Supporting Information

Pd Doping-weakened Intermediate adsorption to Promote Electrocatalytic Nitrate Reduction on TiO$_2$ Nanoarrays for Ammonia Production and Energy Supply with Zinc-Nitrate Batteries

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S1. Experiment section

Chemicals

Sulfuric acid (H$_2$SO$_4$, 98%), palladium chloride (PdCl$_2$, 99.99%), deuterium oxide (D$_2$O, 99.9 atom % D), hydrochloric acid (HCl, 37%), lithium chloride anhydrous (LiCl, 99.0%), sodium hydroxide (NaOH, > 98%), sodium hypochlorite solution (NaClO, available chlorine 4.0 %), p-Dimethylaminobenzaldehyde (C$_9$H$_{11}$NO), lithium nitrate (LiNO$_3$, 99.99%), salicylic acid (C$_7$H$_6$O$_3$, 99%), ethanol (C$_2$H$_5$OH, 99.7%), hydrogen peroxide (H$_2$O$_2$, 30%), trisodium citrate (C$_6$H$_5$Na$_3$O$_7$, 98%), sodium nitroferricyanide dehydrate (C$_5$FeN$_6$Na$_2$O·2H$_2$O, 99%), 2-propanol (C$_3$H$_8$O, 99.5%), titanium butoxide (C$_{16}$H$_{36}$O$_4$Ti, 99%), N-(1-naphthyl) ethylenediamine dihydrochloride (C$_{12}$H$_{14}$N$_2$·2HCl, 98%), tetrahydrofuran (C$_4$H$_8$O, 99.5%), trimethylamine (C$_3$H$_9$N, 30 wt.% in H$_2$O), and 1-butyl-3-methylimidazolium chloride (C$_8$H$_{15}$ClN$_2$, 97%) were purchased from Shanghai Macklin Biochemical Co., Ltd. Nitric acid (65%) was purchased from Sigma-Aldrich. Ar gas (99.999 % purity) were supplied by Linde HKO Ltd. W1S1005 carbon cloth was purchased from Fuel Cell Store Ltd.

Synthesis of TiO$_2$ array on CC

The CC-supported TiO$_2$ array was prepared by a seed-assisted approach. Typically, the CC (3 cm×5 cm) was pre-treated by acetone and ethanol several times and then dried at room temperature. The dried CC was immersed in 2-propanol solution containing 0.075 M titanium butoxide and tried in an oven at 60°C for 3 times. Then, the CC was subjected to heat treatment in air at 500°C for 30 min to form TiO$_2$ seeds. Subsequently,
the TiO$_2$ seed decorated CC was placed into a Teflon-lined stainless-steel autoclave (80 mL) which contains 30 mL 2-propanol, 30 mL concentrated HCl, and 1.32 mL titanium butoxide, and then the stainless steel autoclave was transferred to an oven at 150°C for 6 h. when autoclave was cooled down to room temperature, the CC was removed from it and rinsed with distilled water several times and dried. The Ti(OH)$_2$Cl$_2$(OH)$_2$ precursor nanoarray on CC was obtained. Finally, the precursor array was annealed at 550°C under ambient conditions for 4 hours to form TiO$_2$ array on CC with the loading mass of around 10 mg/cm$^2$.

**Synthesis of Pd/TiO$_2$ array on CC**

Pd/TiO$_2$ array was prepared by ion exchange between Pd$^{2+}$ and H$^+$. Typically, 3 cm×5 cm Ti(OH)$_2$Cl$_2$(OH)$_2$ precursor array was transferred into a Teflon-lined stainless steel autoclave (80 mL) which contains 10 mM PdCl$_2$ and 20 mM HCl. Then the autoclave was placed in an oven at 90°C for 12 h. After cooling down to room temperature, the as-obtained array was rinsed with distilled water for 3 times and annealed at 550°C for 4 hours in the Ar atmosphere. Lastly, the Pd/TiO$_2$ array on CC was obtained with the loading mass of around 10 mg/cm$^2$.

**Synthesis of Pd/TiO$_2$ NPs**

2 g of commercial TiO$_2$ NPs (anatase phase) was annealed at 950°C for 6 h under ambient conditions to obtain rutile TiO$_2$ nanoparticles. Then, 0.5 g of rutile TiO$_2$ NPs was placed into a Teflon-lined stainless steel autoclave (80 mL) which contains 10 mM PdCl$_2$ and 20 mM HCl. Afterward, the autoclave was transferred to an oven at 90°C for
12 h. After cooling down, Pd/TiO\textsubscript{2} NPs was achieved by washing TiO\textsubscript{2} NPs with distilled water for 3 times and annealing at 550°C for 4 hours in the Ar atmosphere.

