Supporting Information

Atomically Dispersed Pd on ZrO$_2$ for Efficient Nitrite Electroreduction to Ammonia

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**Experimental section**

7.40 g of ZrO(NO$_3$)$_2$·xH$_2$O and 19.22 g of urea were dissolved in 80 mL of deionized water. And the mixed solution was transferred to a Teflon-lined stainless steel autoclave and kept under 160 °C for 20 h. After cooling, the precipitates were washed with deionized water several times and dried at 80 °C for 12 h. The dried precipitates were then calcined in a muffle furnace at 500 °C for 3 h to obtain ZrO$_2$. To prepare Pd$_1$/ZrO$_2$, an impregnation solution was used by dissolving 0.30 g of PdCl$_2$ in 30 mL of deionized water. The as-prepared ZrO$_2$ was then immersed in impregnation solution for 1 h, followed by drying under vacuum at 110 °C to obtain Pd$_1$/ZrO$_2$.

**Electrochemical experiments**

Electrochemical measurements were carried out on a CHI-760E electrochemical workstation using a three-electrode cell, with Ag/AgCl (saturated KCl), Pt foil and catalyst coated on carbon cloth (CC, 1 × 1 cm$^2$) as reference, counter and working electrodes, respectively. All potentials were referenced to reversible hydrogen electrode (RHE) in terms of $E$ (V vs. RHE) = $E$ (V vs. Ag/AgCl) + 0.198 V + 0.059 × pH. The CC substrate (1×1 cm$^2$) was pretreated by soaking it in 0.5 M H$_2$SO$_4$ for 12 h, and then washed with deionized water several times and dried at 60 °C for 24 h. The catalyst ink was prepared by dispersing 1 mg of the catalysts in 100 μL of ethyl alcohol containing 5 μL of Nafion (5 wt%) under ultrasonication. The catalyst inks were dropped onto CC (0.2 mg·cm$^{-2}$) to form the working electrodes. The electrochemical NO$_2$RR measurements were performed 0.5 M Na$_2$SO$_4$ solution containing 0.1 M NaNO$_2$ using an H-type electrochemical cell separated by a Nafion 211 membrane. After each chronoamperometry test at certain potential for 1 h, the liquid products were analyzed by various colorimetric methods using UV-vis absorbance spectrophotometer (MAPADA P5), while the gas products (H$_2$, N$_2$) were analyzed by gas chromatography (Shimadzu GC2010).

**Determination of NH$_3$**

The generated NH$_3$ was determined by the indophenol blue method$^1$. Typically, 0.5 mL of electrolyte was removed from the electrochemical reaction vessel and...
diluted 50 times with deionized water. Then 2 mL of diluted solution was removed into a clean vessel followed by sequentially adding NaOH solution (2 mL, 1 M) containing C$_7$H$_6$O$_3$ (5 wt.%) and C$_6$H$_5$Na$_3$O$_7$ (5 wt.%), NaClO (1 mL, 0.05 M), and Na$_2$Fe(CN)$_5$NO·2H$_2$O (0.2 mL, 1 wt.%) aqueous solution. After the incubation for 2 h at room temperature, the mixed solution was subjected to UV-vis measurement using the absorbance at 655 nm wavelength. The concentration-absorbance curves were calibrated by the standard NH$_4$Cl solution with a series of concentrations.

**Calculations of NH$_3$ yield rate and NH$_3$-Faradaic efficiency**

\[
\text{NH}_3\text{ yield rate (μg·h}^{-1}·\text{mg}_\text{cat}^{-1}) = \frac{C_{\text{NH}_3} \times V}{t \times A}
\]  

\[
\text{NH}_3 - \text{Faradaic efficiency(%) =} \frac{6 \times F \times C_{\text{NH}_3} \times V}{17 \times Q} \times 100\%
\]

where $c_{\text{NH}_3}$ (μg mL$^{-1}$) is the measured NH$_3$ concentration, $V$ (mL) is the volume of the electrolyte, $t$ (h) is the reduction time, $A$ (cm$^2$) is the surface area of CC (1 × 1 cm$^2$), $F$ (96500 C mol$^{-1}$) is the Faraday constant, $Q$ (C) is the quantity of applied electricity.

