Electronic Supplementary Information for

**Boron-doped silver nanosponges with enhanced performance towards electrocatalytic nitrogen to ammonia**

Yinghao Li, Hongjie Yu, Ziqiang Wang,* Songliang Liu, You Xu, Xiaonian Li, Liang Wang,* Hongjing Wang*

State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.

E-mails: zqwang@zjut.edu.cn; wangliang@zjut.edu.cn; hjw@zjut.edu.cn
1. Materials synthesis

1.1 Materials and Chemicals. Ammonium chloride (NH₄Cl, 99.999%) and sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O, ≥99.0%) were purchased from MACKLIN. Silver nitrate (AgNO₃, 99.8%), salicylic acid (C₇H₆O₃, 99.5%), sodium borohydride (NaBH₄, 96%), para-(dimethylamino) benzaldehyde (C₉H₁₁NO, 99%), N,N-dimethylformamide (DMF, 99.5%), sodium hypochlorite solution (NaClO, available chlorine 6.0−14.0%), concentrated hydrochloric acid (HCl, 37 wt%), ethanol (C₂H₅OH, ≥99.8%), and hydrazine monohydrate (N₂H₄·H₂O, ≥99%) were purchased from Aladdin. Nafion solution (5 wt%) was ordered from the Sigma-Aldrich. Carbon paper and Nafion 117 membranes were received from Shanghai Hesen Electric Co., Ltd.

1.2 Synthesis of B-Ag NSs. In a typical preparation of B-Ag NSs, 17 mg of AgNO₃ was dissolved in 1 mL of DMF under ultrasonication. Then 5 mL of DMF containing 18.9 mg of NaBH₄ was quickly injected into above solution, which was maintained in an ice bath for 2 h with vigorous stirring. Finally, the final product was collected by centrifugation and washed several times with ethanol and water.

2. Characterization

Scanning electron microscopy (SEM) images were obtained by a JSM-2010 scanning electron microscope. Transmission electron microscopy (TEM) and elemental analysis mapping were performed on a JEOL JEM-2100 equipped with an energy dispersive X-ray (EDX) spectroscopy. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an ESCALAB MK II spectrometer. The X-ray diffraction (XRD) patterns were collected on an X-ray diffractometer (Shimadzu, XRD-6000) with Cu Kα radiation. The compositions of the catalysts were measured by inductively coupled plasma mass spectrometry (ICP-MS) (Elan DRC-e instrument).

3. Electrochemical measurements

All electrochemical measurements were performed in a two-compartment cell separated by a Nafion 117 membrane at ambient temperature. Three-electrode system was employed to estimate electrochemical performance by a CHI 660E apparatus, where modified carbon cloth, saturated
Ag/AgCl electrode and carbon rod were used as the working electrode, reference electrode and counter electrodes, respectively. For preparation of the working electrode, 5 mg of catalyst was mixed with 50 μL of Nafion solution (5 wt%), 300 μL of ultrapure water and 650 μL of ethanol with sonication for 2 h. Then 20 μL of electrocatalyst ink was loaded onto carbon paper (0.5×0.5 cm²) and dried under room temperature. Before N₂ reduction experiments, the electrolyte (0.1 M HCl) was purged with N₂ for 30 min. Linear sweep voltammetry (LSV) curves of catalysts were conducted in N₂- or Ar-saturated 0.1 M HCl solution. The chronoamperometry test was performed at different potentials in the N₂-saturated 0.1 M HCl solution with continual bubble of N₂. Potentials were recorded on the reversible hydrogen electrode, and current densities were normalized to geometric area of carbon cloth.

4. Production Quantification

The concentration of produced NH₃ was determined by the indophenol blue method. In detail, 2 mL of electrolyte after electrolysis was mixed with 2 mL of 1.0 M NaOH solution containing C₇H₆O₃ (5 wt%) and C₆H₅Na₃O₇ (5 wt%), 1 mL of 0.05 M NaClO solution, and 0.2 mL of C₅FeN₆Na₂O solution (1 wt%). After standing at 25 °C for 2 h in the dark, the absorption spectrum was detected by an ultraviolet-visible (UV-vis) spectrophotometer. The known concentration NH₄⁺ solutions were used to calibrate the concentration-absorbance standard curve. On the other hand, the probable by-product hydrazine was estimated by the method of Watt and Chrisp. Typically, the mixture solution containing 5.99 g of C₉H₁₁NO, 300 mL of ethanol and 30 mL of HNO₃ was used as a color reagent. Then, 5 mL of electrolyte after electrolysis was added into 5 mL of color reagent. After standing for 10 min, the UV-vis absorption spectra were measured. The known concentration hydrazine monohydrate solutions were used to calibrate the concentration-absorbance standard curve. The rate of formation of NH₃ (v_NH₃) was calculated according to the following equation:

\[ v_{NH₃} = \frac{c_{NH₃} \times V \times t \times m}{17 \times Q} \]  

The FE was calculated based on the following equation:

\[ FE = 3F \times c_{NH₃} \times V / (17 \times Q) \]
where $c_{\text{NH}_3}$ is the concentration of NH$_3$ in the electrolyte; $V$ is the volume of electrolyte; $t$ is the electrolysis time; $m$ is the mass of catalysts; $F$ is the Faraday constant; and $Q$ is the total quantity of applied electricity.
Fig. S1 XPS Ag 3d spectra of the B-Ag NSs and Ag NSs.

