Electronic Supplementary Information

Morphology-dependent electrocatalytic nitrogen reduction on Ag triangular nanoplates

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Materials and Methods

Chemicals

Sodium borohydride (NaBH₄), potassium sulfate (K₂SO₄, 99%), carbon black (CB) were all purchased from Alfa Aesar (USA). Sulfuric acid (H₂SO₄, 98%), silver nitrate (AgNO₃), ethanol (CH₃CH₂OH, 98%) and hydrogen peroxide (H₂O₂, 30 wt%) were purchased from Beijing Chemical Reagent Co. Ltd. (Beijing, China). Nafion (5% in methanol) was purchased from Sigma-Aldrich (USA). The carbon paper (CP) was purchased from TORAY. The Nessler’s reagent was purchased from Aladdin (China). The water (18 MΩ cm) used in all experiments was prepared by passing through an ultra-pure purification system (Milli-Q). All chemicals are of analytical grade without any further purification. High-purity nitrogen (N₂, 99.9999%) and argon (Ar, 99.9999%) were purchased from Beijing AP BAIF Gases Industry Co., Ltd (Air Products).

Preparation of Ag triangular nanoplates (AgTPs) and Ag nanoparticles (AgNPs)

AgTPs were prepared through a modified method reported previously.[1–3] Typically, a 24.75 mL aqueous solution containing silver nitrate (0.05 M, 50 µL), trisodium citrate (75 mM, 0.5 mL) and H₂O₂ (30 wt%, 60 µL) was vigorously stirred at room temperature. Sodium borohydride (NaBH₄, 100 mM, 250 µL) was rapidly injected into the mixture solution to initiate the reduction of Ag⁺, immediately leading to a light-yellow solution. After about 3 min, the colloidal solution turned to deep yellow. Afterwards, the solution color changed from deep yellow to red, green, and finally blue in 2–3 min. The resulting product was collected by centrifugation and washed with deionized water.

Structure and composition characterization

Powder X-ray diffraction (XRD) was performed on a Rigaku MiniFlex 600 diffractometer with a Cu-Kα X-ray radiation source (λ = 0.154056 nm) at the scan rate of 1 °/min. Transmission electron microscopy (TEM) studies were performed on a JEM-2100 (JEOL, Japan) transmission electron microscope operating at 200 kV. All the absorbance of samples was measured by the UV-vis spectrophotometer (Shimadzu, UV-2600).

Electrochemical tests

All the electrochemical measurements were carried out in a standard two-compartment cell (H cell) using saturated calomel electrode (SCE) as the reference electrode, a platinum plate as the counter electrode and the catalyst loading carbon paper as the working electrode. In a typical test, 3.04 mg of
CB-supported Ag catalysts (1.04 mg of Ag catalyst and 2 mg of CB) were dispersed in a mixed solvent containing 200 µL of deionized water, 64 µL of ethanol and 32 µL of Nafion to form a homogeneous ink after 1 h of sonication. The catalysts were then applied to a carbon paper (0.6 cm × 1.2 cm²) with a total loading of 0.15 mg through the dip-coating method. The working electrodes (Ag/CB/CP) were dried in Argon at room temperature before testing. The Nafion 115 membrane separating the cathodic was pretreated in boiled 5% H₂O₂ solution for 1 h, then in boiled 0.5 M H₂SO₄ solution for another 1 h, and finally washed with deionized water for several times. All potentials in this study were measured against the SCE and converted to the reversible hydrogen electrode (RHE) reference scale.

\[ \text{Potential (V vs RHE)} = \text{Applied potential (V vs SCE)} + 0.241 \text{ V} + 0.0592 \times \text{pH} \quad (1) \]

The electrochemical nitrogen reduction was carried out in N₂-saturated acidic 0.5 M K₂SO₄ solution (pH = 3.5) at room temperature and pressure. To produce enough ammonia for quantification, the electrolysis reaction was kept for 4000 s or even longer. Before electrolysis, we bubbled high-purity N₂ (99.9999%) gas into the cathodic electrolyte for at least 30 min to realize nitrogen gas saturation.