**Characterization**

The crystalline, morphologies and microstructures of samples were investigated by XRD using a Bruker D2 Phaser diffractometer with Cu K\(\alpha\) irradiation (\(\lambda = 1.54 \text{ Å}\)), field-emission scanning electron microscopy (FEI Quanta 450 FEG) and JEOL-2001F field-emission TEM (JEOL-2001F). The surficial chemical states and compositions of the as-obtained products were investigated by XPS (ESCALB 250) with an Al K\(\alpha\) X-ray beam (E = 1486.6 eV). \(^1\)H-NMR measurements were performed on Bruker 600MHz ASCEND AVANCE III HD Nuclear Magnetic Resonance System (NMR-600). UV-vis spectroscopy measurements were carried out using a UV/VIS Spectrometer Lambda 2S.

**Computational Details**

All the computations were conducted based on the density functional theory (DFT) using the Cambridge Sequential Total Energy Package (CASTEP) code of the Mastersials Studio 2018 software. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional were used to describe the electronic exchange and correlation effects. The kinetic-energy cutoff was set as 500 eV. The geometry optimization within the conjugate gradient method was performed with forces on each atom less than 0.05 eV/Å. An energy tolerance is \(5.0 \times 10^{-6}\) eV per atom, and a maximum displacement of 0.001Å was considered. A p(1 \times 3) unit cell of TiO\textsubscript{2} (110)
surface with a two-layer model of the crystal plane was used to simulate the exposed surface of the catalysts accompanying with a sufficient vacuum gap of 15 Å. Bottom atomic Ti-O layer was fixed while other layers and the adsorbates were fully relaxed during structural optimizations. The Brillouin zone was sampled by a k-point mesh of $4 \times 4 \times 1$.

The $\text{NO}_3^-$ reduction reaction on the catalysts surfaces was simulated according to the following reactions (J. Am. Chem. Soc. 2020, 142, 5702-5708):

\begin{align*}
&\text{NO}_3^- + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{NO}_2 + 2\text{OH}^- \\
&\text{NO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{NO} + 2\text{OH}^- \\
&\text{NO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{N} + 2\text{OH}^- \\
&\text{N} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{NH} + \text{OH}^- \\
&\text{NH} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{NH}_2 + \text{OH}^- \\
&\text{NH}_2 + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{NH}_3 + \text{OH}^- 
\end{align*}

Where * represent the adsorption site, the free energies for each reaction were given after correction:

$$\Delta G = \Delta E - T\Delta S$$

Where $\Delta E$ is the reaction energy obtained by the difference between reactants and products; $\Delta S$ is the change in entropy for each reaction. Entropy values are taken from the standard database in the NIST webbook (J. Phys. Chem. Ref. Data 1996, 25, 551-603.). The entropies of adsorbate and adsorption site are negligible.

**Electrochemical measurements**
All electrochemical measurements were carried out in the Ar atmosphere. The CC-supported TiO$_2$ or Pd/TiO$_2$ (1×1 cm$^2$), Ag/AgCl (3 M KCl), and Pt plate (1 cm×1 cm) were used as the work electrode, the reference electrode and the counter electrode, respectively. The Pd/TiO$_2$ NPs modified electrode was prepared as following: first, 100 µL of Pd/TiO$_2$ NPs ink with 5 mg/mL of alcohol/water (v/v=1:1) solution was dropped onto a CC (1×1 cm$^2$); then CC with the loading mass of 0.5 mg/cm$^2$ was dried under ambient conditions for 2 hours. Before all electrochemical tests, a 50-cycle CV test with a scan rate of 0.1 V/s was performed to make the catalyst electrode reach the steady-state. LSV tests were conducted with the scan rate of 5 mV/s in the three-electrode system. 40 mL of the Ar-saturated electrolyte containing 1 M LiCl or 1 M LiCl + 0.25 M LiNO$_3$. The chronoamperometry tests were conducted at a series of applied potentials in a typical H-type cell that contains 40-mL electrolyte separated by a membrane (Nafion 117) on the electrochemical workstation (CHI 760E, Chenhua, China). All potentials in this work refer to RHE, E(RHE) = E(Ag/AgCl) + 0.222 + 0.059pH, where pH=7. Nafion membrane was pretreated in 5 wt% H$_2$O$_2$ aqueous solution at 80 °C for 1 h and then in ultrapure water at 80 °C for another 1 h. For isotope labeling experiments, 40-mL solution containing 0.25 M K$^{15}$NO$_3$+1 M LiCl was used as the NORR electrolyte. The 1-h chronoamperometry tests were conducted at the optimal potential of -0.7 V (vs RHE) in the Ar atmosphere. Then, 0.45-mL diluted electrolyte and 0.05-mL deuterium oxide (D$_2$O) were added into the NMR tube for further NMR (600 MHz) detection. The calibration curve was drawn by detecting the adsorption intensities of a series of ($^{15}$NH$_4$)$_2$SO$_4$ with the given concentration in H$_2$SO$_4$
(0.05 M) solution. Finally, the calibration curve was created by using the area integral value of two peaks. EIS measurement was carried out in an H-type cell at 1.27 V (vs Zn) in the frequency range from 0.1 Hz to $10^5$ Hz with 5 mV amplitude.