**Characterizations**

X-ray diffraction (XRD) pattern was collected on a Rigaku D/max 2400 diffractometer. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a PHI 5702 spectrometer. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were recorded on a Tecnai G2 F20 microscope. Spherical aberration-corrected scanning transmission electron microscopy (AC-STEM) was performed on a Titan Cubed Themis G$^2$ 300 microscope. Online differential electrochemical mass spectrometry (DEMS, QAS 100) was performed by QAS 100 spectrometer. Various products during the electrolysis reactions were monitored at different values of m/z ionic signals.

**Calculation details**

Cambridge sequential total energy package (CASTEP) module was employed for the density functional theory (DFT) calculations. Electron-exchange correlations were represented by the functional of Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA). The van der Waals interactions were
evaluated by employing the Grimme (DFT+D) scheme. The convergence criteria for structure optimization were set to: (1) energy tolerance of $1 \times 10^{-5}$ eV, (2) maximum force tolerance of 0.02 eV Å$^{-1}$, (3) Monkhorst-Pack k-point sampling: $2 \times 2 \times 1$. The cutoff energy for the plane wave basis was set at 420 eV. Monoclinic ZrO$_2$ (-111) was modeled by a $3 \times 3$ supercell, and a vacuum region of 15 Å was used to separate adjacent slabs.

The free energies ($\Delta G$, 298 K) for each reaction were given after correction$^5$:

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

where $\Delta E$ is the adsorption energy, $\Delta ZPE$ is the zero-point energy difference and $T\Delta S$ is the entropy difference between the gas phase and adsorbed state.

The Forcite module was employed for the MD simulations$^6$. The electrolyte system was modeled by a cubic cell with placing catalyst at the center of the cell and randomly filling 1000 H$_2$O, 50 NO molecules, and 50 H atoms. The force field type was chosen as universal. After geometry optimization, the MD simulations were carried out with the total simulation time of 1 ns at a time step of 1 fs. The radial distribution function (RDF) is calculated by$^7$:

$$
g(r) = \frac{dN}{4\pi \rho r^2 dr}
$$

where $dN$ is the amount of NO$_2^-$ in the shell between the central particle $r$ and $r+dr$, $\rho$ is the number density of NO$_2^-$ and H.
Figure S1. TEM image of ZrO$_2$. 
Figure S2. XANES fitted curve to determine the average Pd valence state of Pd$_1$/ZrO$_2$. 

![Graph showing XANES fitted curve for Pd valence state determination.](image)
Figure S3. XPS Pd 3d spectra of Pd$_1$/ZrO$_2$. 
Figure S4. PDOS profiles of ZrO$_2$ and Pd$_x$/ZrO$_2$. 
Figure S5. Average potential profiles along c-axis direction for calculating the work functions (Φ) of (a) ZrO$_2$ and (b) Pd$_1$/ZrO$_2$. 
Figure S6. UV-vis absorption spectra of NH$_4^+$ assays after incubated for 2 h at ambient conditions. (b) Calibration curve used for the calculation of NH$_3$ concentrations.
Figure S7. Chronoamperometry test of ZrO$_2$ in H cell.
Figure S8. Comparison of NO$_2$RR performance between ZrO$_2$ and Pd$_1$/ZrO$_2$. 
Figure S9. CV measurements at different scanning rates and calculated electrochemically active surface area (ECSA) for (a, b) ZrO$_2$, (c, d) Pd$_x$/ZrO$_2$. 
Figure S10. ECSA-normalized NH$_3$ yield rate and FE$_{NH3}$ of ZrO$_2$ and Pd$_1$/ZrO$_2$ at -0.6 V.
Figure S11. Amounts of produced NH$_3$ on Pd$_x$/ZrO$_2$ under different conditions: (1) electrolysis in NO$_2^-$-containing solution at -0.6 V, (2) before electrolysis, (3) electrolysis in NO$_2^-$-free solution at -0.6 V; (4) electrolysis in NO$_2^-$-containing solution at open-circuit potential (OCP).
Figure S12. Alternating cycling test on Pd$_{1}$/ZrO$_2$ with/without NO$_2^-$ at -0.6 V.
Figure S13. Free energy diagrams of various NO$_2$RR pathways (NHO/NOH) on ZrO$_2$. 

Reaction coordinate

Free Energy (eV)

ZrO$_2$
Figure S14. Free energy diagrams of various NO$_2$RR pathways (NHO/NOH) on Pd$_{1}$/ZrO$_2$. 
Figure S15. Optimized structures of the reaction intermediates involved in NHO/NOH pathways on ZrO$_2$. 
Figure S16. Optimized structures of the reaction intermediates involved in NHO/NOH pathways on Pd$_1$/ZrO$_2$. 
Figure S17. Online DEMS spectra of ZrO$_2$ during NO$_2$RR electrolysis at -0.6 V.
Figure S18. *NO₂/*H snapshots of Pd₁/ZrO₂ before and after simulation.
Table S1. Pd K-edge EXAFS fitting results of Pd$_1$/ZrO$_2$.

| Sample      | Shell | CN | R (Å) | $\sigma^2 (10^{-3} \text{Å})$ | $|\Delta E_0| (\text{eV})$ | R factor |
|-------------|-------|----|-------|----------------------------|-----------------|---------|
| Pd$_1$/ZrO$_2$ | Pd-O  | 1.25 | 2.01  | 6.1                        | 4.9             | 0.12    |
|             | Pd-Zr | 1.17 | 2.78  |                            |                 |         |

CN is the coordination number, R is interatomic distance, $\sigma^2$ is Debye-Waller factor, $\Delta E_0$ is edge-energy shift, R factor is used to value the goodness of the fitting.
Table S2. Comparison of the optimum NH₃ yield and FE₅NH₃ for the recently reported state of the art NO₂RR electrocatalysts at ambient conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>NH₃ yield rate (μmol h⁻¹ cm⁻²)</th>
<th>FE₅NH₃ (%)</th>
<th>Potential (V vs RHE)</th>
<th>Ref</th>
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<tbody>
<tr>
<td>P-TiO₂/TP</td>
<td>0.1 M Na₂SO₄ (0.1 M NO₂⁻)</td>
<td>560.8</td>
<td>90.6</td>
<td>-0.6 V</td>
<td>8</td>
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<tr>
<td>Cu₃P NA/CF</td>
<td>0.1 M PBS (0.1 M NaNO₂)</td>
<td>95.7±2.1</td>
<td>91.2±2.5</td>
<td>-0.5 V</td>
<td>9</td>
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<tr>
<td>Ag@NiO/CC</td>
<td>0.1 M NaOH (0.1 M Na₂O₃)</td>
<td>338.3</td>
<td>96.1</td>
<td>-0.7 V</td>
<td>10</td>
</tr>
<tr>
<td>CoP NA/TM</td>
<td>0.1 M PBS (500 ppm NO₂⁻)</td>
<td>132.7±3.0</td>
<td>90.0±2.3</td>
<td>-0.2 V</td>
<td>11</td>
</tr>
<tr>
<td>ITO@TiO₂/TP</td>
<td>0.5 M LiClO₄ (0.1 M NO₂)</td>
<td>411.3</td>
<td>82.6</td>
<td>-0.5 V</td>
<td>12</td>
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<tr>
<td>Pd/CuO NOs</td>
<td>0.1 M K₂SO₄ (0.01 M KNO₂)</td>
<td>53.3</td>
<td>91.8</td>
<td>-1.5 V</td>
<td>13</td>
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<tr>
<td>Ni@MDC</td>
<td>0.1 M NaOH (0.1 M NO₂⁻)</td>
<td>300</td>
<td>65.4</td>
<td>-0.8 V</td>
<td>14</td>
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<tr>
<td>CF@Cu₂O</td>
<td>0.1 M PBS (0.1 M NaNO₂)</td>
<td>441.8</td>
<td>94.2</td>
<td>-0.6 V</td>
<td>15</td>
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<tr>
<td>Ni-TiO₂/TP</td>
<td>0.1 M NaOH (0.1 M NO₂⁻)</td>
<td>380.27</td>
<td>94.89</td>
<td>-0.5 V</td>
<td>16</td>
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<tr>
<td>Pd₁/ZrO₂</td>
<td>0.1 M Na₂SO₄ (0.1 M NO₂⁻)</td>
<td>438.06</td>
<td>96.75</td>
<td>-0.6 V</td>
<td>This Work</td>
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</tbody>
</table>
References


7. X. Li, P. Shen, X. Li, D. Ma and K. Chu, Sub-nm RuO$_x$ clusters on Pd metallene for synergistically enhanced nitrate electroreduction to ammonia, *ACS Nano*, 2023, **17**, 1081-1090.


12. S. Li, J. Liang, P. Wei, Q. Liu, L. Xie, Y. Luo and X. Sun, ITO@TiO$_2$ nanoarray: An efficient and robust nitrite reduction reaction electrocatalyst toward NH$_3$ production under ambient conditions, *eScience*, 2022, **2**, 382-388.

