Supporting Information

ZrB$_2$ as an earth-abundant metal diboride catalyst for electroreduction of dinitrogen to ammonia

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Experimental Section

Synthesis of ZrB$_2$ nanocubes

All the chemicals are of analytical grade and used as received. The ZrB$_2$ nanocubes were prepared by a simple molten-salt method based on a reported method with a slight modification[1]. In brief, 1 mmol of ZrCl$_4$ and 2 mmol of MgB$_2$ were vacuum-sealed into a quartz tube, which was then transferred into a furnace. The tube was firstly heated from room temperature to 200 °C with a heating rate of 5 °C min$^{-1}$ and kept for 2 h. Subsequently, the temperature was further increased to 900 °C with a heating rate of 3 °C min$^{-1}$ and kept for another 5 h. After cooling down to room temperature, we got the final ZrB$_2$ nanocubes.

Electrochemical experiments

Electrochemical measurements were carried out on a CHI-760E electrochemical workstation by means of a conventional three-electrode cell. The catalyst dropped on carbon cloth (CC) was used as the working electrode, Ag/AgCl (saturated KCl) electrode was used as the reference electrode, and graphite rod was used as the counter electrode. All potentials were referenced to reversible hydrogen electrode (RHE) by following equation: $E_{\text{RHE}}$ (V)$=E_{\text{Ag/AgCl}}$+0.197+0.059×pH. The CC substrate 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. To prepare working electrode, 1 mg of samples was dispersed in 100 μL of ethyl alcohol/Nafion (1:19 v/v) hybrid solutions and ultrasonically dispersed to form a homogeneous ink. Then, 20 μL of ink was dropped onto the 1×1 cm$^2$ CC substrate (mass loading: 0.2 mg cm$^{-2}$), and dried naturally. The NRR test was performed on an H-type two-compartment electrochemical cell separated by a Nafion 211 membrane [2-4]. The Nafion membrane was pretreated by boiling it in 5% H$_2$O$_2$ solution for 1 h, 0.5 M H$_2$SO$_4$ for 1 h and deionized water for 1 h in turn. Prior to electrolysis, the feeding gases were purified through 0.05 M H$_2$SO$_4$ solution to remove any possible contaminants (NH$_3$ and NO$_x$). During each electrolysis, ultra-high-purity N$_2$ gas (99.999%) was continuously purged into the cathodic chamber at a flow rate of 20 mL min$^{-1}$. After
each NRR electrolysis, the produced NH$_3$ and possible N$_2$H$_4$ were quantitatively determined by the indophenol blue method[5], and approach of Watt and Chrisp[6], respectively.

**Determination of N$_2$H$_4$**

5 mL of electrolyte was removed from the electrochemical reaction vessel. The 330 mL of color reagent containing 300 mL of ethyl alcohol, 5.99 g of C$_9$H$_{11}$NO and 30 mL of HCl were prepared, and 5 mL of color reagent was added into the electrolyte. After stirring for 10 min, the UV-Vis absorption spectrum was measured and the concentration-absorbance curves were calibrated by the standard N$_2$H$_4$ solution with a series of concentrations.

**Determination of NH$_3$**

4 mL of electrolyte was removed from the electrochemical reaction vessel. Then 50 μL of solution containing NaOH (0.75 M) and NaClO ($\rho_{\text{Cl}}=\sim4$), 500 μL of solution containing 0.32 M NaOH, 0.4 M C$_7$H$_6$O$_3$, and 50 μL of C$_5$FeN$_6$Na$_2$O solution (1 wt%) were respectively added into the electrolyte. After standing for 2 h, the UV-Vis absorption spectrum was measured and the concentration-absorbance curves were calibrated by the standard NH$_4$Cl solution with a series of concentrations.

\[
\text{NH}_3 \text{ yield (μg h}$^{-1}$ \text{ mg}^{-1} \text{cat.}) = \frac{c_{\text{NH}_3} \times V}{t \times m}
\]  

Faradaic efficiency was calculated by the following equation:

\[
\text{Faradaic efficiency (％)} = \frac{3 \times F \times c_{\text{NH}_3} \times V}{17 \times Q} \times 100\%
\]

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 and $m$ (mg) is the mass loading of the catalyst on CC. $F$ (96500 C mol$^{-1}$) is the Faraday constant, $Q$ (C) is the quantity of applied electricity.