**Assembly of the zinc-nitrate battery and electrochemical test.**

The CC-supported Pd/TiO$_2$ (1×1 cm$^2$) and Zn plate (1.5×2 cm$^2$) were employed as the cathode for zinc-nitrate battery. A typical H-type cell that contains 20-mL cathode electrolyte (0.25 M LiNO$_3$ + 5 M LiCl) and 20-mL anode electrolyte (5 M KOH) separated by a bipolar membrane (Nafion 117). The discharging polarization curves with a scan rate of 5 mV/s and galvanostatic tests were conducted using CHI 760E workstation and Land 2001A battery test system at room temperature, respectively. After electrochemical test, the electrolyte was diluted 5 times with distilled water, and then diluted to a certain concentration with 1 M LiCl solution for the next detection.

The power density ($P$) of zinc-nitrate battery was determined by $P = I \times V$, where $I$ and $V$ are the discharge current density and voltage, respectively.

The electrochemical reactions in Zn-nitrate battery are presented as following:

Cathode reaction: $\text{NO}_3^- + 7\text{H}_2\text{O} + 8e^- \rightarrow \text{NH}_4\text{OH} + 9\text{OH}^-$

Anode reaction: $4\text{Zn} + 8\text{OH}^- \rightarrow 4\text{ZnO} + 4\text{H}_2\text{O} + 8e^-$

Overall reaction: $4\text{Zn}^+ \text{NO}_3^- + 3\text{H}_2\text{O} \rightarrow 4\text{ZnO} + \text{NH}_4\text{OH} + \text{OH}^-$

Since cathode and anode are separated by a bipolar membrane, the electrode potentials should be calculated individually:

$$E_{\text{cathode}} = -\frac{1}{nF} (\Delta G_{\text{cat}} + RT \ln \frac{[\text{OH}^-]^9[\text{NH}_4\text{OH}]}{[\text{NO}_3^-]})$$

$$= 0.6 \text{ V}$$
\[ E_{\text{anode}} = \frac{-1}{nF} (\Delta G_{\text{ano}} + RT \ln \left[ \frac{1}{[OH^-]^2} \right]) = -1.27 \text{ V} \]

Where \( n, F, \Delta G, R, \) and \( T \) are electron transfer number, the Faraday constant (96485 C/mol), standard molar Gibbs free energy change of chemical reaction at 298 K, gas constant (8.314 J/(mol K)), and reaction temperature (298 K), respectively. The concentrations of [OH\(^-\)] in cathode cell and anode cell are 10\(^{-7}\) and 5 mol/L, respectively. [NO\(_3\)] is 0.25 mol/L. Assuming [NH\(_4\)OH] is 10\(^{-3}\) mol/L in cathode cell. Therefore, we have \( E_{\text{overall}} = E_{\text{cathode}} - E_{\text{anode}} = 1.87 \text{ V} \)

**Determination of ammonia**

The amount of the produced NH\(_3\) was detected with the indophenol blue method. To minimize the experimental error in quantification of ammonia, all data was recorded three times to obtain the error bar. In detail, 1-mL electrolyte was taken out after NO\(_3\)RR test and diluted with 1 M LiCl, and 1.25 mL of solution containing 0.625 M NaOH, 0.36 M salicylic acid and 0.17 M sodium citrate was added. Then 150 \( \mu \)L sodium nitroferricyanide solution (10 mg/mL) and 75 \( \mu \)L NaClO (available chlorine 4.0 wt\%) solution were added. After 2 h under ambient conduction, UV-Vis absorption spectrum was recorded, and the absorbance value was obtained at the wavelength of 658 nm. The standard NH\(_4^+\) solutions with the given concentrations of (NH\(_4\))\(_2\)SO\(_4\) in 0.05 M H\(_2\)SO\(_4\) were prepared for building the calibration curve.

