsorption can be described as * + HNO₃(g) → *NO₃ + H⁺ + e⁻.

Correspondingly, the adsorption energy of NO₃⁻, which is defined as ΔG(*NO₃), can be approximated by ΔG(*NO₃) = G(*NO₃) – G(*) - G(HNO₃, g) + 1/2 G(H₂) + 0.3917 eV

where G(*NO₃) is the Gibbs free energy of NO₃⁻ adsorbed on catalysts; G(*) is the free energy of catalysts, and G(HNO₃, g); G(H₂, g) are the free energy of HNO₃ and H₂ molecules in the gas phase, respectively.

In the view of computational hydrogen electrode (CHE) model, the ΔG of each elementary step is defined as ΔG = ΔE + ΔZPE - TΔS + ΔGₚH

where ΔE denotes the energy change obtained from DFT calculations; ΔZPE and ΔS are the correction of zero-point energy and entropy, respectively; T is equal to 298.15 K. The pH effect can be corrected by ΔGₚH = pH × kₐ ln 10.
Fig. S23 Solar-driven NARR in NH$_3$ production as well as carbon emission reduction under different light intensities. Notably, the carbon emission reduction was calculated based on the carbon footprint (about 2.16 tons of CO$_2$ emission per ton of NH$_3$ produced) in Haber-Bosch process.$^{1,2}$
Table S1. Comparison of NARR performance between RM and other reported NARR catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Mediums</th>
<th>E / V vs. RHE</th>
<th>$\text{FE}_{\text{NH}_3}$ / %</th>
<th>$r_{\text{NH}_3}$ / mmol cm$^{-2}$ h$^{-1}$</th>
<th>$\text{EE}_{\text{NH}_3}$ / %</th>
<th>Electric power consumption / kWh kg$\text{NH}_3^{-1}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>RM</td>
<td>1 M PBS + 1 M KNO$_3$</td>
<td>-0.73</td>
<td>92.8</td>
<td>0.16</td>
<td>33.2%</td>
<td>29.4</td>
<td>This work.</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/SS</td>
<td>0.1 M NaOH + 0.1 M NaNO$_3$</td>
<td>-0.5</td>
<td>91.5</td>
<td>0.596</td>
<td>-</td>
<td>-</td>
<td>Nano Res. 2022, 15, 3050</td>
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<tr>
<td>Co-doped Fe/Fe$_2$O$_3$</td>
<td>0.1 M Na$_2$SO$_4$ + 500 ppm NO$_3$-N</td>
<td>-0.75</td>
<td>85.2</td>
<td>0.0886</td>
<td>-</td>
<td>-</td>
<td>Proc. Natl. Acad. Sci. U.S.A. 2022, 119, e2115504119</td>
</tr>
<tr>
<td>FeOOH/CP</td>
<td>0.1 M PBS + 0.1 M NaNO$_3$</td>
<td>-0.5</td>
<td>92</td>
<td>0.053</td>
<td>-</td>
<td>-</td>
<td>ACS Appl. Mater. Interfaces 2022, 14, 17312</td>
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<tr>
<td>2D Fe-cyano</td>
<td>1 M KOH + 0.1 M KNO$_3$</td>
<td>-0.5</td>
<td>90.2</td>
<td>4.95</td>
<td>26.2</td>
<td>-</td>
<td>ACS Nano 2022, 16, 1072</td>
</tr>
<tr>
<td>TiO$_2$ microspheres</td>
<td>1.0 M PBS + 0.4 M KNO$_3$</td>
<td>-1.0</td>
<td>90.5</td>
<td>0.160</td>
<td>-</td>
<td>-</td>
<td>ChemSusChem 2022, e202102450</td>
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<td>Fe-doped Co$_3$O$_4$</td>
<td>0.1 M PBS + 50 mM KNO$_3$</td>
<td>-0.7</td>
<td>95.5</td>
<td>0.0367</td>
<td>-</td>
<td>-</td>
<td>J. Colloid Interface Sci. 2022, 615, 636</td>
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<td>Fe-PPy SACs</td>
<td>0.1 M KOH + 0.1 M KNO$_3$</td>
<td>-0.7</td>
<td>98.4</td>
<td>0.16</td>
<td>27.5</td>
<td>24.38</td>
<td>Energy Environ. Sci. 2021, 14, 3522</td>
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<td>Fe SAC</td>
<td>0.50 M KNO$_3$ + 0.10 M K$_2$SO$_4$</td>
<td>-0.66</td>
<td>75</td>
<td>0.308</td>
<td>-</td>
<td>-</td>
<td>Nat. Commun. 2021, 12, 2870</td>
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<td>Strained Ru nanoclusters</td>
<td>1 M KOH + 1 M KNO$_3$</td>
<td>-0.2</td>
<td>~100</td>
<td>1.029</td>
<td>26.6</td>
<td>25.6</td>
<td>J. Am. Chem. Soc. 2020, 142, 5702</td>
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<td>Cu-Ni alloy</td>
<td>1 M KOH + 1 M KNO$_3$</td>
<td>-0.15</td>
<td>~100</td>
<td>4.16</td>
<td>29.71</td>
<td>17.41</td>
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<td>Cu/Cu$_2$O</td>
<td>0.5 M</td>
<td>-0.85</td>
<td>81.2</td>
<td>0.24</td>
<td>16.01</td>
<td>26.23</td>
<td>Angew. Chem.</td>
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<td>nanowire arrays</td>
<td>Na$_2$SO$_4$ + 200 ppm NaNO$_3$-N</td>
<td></td>
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<td>( \text{Int. Ed. 2020, 59, 5350} )</td>
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<tr>
<td>O-Cu–PTCDA</td>
<td>0.1 M PBS + 500 ppm KNO$_3$</td>
<td>-0.4</td>
<td>77</td>
<td>0.0256</td>
<td>19.37</td>
<td>20.56</td>
<td>( \text{Nat. Energy 2020, 5, 605} )</td>
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<tr>
<td>Au/C</td>
<td>0.5 M K$_2$SO$_4$ + 1 mM KNO$_3$</td>
<td>-0.3</td>
<td>26</td>
<td>( 1.58 \times 10^{-3} )</td>
<td>6.97</td>
<td>19.30</td>
<td>( \text{ACS Energy Lett. 2020, 5, 2095} )</td>
</tr>
<tr>
<td>TiO$_{2-x}$ NTs</td>
<td>0.5 M Na$_2$SO$_4$ + 50 ppm nitrate N (NaNO$_3$)</td>
<td>-1.6 (vs. SCE)</td>
<td>87.1</td>
<td>0.045</td>
<td>16.43</td>
<td>27.41</td>
<td>( \text{ACS Catal. 2020, 10, 3533} )</td>
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</table>

References