Fig. S2 SEM images of the samples prepared with different solvents: (a) H$_2$O and (b) DMF.
Fig. S3 SEM images of the samples prepared with different concentrations of NaBH$_4$: (a) 20 mM and (b) 0.5 M.

Fig. S4 SEM image of the sample prepared at room temperature.
**Fig. S5** SEM images of the samples prepared with different amounts of reducing agent and metallic precursor: (a) NaBH₄ (1 mL, 0.1 M), AgNO₃ (1 mL, 0.1 M); (b) NaBH₄ (1 mL, 0.1 M), AgNO₃ (3 mL, 0.1 M); and (c) NaBH₄ (1 mL, 0.1 M), AgNO₃ (10 mL, 0.1 M).

**Fig. S6** Absolute calibration of the indophenol blue method using ammonium chloride solutions of known concentrations as standards. (a) UV-vis absorption spectra of indophenol assays with NH₄⁺ ions after incubation for 2 h at room temperature. (b) Calibration curve used for estimation of NH₃ by NH₄⁺ concentrations. The absorbance at 655 nm was measured by UV-vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with NH₃ concentrations.
Fig. S7 Absolute calibration of the Watt and Chrip (para-dimethylaminobenzaldehyde) method for the estimating of N$_2$H$_4$·H$_2$O concentration using N$_2$H$_4$·H$_2$O solutions with known concentration as standards. (a) UV-Vis curves of various N$_2$H$_4$·H$_2$O concentration after incubated for 10 min at room temperature. (b) Calibration curve used for estimation of N$_2$H$_4$·H$_2$O concentration. The absorbance at 458 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with N$_2$H$_4$·H$_2$O concentration of three times independent calibration curves.

Fig. S8 Yield rate of N$_2$H$_4$ formation for the B-Ag NSs at selected potentials.
**Fig. S9** (c) UV-vis absorption spectra of the electrolyte catalysed by the B-Ag NSs and Ag NSs. (b) Yield rate of NH$_3$ and corresponding FE of the B-Ag NSs and Ag NSs.

**Fig. S10** N$_2$-TPD profiles of Ag NSs and B-Ag NSs.
Fig. S11 cyclic voltammetry curves of the (a) B-Ag NSs and (b) Ag NSs at different scan rates in the potential range of -0.07 and 0.03 V.

Fig. S12 Charging current density differences plotted against scan rates for the B-Ag NSs and Ag NSs.
**Fig. S13** UV-vis absorption spectra of HCl electrolytes stained with indophenol indicator after charging at -0.2 V for 2 h under various conditions.

**Fig. S14** (a) Chronoamperometry curve of the B-Ag NSs at the potential of -0.5 V for 20 h. (b) Yield rate of NH$_3$ and corresponding FE before and after the durability tests.
Fig. S15 SEM image of the B-Ag NSs after long-term stability measurement.

Fig. S16 XPS spectra of the Ag 3d, B 1s and O 1s for the B-Ag NSs after stability test.
Table S1. The comparisons of the NRR activity of the B-Ag NSs with the recently reported catalysts under ambient conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>NH₃ yield rate</th>
<th>FE(%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>B-Ag NSs</strong></td>
<td>0.1 M HCl</td>
<td>26.48 μg h⁻¹ mg⁻¹cat.</td>
<td>8.86</td>
<td>This work</td>
</tr>
<tr>
<td>Au-TiO₂ sub nanocluster</td>
<td>0.1 M HCl</td>
<td>21.4 μg h⁻¹ mg⁻¹cat.</td>
<td>8.11</td>
<td>3</td>
</tr>
<tr>
<td>α-Au/CeOₓ-rGO</td>
<td>0.1 M HCl</td>
<td>8.3 μg h⁻¹ mg⁻¹cat.</td>
<td>10.1</td>
<td>4</td>
</tr>
<tr>
<td>VN nanosheet array</td>
<td>0.1 M HCl</td>
<td>5.6 μg h⁻¹ mg⁻¹cat.</td>
<td>2.25</td>
<td>5</td>
</tr>
<tr>
<td>Pd/C</td>
<td>0.1 M HCl</td>
<td>~2.5 μg h⁻¹ mg⁻¹cat.</td>
<td>~1.0</td>
<td>6</td>
</tr>
<tr>
<td>Ag nanosheets</td>
<td>0.1 M HCl</td>
<td>2.83 μg h⁻¹ mg⁻¹cat.</td>
<td>4.8</td>
<td>7</td>
</tr>
<tr>
<td>MoO₃</td>
<td>0.1 M HCl</td>
<td>29.43 μg h⁻¹ mg⁻¹cat.</td>
<td>1.9</td>
<td>8</td>
</tr>
<tr>
<td>PdRu BPNs</td>
<td>0.1 M HCl</td>
<td>25.92 μg h⁻¹ mg⁻¹cat.</td>
<td>1.53</td>
<td>9</td>
</tr>
<tr>
<td>Au flower</td>
<td>0.1 M HCl</td>
<td>25.57 μg h⁻¹ mg⁻¹cat.</td>
<td>6.05</td>
<td>10</td>
</tr>
<tr>
<td>N-Doped Porous Carbon</td>
<td>0.05 M H₂SO₄</td>
<td>23.8 μg h⁻¹ mg⁻¹cat.</td>
<td>1.42</td>
<td>11</td>
</tr>
<tr>
<td>Fe₂O₃-CNT</td>
<td>diluted KHCO₃</td>
<td>0.22 μg h⁻¹ cm⁻²</td>
<td>0.15</td>
<td>12</td>
</tr>
</tbody>
</table>
References