**Determination of hydrazine**
Hydrazine in the electrolytes was also detected by the Watt-Chrisp method. A mixture of ethanol (100 mL), para(dimethylamino) benzaldehyde (2.0 g) and HCl (concentrated, 12 mL) were used as a color reagent. 2-mL color reagent was added into 2-mL of diluted electrolyte. After 30 min, the absorbance was measured at a wavelength of 458 nm. The standard hydrazine monohydrate solutions with the given concentrations of hydrazine in 0.05 M H₂SO₄ were also prepared for building the calibration curves.

**Colorimetric detection of NO₂⁻**

0.10-mL acidic solution containing 2 M HCl and 10 mg/mL sulfanilamide was dropped into 5 mL of standard or the diluted electrolyte in the test tubes. Subsequently, 0.10-mL N-(1-Naphthyl) ethylenediamine dihydrochloride solution (10 mg/mL) was dropped into the solution. After 30 min, the absorbance of NO₂⁻ was achieved between 600 nm and 450 nm. The final absorbance of NO₃⁻ was obtained at 540 nm. The standard calibration curve can be also obtained with the given concentrations of NaNO₂.

**Faradaic efficiency and ammonia yield rate**

FEs and area-normalized yield rates of NH₃, NO₂⁻, and N₂H₄ were calculated:

\[
\text{FE (NH}_3\text{)} = \frac{(8F \times C \times V \times n)}{Q}
\]

\[
\text{Yield rate (NH}_3\text{)} = \frac{(17C \times V \times n)}{(t \times A)}
\]

\[
\text{FE (NO}_2\text{)} = \frac{(2F \times C \times V \times n)}{Q}
\]

\[
\text{Yield rate (NO}_2\text{)} = \frac{(46C \times V \times n)}{(t \times A)}
\]

\[
\text{FE (N}_2\text{H}_4\text{)} = \frac{(7F \times C \times V \times n)}{Q}
\]
Yield rate \((N_2H_4) = (32C \times V \times n) / (t \times A)\)

Where \(F\) is the Faraday constant (96485 C/mol), \(C\) is the measured NH\(_3\) concentration, \(V\) is the volume of electrolyte, \(Q\) is the total charge passed through the electrode, \(n\) is the dilution factor and \(A\) is the geometric area of the working electrode (1×1 cm\(^2\)).
S2. Figures and tables

**Figure S1.** SEM images of the pristine CC (a), TiO$_2$ (b), and Pd/TiO$_2$ nanoarrays (c).

**Figure S2.** EDX spectra for Pd/TiO$_2$ nanoarrays (a) and TiO$_2$ nanoarrays (b).
Figure S3. TEM images (a-b) and EDX elemental mapping of TiO$_2$ nanoarrays.

Figure S4. The high-resolution Pd 3 XPS spectrum of the Pd/TiO$_2$ nanoarrays.
Figure S5. The optimized structures for (a) TiO$_2$ and (b) Pd/TiO$_2$.

Figure S6. DOS of the free NO$_3^-$.
**Figure S7.** Top views of electron density difference mappings for the optimized Pd/TiO$_2$-NO$_3^-$ (a) and TiO$_2$-NO$_3^-$ (b) structures.

**Figure S8.** Stable configurations of the intermediates on TiO$_2$. The most stable adsorption configurations of *NO$_3$, *NO$_2$, *NO, *N, *NH, *NH$_2$, and *NH$_3$. 
Figure S9. Stable configurations of the intermediates on Pd/TiO₂. The most stable adsorption configurations of *NO₃, *NO₂, *NO, *N, *NH, *NH₂, and *NH₃.

As presented in Figures S8-S9, we adopted a side-on adsorption model for NO₃⁻ on the surfaces of TiO₂ and Pd/TiO₂ based on previous works (J. Am. Chem. Soc., 2020, 142, 5702-5708, ACS Catal., 2019, 9, 7052-7064.), where two Ti atoms or a Pd atom and a Ti atom cooperatively act as the active sites for adsorbing NO₃⁻ and proceeding to the subsequent elemental reactions. Pd and Ti atoms in Pd/TiO₂ synergistically promote the NORR process.
Figure S10. (a, c) The cyclic voltammetry profiles obtained on the pristine TiO$_2$ and the Pd/TiO$_2$ nanoarrays at the sweep rates of 20, 40, 60, 80 and 100 mV s$^{-1}$. (b, d) The determination of double layer capacitance for each catalyst.

The ECSA is estimated from the electrochemical double-layer capacitance of the catalytic surface. The double layer capacitance (Cdl) has been calculated based on the plot of current density against scan rate. ECSA of working electrode can be calculated according to the equation:

$$\text{ECSA} = R_f \times S$$

where $S$ is generally equal to the geometric area of electrode (in this work, $S = 1 \text{ cm}^{-2}$). $R_f$ is the roughness factor of working electrode and determined by the relation:

$$R_f = \frac{\text{Cdl}}{40 \mu \text{F cm}^{-2}}$$
Figure S11. LSV curves over the Pd/TiO$_2$ nanoarrays (a) and the TiO$_2$ nanoarrays (b) obtained in 1 M LiCl electrolyte with different LiNO$_3$ that exhibit that both catalysts present the gradual increased current density as the LiNO$_3$ concentration increases in 1 M LiCl electrolyte. Pd/TiO$_2$ delivers a much larger current density in the electrolyte with an identical concentration of NO$_3^-$ than that of TiO$_2$. This demonstrates Pd/TiO$_2$ has the superior capacity of the NORR to TiO$_2$.

Figure S12. ECSA-normalized current densities for TiO$_2$ and Pd/TiO$_2$. 
**Figure S13.** The photograph of the zinc-nitrate battery.

**Figure S14.** $j$-$t$ curves of the NORR with a Zn-nitrate battery system at different current densities.
**Figure S15.** The UV-Vis curves and calibration curves of the electrolyte with the given NH$_3$ concentrations.

**Figure S16.** SEM images of Pd/TiO$_2$ after a 12-h long-term stability test with a Zn-nitrate battery.
Figure S17. CA curves (a) and (b-d) UV-Vis curves of the Pd/TiO$_2$ array electrode achieved in the electrolyte with 0.02 M NaOH, (b) NH$_3$, (c) NO$_2^-$, and (d) hydrazine.

Figure S18. Yields and FEs of the Pd/TiO$_2$ array electrode achieved in the electrolyte with 0.02 M NaOH.
Figure S19. (a) Photographs of the pristine CC and the recycled Zn on CC. (b) SEM image and (c) XRD pattern of the recycled Zn on CC.

Figure S20. UV-Vis curves of the Pd/TiO$_2$ catalyst against various work potentials obtained in NO$_3^-$ electrolyte after the NORR test.
**Figure S21.** CA curves and UV-Vis curves of the TiO$_2$ catalyst against various work potentials obtained in NO$_3^-$ electrolyte after the NORR test.

**Figure S22.** (a-b) Schematic illustrations for the bipolar membrane (a) and the proton exchange membrane (b). (c) EIS plots achieved in two difference cell configurations.
Figure S23. UV-Vis curves and NO$_2^-$ yield and FE of the Pd/TiO$_2$ nanoarrays (a-b) and the TiO$_2$ nanoarrays (c-d) against various work potentials obtained in 1 M LiCl + 0.25 M LiNO$_3$ electrolyte.

Figure S24. The UV-Vis curves and calibration curves of the electrolyte with the given NO$_3^-$ concentrations.
Figure S25. UV-Vis curves and hydrazine yield and FEs of the Pd/TiO$_2$ nanoarrays (a-b) and the TiO$_2$ nanoarrays (c-d) against various work potentials obtained in 1 M LiCl + 0.25 M LiNO$_3$ electrolyte.

Figure S26. The UV-Vis curves and calibration curves of the electrolyte with the given hydrazine concentrations.
Figure S27. (a) XRD pattern and (b) SEM images of Pd/TiO$_2$ NPs.

Figure S28. CA curves (a) and (b-d) UV-Vis curves of the Pd/TiO$_2$ NPs catalyst against various work potentials obtained in NO$_3^-$ electrolyte after the NORR test, (b) NH$_3$, (c) NO$_2^-$ and (d) hydrazine.
**Figure S29.** (a-c) yields and FE of the Pd/TiO\textsubscript{2} NPs catalyst against various work potentials, (a) NH\textsubscript{3}, (b) NO\textsubscript{2}\textsuperscript{-}, and (c) hydrazine. (d) Total FE of the Pd/TiO\textsubscript{2} NPs catalyst achieved at different potentials.