Linear sweep voltammogram (LSV) curves were collected at a scan rate of 50 mV s⁻¹. N₂ (99.9999%) was continuously bubbled into the cathodic electrolyte with magnetic stirring (300 rpm) during the electrolysis measurements. Electrochemical measurements with Ar as gas supply were carried out under the same experiment condition. All current densities were normalized to the geometrical area of electrode.

**Quantification of NH₃ using Nessler’s reagents**

The concentration of produced NH₃ was spectrophotometrically determined by colorimetric assays using the Nessler’s reagent. Before UV-vis adsorption tests, all the test solution was kept in dark place at 25 °C for 20 min. Then we took the absorbance test at 420 nm with a UV-vis spectrophotometer (Shimadzu, UV-2600). The calibration curve (ammonium concentration versus absorbance) was plotted by measuring the UV-vis absorbance at 420 nm of series reference solutions at known concentrations of NH₄Cl. The concentration of ammonia in electrolytes can be calculated through the standard curve.

**Quantification of NH₃ using indophenol-blue method**

The quantity of the produced ammonia could also be measured with the indophenol-blue method.[4] Typically, 2 mL of sample solution was taken from the cathodic compartment and transferred into a 10 mL plastic tube. Then, 2 mL of 1 M NaOH solution (containing 5% salicylic acid and 5% sodium citrate), 1 mL of 0.05 M NaClO and 0.2 mL of 1% C₅FeN₆Na₂O·2H₂O were added into the above solution. After being kept in dark at 25 °C for 2 h, the UV-Vis absorption at the wavelength of 660 nm
for the solution was measured. The calibration curve was calibrated using standard NH₄Cl solution with a series of concentrations. The concentration of ammonia in the electrolytes can be calculated through the standard curve.

**Quantification of N₂H₄ using Watt and Chrisp method**

Typically, a mixture solution of hydrochloric acid (concentrated, 30 mL), ethanol (300 mL) and 4-(dimethylamino) benzaldehyde (5.99 g) was used as color reagent. A series of reference solutions with suitable N₂H₄·H₂O concentrations were made to measure their UV-vis absorbance at 455 nm to obtain the calibration curve. After ENRR experiments, 5 mL of electrolyte was pipetted out and mixed with 5 mL of the above as-prepared color reagent. Then, the mixture solution was kept under dark condition at 25 °C for 20 min before UV-vis adsorption tests. At last, the concentration of hydrazine in electrolytes was calculated via the as-obtained calibration curve.

**Nuclear magnetic resonance (NMR) measurements**

After electrochemical nitrogen reduction reactions, 100 µL of 20% DMSO-d6 (Sigma) was mixed with 500 µL of the resultant electrolytes and then measured with a Bruker Ascend 700-MHz NMR system.

**Faradaic efficiency calculation**

The NH₃ concentration was calculated from the calibration curve and the NH₃ yield \((r)\) normalized to catalyst (Ag) mass was calculated using the following equation:

\[
r = \frac{17 \times c(\text{NH}_3) \times V}{m \times t}
\]  

(2)

The Faradic efficiency \((\text{FE})\) for N₂ reduction could be calculated as follows:

\[
\text{FE} = \left[\frac{3 \times F \times c(\text{NH}_3) \times V}{Q}\right] \times 100\%
\]  

(3)