**Characterizations**

Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray (EDX) were carried out on a Tecnai G$^2$ F20 microscope. X-ray diffraction (XRD) pattern was recorded on a
Rigaku D/max 2400 diffractometer. X-ray photoelectron spectroscopy (XPS) was conducted on a PHI 5702 spectrometer. The UV-vis absorbance measurements were recorded on a MAPADA P5 spectrophotometer. \textsuperscript{1}H nuclear magnetic resonance (NMR) measurements were performed on a 500 MHz Bruker superconducting-magnet NMR spectrometer. Prior to NMR measurements, all the feeding gases were respectively purified by an acid trap (0.05 M H\textsubscript{2}SO\textsubscript{4}) to eliminate the potential NO\textsubscript{x} and NH\textsubscript{3} contaminants [7].

**Calculation details**

Spin-polarized density functional theory (DFT) calculations were carried out using a Cambridge sequential total energy package (CASTEP). The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) functional was used for the exchange-correlation potential [8]. The DFT-D correction method was considered for van der Waals forces. During the geometry optimization, the convergence tolerance was set to be $2.0 \times 10^{-5}$ eV for energy and 0.05 eV Å\textsuperscript{-1} for force. The Brillouin zone was sampled in a 4×4×1 mesh. The electron wave functions were expanded using plane waves with a cutoff energy of 400 eV. The ZrB\textsubscript{2} (001) was modeled by a 2×2 supercell, and a vacuum region of 15 Å was used to separate adjacent slabs.

The Gibbs free energy ($\Delta G$, 298 K) of reaction steps is calculated by [9]:

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

(3)

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 entropies of free gases were acquired from the NIST database.
Fig. S1. (a) UV-vis absorption spectra of indophenol assays with NH$_4$Cl after incubated for 2 h at ambient conditions. (b) Calibration curve used for calculation of NH$_3$ concentrations.
Fig. S2. (a) UV-vis absorption spectra of $N_2H_4$ assays after incubated for 20 min at ambient conditions. (b) Calibration curve used for calculation of $N_2H_4$ concentrations.
Fig. S3. pH effect of 0.5 M LiClO$_4$ on the NH$_3$ yield of ZrB$_2$ NCs
Fig. S4. NH$_3$ yields and FEs of ZrB$_2$ NCs in 0.1 M Na$_2$SO$_4$ electrolyte at various potentials.
Fig. S5. (a, b) Morphologies of ZrB$_2$ NCs and ZrO$_2$ NCs and (c) their NH$_3$ yields at -0.3 V. ZrO$_2$ NCs were prepared by annealing ZrB$_2$ NCs in a muffle furnace at 300 °C for 2 h under air atmosphere.
Fig. S6. UV-vis spectra of the electrolytes (stained with the chemical indicator based on the method of Watt and Chrisp) after 2 h of electrolysis on ZrB$_2$ NCs at various potentials.
Fig. S7. Mass of produced NH$_3$ after NRR electrolysis at various times (1-5 h) on ZrB$_2$ NCs at -0.3 V.
Fig. S8. UV-vis absorption spectra of the electrolytes for initial and post-NRR electrolysis (after 20 h) on ZrB$_2$ NCs at -0.3 V.
Fig. S9. TEM image of ZrB$_2$ NCs after stability test.
Fig. S10. XPS spectra of ZrB<sub>2</sub> NCs after stability test. (a) Zr3d. (b) B1s.
Fig. S11. Projected density of states (PDOS) of ZrB$_2$(001).
Fig. S12. Average potential profiles along c-axis direction for calculating the work function of ZrB$_2$ (001).
Table S1. Comparison of optimum NH$_3$ yield and Faradic efficiency (FE) for recently reported state-of-the-art NRR electrocatalysts at ambient conditions

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Determination method</th>
<th>Optimum Potential (V vs RHE)</th>
<th>NH$_3$ yield</th>
<th>FE (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO particles</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.39</td>
<td>7.92 μg h$^{-1}$ mg$^{-1}$</td>
<td>8.02</td>
<td>[10]</td>
</tr>
<tr>
<td>Mn$_3$O$_4$ nanocubes</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.8</td>
<td>11.6 μg h$^{-1}$ mg$^{-1}$</td>
<td>3</td>
<td>[11]</td>
</tr>
<tr>
<td>La$_2$O$_3$ nanoplate</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.8</td>
<td>17.04 μg h$^{-1}$ mg$^{-1}$</td>
<td>4.76</td>
<td>[12]</td>
</tr>
<tr>
<td>Y$_2$O$_3$ Nanosheet</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.9</td>
<td>1.06 × 10$^{-10}$ mol s$^{-1}$ cm$^{-2}$</td>
<td>2.53</td>
<td>[13]</td>
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<tr>
<td>B$_4$C nanosheet</td>
<td>0.1 M HCl</td>
<td>Indophenol blue method</td>
<td>-0.75</td>
<td>26.57 μg h$^{-1}$ mg$^{-1}$</td>
<td>15.95</td>
<td>[14]</td>
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<tr>
<td>MoS$_2$ nanosheet</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.5</td>
<td>8.08 × 10$^{-11}$ mol s$^{-1}$ cm$^{-2}$</td>
<td>1.17</td>
<td>[15]</td>
</tr>
<tr>
<td>Defect-rich MoS$_2$ nanoflower</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.4</td>
<td>29.28 μg h$^{-1}$ mg$^{-1}$</td>
<td>8.34</td>
<td>[16]</td>
</tr>
<tr>
<td>Au-TiO$_2$ sub-nanocluster</td>
<td>0.1 M HCl</td>
<td>Indophenol blue method</td>
<td>-0.2</td>
<td>21.4 μg h$^{-1}$ mg$^{-1}$</td>
<td>8.11</td>
<td>[17]</td>
</tr>
<tr>
<td>Au nanorods</td>
<td>0.1 M KOH</td>
<td>Nessler’s reagent method</td>
<td>-0.2</td>
<td>1.65 μg cm$^{-2}$ h$^{-1}$</td>
<td>4.02</td>
<td>[18]</td>
</tr>
<tr>
<td>Mo$_2$C/C</td>
<td>0.5 M Li$_2$SO$_4$</td>
<td>Nessler’s reagent method</td>
<td>-0.3</td>
<td>11.3 μg h$^{-1}$ mg$^{-1}$</td>
<td>7.8</td>
<td>[19]</td>
</tr>
<tr>
<td>MXene</td>
<td>0.5 M Li$_2$SO$_4$</td>
<td>Nessler’s reagent method</td>
<td>-0.1</td>
<td>4.7 μg cm$^{-2}$ h$^{-1}$</td>
<td>5.78</td>
<td>[20]</td>
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<tr>
<td>Mosaic Bi nanosheets</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.8</td>
<td>13.23 μg h$^{-1}$ mg$^{-1}$</td>
<td>10.46</td>
<td>[21]</td>
</tr>
<tr>
<td>Porous Au Film</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.2</td>
<td>9.42 μg cm$^{-2}$ h$^{-1}$</td>
<td>13.36</td>
<td>[22]</td>
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<tr>
<td>B-doped graphene</td>
<td>0.05 M H$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.5</td>
<td>9.8 μg cm$^{-2}$ h$^{-1}$</td>
<td>10.8</td>
<td>[23]</td>
</tr>
<tr>
<td>Boron nitride nanosheet</td>
<td>0.1 M HCl</td>
<td>Indophenol blue method</td>
<td>-0.75</td>
<td>22.4 μg h$^{-1}$ mg$^{-1}$</td>
<td>4.7</td>
<td>[24]</td>
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<tr>
<td>Defect-rich fluoro graphene nanosheet</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.7</td>
<td>9.3 μg h$^{-1}$ mg$^{-1}$</td>
<td>4.2</td>
<td>[25]</td>
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<tr>
<td>ZrB$_2$ NCs</td>
<td>0.5 M LiClO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.3</td>
<td>37.7 μg h$^{-1}$ mg$^{-1}$</td>
<td>18.2</td>
<td>This work</td>
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Supplementary references