**Figure S30.** (a) \textsuperscript{1}H NMR spectra of the electrolyte and (\textsuperscript{15}NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} reference with the given concentrations. (b) The corresponding calibration curve from \textsuperscript{1}H NMR spectra.
Supporting Information

Table S1. The theoretical data for several types of metal-based batteries.

<table>
<thead>
<tr>
<th>Battery type</th>
<th>Chemical reaction</th>
<th>Theoretical Voltage (V)</th>
<th>Theoretical Capacity* (mAh g⁻¹)</th>
<th>Energy Density* (Wh kg⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>Li-S</td>
<td>2 Li + S = Li₂S</td>
<td>2.2</td>
<td>1167</td>
<td>2566</td>
</tr>
<tr>
<td>Li-O₂</td>
<td>2 Li + O₂ = Li₂O₂</td>
<td>3.0</td>
<td>1168</td>
<td>3504</td>
</tr>
<tr>
<td>Li-CO₂</td>
<td>4 Li + 3CO₂ = C + 2 Li₂CO₃</td>
<td>2.7</td>
<td>67</td>
<td>1809</td>
</tr>
<tr>
<td>Li-N₂</td>
<td>6 Li + N₂ = 2 Li₃N</td>
<td>0.54</td>
<td>2311</td>
<td>1248</td>
</tr>
<tr>
<td>Zn-CO₂</td>
<td>Zn + CO₂ + H₂O = ZnO + HCOOH</td>
<td>0.955</td>
<td>421</td>
<td>402</td>
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<tr>
<td>Al-N₂</td>
<td>2Al + N₂ = 2AlN</td>
<td>0.99</td>
<td>1961</td>
<td>1941</td>
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<tr>
<td>Zn-Air</td>
<td>2 Zn + O₂ = 2 ZnO⁺</td>
<td>1.65</td>
<td>670</td>
<td>1105</td>
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<tr>
<td>Zn-nitrate</td>
<td>4Zn+ NO₃⁻ + 3H₂O → 4ZnO + NH₄OH + OH⁻</td>
<td>1.85</td>
<td>568</td>
<td>1051</td>
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</table>

*This calculated value is based on the reaction products of the battery reaction equation.
Table S2. Performance comparison of the well-developed catalysts for NORR and NRR.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NH$_3$ FE (%)</th>
<th>NH$_3$ Yield (mg·cm$^{-2}$·h$^{-1}$)</th>
<th>Reference</th>
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<tr>
<td>Electro-reduction of nitrate into ammonia</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd/TiO$_2$</td>
<td>92.05</td>
<td>1.12</td>
<td>This work</td>
</tr>
<tr>
<td>PTCDA/O-Cu</td>
<td>77</td>
<td>0.436</td>
<td>S1</td>
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<tr>
<td>TiO$_{2.8}$</td>
<td>85</td>
<td>0.765</td>
<td>S2</td>
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<tr>
<td>Cu/Cu$_2$O NWAs</td>
<td>81.2</td>
<td>0.1633</td>
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<tr>
<td>Ti/RuO$_2$</td>
<td>52.1</td>
<td>0.271</td>
<td>S4</td>
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<tr>
<td>Cu/Ni</td>
<td>76.5</td>
<td>0.35</td>
<td>S5</td>
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<tr>
<td>Fe$^{0}$/Fe$_3$O$_4$</td>
<td>32</td>
<td>0.0775</td>
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<td>Co$_3$O$_4$/Ti</td>
<td>80</td>
<td>0.634</td>
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<tr>
<td>ZVT sheets</td>
<td>6</td>
<td>0.0588</td>
<td>S8</td>
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<tr>
<td>Electro-reduction of N$_2$ into ammonia</td>
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<tr>
<td>Pd$_3$Cu$_1$</td>
<td>1.22</td>
<td>0.0399</td>
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<tr>
<td>Fe/TiO$_2$</td>
<td>25.6</td>
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<td>Bi-TiO$_2$</td>
<td>17.3</td>
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<td>PdPb</td>
<td>5.79</td>
<td>0.02568</td>
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<tr>
<td>TiO$_2$/rGO</td>
<td>3.3</td>
<td>0.01513</td>
<td>S13</td>
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<td>Pd/C</td>
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<td>S14</td>
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<td>PdO/Pd</td>
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<td>PdH</td>
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<td>V-TiO$_2$</td>
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<td>PdRu</td>
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<tr>
<td>TiO$_2$(V$_2$O$_5$)</td>
<td>6.5</td>
<td>0.003</td>
<td>S19</td>
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</tbody>
</table>
S3. Reference