where the amount of the produced ammonia is in mole measured by colorimetry with Nessler’s reagent, \(F\) is the Faradaic constant \((96485 \text{ C mol}^{-1})\), \(V\) is the volume of the electrolytes in the cathodic compartment, \(m\) is the mass of catalyst (Ag), \(t\) is the total reaction time for nitrogen reduction, and \(Q\) is the electric charge (in C).
**Fig. S1** Transmission electron microscopy (TEM) images for the carbon black (CB) supported Ag catalysts. (a–b) AgTPs/CB and (c–d) AgNPs/CB.
Fig. S2 UV-vis measurements of the concentrations of ammonium in standard solutions with Nessler’s reagents. (a) UV-vis spectra for standard solutions. (b) Calibration curve for ammonium concentration vs absorbance. $R^2 = 0.999$. 
Fig. S3 UV-vis measurements of the electrolytes with Ar and N₂ as gas feed, respectively. (a) UV-vis spectra for electrolytes after electro-reduction reactions under Ar atmosphere. (b) None ammonium can be detected during the 4 h of electrolysis reduction. (c) UV-vis spectra for after nitrogen electro-reduction reactions with N₂ as feed gas. (d) Ammonia yield increases linearly with time.
Fig. S4  UV-vis measurements of the concentrations of ammonium in standard solutions with the indophenol-blue method. (a) UV-vis spectra for standard solutions. (b) Calibration curve for ammonium concentration vs absorbance at 660 nm. $R^2 = 0.999$. 
**Fig. S5** UV-vis spectra for electrolytes after 4 h of nitrogen reduction reactions. The corresponding FE for ammonia was calculated to be 23.9% with the ammonia yield of 56.5 mg g$_{Ag}^{-1}$ h$^{-1}$.
**Fig. S6** NMR & isotope-labelled experiments. (a) NMR spectra for the resultant electrolytes after 5 h of electrolysis with $^{15}\text{N}_2$, $^{14}\text{N}_2$ and Ar as feed gas, respectively. (b) NMR spectra for $\text{NH}_4^+$ in the electrolytes extracted from the ENRR system at 5, 10 and 15 h, respectively, showing the increasing amount of $\text{NH}_4^+$ during the electroreduction reaction.
Fig. S7 Quantification of N$_2$H$_4$ with the Watt and Chrisp method. (a) UV-vis spectra for standard solutions. (b) Calibration curve for N$_2$H$_4$ concentrations. R$^2 = 0.999$. 
Fig. S8 UV-vis absorption spectra for the electrolytes after 7000 s of electrolysis at −0.25 V for hydrazine quantification. Negligible hydrazine could be found (FE < 0.4%).
Fig. S9 Promotion of nitrogen reduction by different alkali metal cations (e.g. Li⁺, Na⁺, K⁺) (1.0 mol L⁻¹). (a) FE for ENRR on AgTPs at −0.25 V vs RHE. K⁺ cations exhibited superior ENRR promotion to the other two alkali metal cations. Na⁺ and Li⁺ cations showed lower FE of 15.64% and 7.35%, respectively. (b) Effective current density for ENRR on AgTPs at −0.25 V vs RHE.
**Table S1.** The metal content of the as-prepared metal/CB catalysts determined by ICP-AES and the metal loading on working electrodes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal content (wt.%)</th>
<th>Ag/CB loading on CP (µg)</th>
<th>Ag loading on CP (mg cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgTPs/CB on CP</td>
<td>25.3</td>
<td>150.0</td>
<td>0.053</td>
</tr>
<tr>
<td>AgNPs/CB on CP</td>
<td>25.0</td>
<td>150.0</td>
<td>0.052</td>
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</table>
Table S2. Quantification of ion content in electrolytes before and after reaction by ion chromatography method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NH$_4^+$ (mg L$^{-1}$)</th>
<th>NO$_3^-$ (mg L$^{-1}$)</th>
<th>NO$_2^-$ (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&lt;0.05 (50 ppb)</td>
<td>&lt;0.05 (50 ppb)</td>
<td>&lt;0.05 (50 ppb)</td>
</tr>
<tr>
<td>2</td>
<td>&lt;0.05 (50 ppb)</td>
<td>&lt;0.05 (50 ppb)</td>
<td>&lt;0.05 (50 ppb)</td>
</tr>
<tr>
<td>3</td>
<td>0.32</td>
<td>&lt;0.05 (50 ppb)</td>
<td>&lt;0.05 (50 ppb)</td>
</tr>
</tbody>
</table>

No detectable NH$_4^+$, NO$_3^-$ or NO$_2^-$ could be found (i.e. the concentrations were well below the detection limit of ion chromatography, <50 ppb) in the electrolytes (30 mL) bubbled by direct nitrogen flow (Sample 1, 50 mL min$^{-1}$, 4 h) or cycling nitrogen (Sample 2, 1 L, 4 h).

After 4 hours of electrolysis reaction, a significant increase (0.32 mg L$^{-1}$) in ammonia concentration could be detected in the electrolyte (Sample 3) while no NO$_3^-$ or NO$_2^-$ could be found.

The corresponding FE was calculated to be 25.7%, which was in well agreement with the results acquired by the colorimetric methods.
Table S3. ENRR Performance for typical transition metal electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>T (°C)</th>
<th>Potential (V vs RHE)</th>
<th>NH₃ yield</th>
<th>FE (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgTPs</td>
<td>0.5 M K₂SO₄</td>
<td>25</td>
<td>−0.25</td>
<td>58.5 mg g⁻¹ h⁻¹</td>
<td>25</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>pH = 3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgNPs</td>
<td>0.5 M K₂SO₄</td>
<td>25</td>
<td>−0.35</td>
<td>38 mg g⁻¹ h⁻¹</td>
<td>16</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>pH = 3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag nanosheet</td>
<td>0.1 M HCl</td>
<td>25</td>
<td>−0.6</td>
<td>1.66 × 10⁻⁷ mol cm⁻² h⁻¹</td>
<td>4.8</td>
<td>4</td>
</tr>
<tr>
<td>Au nanorod</td>
<td>0.1 M KOH</td>
<td>25</td>
<td>−0.2</td>
<td>1.648 µg cm⁻² h⁻¹</td>
<td>4.02</td>
<td>5</td>
</tr>
<tr>
<td>Au/TiO₂</td>
<td>0.1 M HCl</td>
<td>20</td>
<td>−0.2</td>
<td>21.4 mg g⁻¹ h⁻¹</td>
<td>8.11</td>
<td>6</td>
</tr>
<tr>
<td>Au/CeOₓ-rGO</td>
<td>0.1 M HCl</td>
<td>RT</td>
<td>−0.2</td>
<td>8.3 mg g⁻¹ h⁻¹</td>
<td>10.1</td>
<td>7</td>
</tr>
<tr>
<td>Au/C₃N₄</td>
<td>5 mM H₃SO₄</td>
<td>RT</td>
<td>−0.1</td>
<td>1305 mg g⁻¹ h⁻¹</td>
<td>11.1</td>
<td>8</td>
</tr>
<tr>
<td>MoSAs</td>
<td>0.1 M KOH</td>
<td>RT</td>
<td>−0.3</td>
<td>(34.0 ± 3.6) mg g⁻¹ h⁻¹</td>
<td>14.6 ± 1.6</td>
<td>9</td>
</tr>
<tr>
<td>AuHNCs</td>
<td>0.5 M LiClO₄</td>
<td>20</td>
<td>−0.4</td>
<td>3.9 µg cm⁻² h⁻¹</td>
<td>30.2</td>
<td>10</td>
</tr>
<tr>
<td>Rh nanosheet</td>
<td>0.1 M KOH</td>
<td>25</td>
<td>−0.2</td>
<td>23.88 mg g⁻¹ h⁻¹</td>
<td>0.217</td>
<td>11</td>
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<tr>
<td>RuSAs@ZrO₂</td>
<td>0.1 M HCl</td>
<td>RT</td>
<td>−0.11</td>
<td>3665 mg g⁻¹ h⁻¹</td>
<td>21</td>
<td>12</td>
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<tr>
<td>RuSAs/N-C</td>
<td>0.05 M H₃SO₄</td>
<td>RT</td>
<td>−0.2</td>
<td>120.9 mg g⁻¹ h⁻¹</td>
<td>29.6</td>
<td>13</td>
</tr>
<tr>
<td>AuNCs/CB</td>
<td>0.5 M K₂SO₄</td>
<td>25</td>
<td>−0.3</td>
<td>13 mmol g⁻¹ h⁻¹</td>
<td>22.5</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>pH = 3.5</td>
<td></td>
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<tr>
<td>PtNCs</td>
<td>0.5 M K₂SO₄</td>
<td>25</td>
<td>−0.025</td>
<td>1.3 mmol g⁻¹ h⁻¹</td>
<td>1.0</td>
<td>14</td>
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<td></td>
<td>pH = 3.5</td>
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</table>
References and Notes:


