Electronic Supplementary Information

Experimental section

**Materials:** sodium sulfide (Na$_2$S), sodium sulfate (Na$_2$SO$_4$), ammonium chloride (NH$_4$Cl), anhydrous lithium perchlorate (LiClO$_4$), hydrazine hydrate (N$_2$H$_4$·H$_2$O), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), sodium salicylate (C$_7$H$_5$O$_3$Na), ethanol (CH$_3$CH$_2$OH), and carbon paper were bought from Beijing Chemical Corporation. Para-(dimethylamino) benzaldehyde (C$_9$H$_{11}$NO), sodium nitroferricyanide (III) dihydrate (Na$_2$Fe(CN)$_5$NO·2H$_2$O), and Nafion were purchased from Aladdin Ltd. (Shanghai, China). The water used throughout all experiments was purified through a Millipore system.

**Preparation of S, EG, and SDG:** Graphene was prepared from graphite rods by using electrochemical exfoliation which was performed in a two-electrode system. To prepare S and SDG, the titanium mesh and graphite rod were used as working anode, respectively, and the graphite rod as the counter electrode. The distance between the electrodes was 2 ± 0.5 cm and was kept constant throughout the electrochemical process. The electrolyte for the deposition was prepared by dispersing Na$_2$SO$_4$ (0.05 M, 0.710 g) and Na$_2$S (1.20 g) in 100 mL of DI water. For comparison, EG was also prepared by same method of SDG except the addition of Na$_2$S.

**Pretreatment of titanium mesh and graphite rods:** The titanium mesh was placed in a beaker containing a certain amount of concentrated hydrochloric acid and heated in an oil bath (100 °C). The heating was stopped after the hydrochloric acid boiled for five minutes. Graphite rods were directly put into the ultrasonic machine for 30 minutes.

**Preparation of S/CP, EG/CP, SDG/CP:** Carbon paper (CP) was cleaned via brief sonication with ethanol and water for several times. 10 mg sample and 40 µL 5 wt% Nafion solution were dispersed in 960 µL water/ethanol (V : V = 1 : 3) followed by 1-h sonication to form a homogeneous ink. 20 µL ink was loaded onto a CP (1 × 1 cm$^2$) and dried under ambient condition.

**Characterizations:** XRD patterns were obtained from a Shimazu XRD-6100
diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (Japan). SEM images were collected from the tungsten lamp-equipped SU3500 scanning electron microscope at an accelerating voltage of 20 kV (HITACHI, Japan). TEM images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The absorbance data of spectrophotometer were measured on SHIMADZU UV-1800 ultraviolet-visible (UV-Vis) spectrophotometer. The ion chromatography data were collected on Thermofisher ICS 5000 plus using the dual temperature heater, injection valve, conductivity detector, AERS 500 Anions suppressor.

**Electrochemical measurements:** Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) using a standard three-electrode system using SDG/CP as the working electrode, graphite rod as the counter electrode, and saturated Ag/AgCl electrode as the reference electrode. In all measurements, saturated Ag/AgCl electrode was calibrated with respect to reversible hydrogen electrode as following: in 0.5 M LiClO$_4$ aqueous solution, $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.197$ V. All experiments were carried out at room temperature. For N$_2$ reduction experiments, the 0.5 M LiClO$_4$ electrolyte was purged with N$_2$ for 30 min before the measurement. Potentiostatic test was conducted in N$_2$-saturated 0.5 M LiClO$_4$ solution in a two-compartment cell, which was separated by Nafion 117 membrane.

**Determination of NH$_3$:** The produced NH$_3$ was detected with indophenol blue by ultraviolet spectroscopy$^1$ and ion chromatography.$^2$ For the ultraviolet spectroscopy, 4 mL electrolyte was obtained from the cathodic chamber and mixed with 50 µL oxidizing solution containing NaClO ($\rho$Cl = 4 ~ 4.9) and NaOH (0.75 M), 500 µL coloring solution containing 0.4 M C$_7$H$_6$O$_3$Na and 0.32 M NaOH, and 50 µL catalyst solution (1 wt% Na$_2$[Fe(CN)$_5$NO]) for 1 h. Absorbance measurements were performed at $\lambda = 655$ nm. The concentration-absorbance curve was calibrated using standard NH$_4^+$ solution with a serious of concentrations. The fitting curve ($y = 0.353x$
+ 0.009, $R^2 = 0.999$) shows good linear relation of absorbance value with NH$_4^+$ concentration.

**Determination of N$_2$H$_4$:** The N$_2$H$_4$ present in the electrolyte was determined by the method of Watt and Chrisp.$^3$ The mixture of C$_9$H$_{11}$NO (5.99 g), HCl (30 mL), and C$_2$H$_5$OH (300 mL) was used as a color reagent. In detail, 5 mL electrolyte was removed from the electrochemical reaction vessel, and added into 5 mL above prepared color reagent and stirring 10 min at room temperature. Moreover, the absorbance of the resulting solution was measured at a wavelength of 460 nm. The concentration absorbance curves were calibrated using standard N$_2$H$_4$ solution with a series of concentrations. The fitting curve ($y = 0.627x + 0.047$, $R^2 = 0.999$) shows good linear relation of absorbance value with N$_2$H$_4$ concentration.

**Calculations of NH$_3$ yield and FE:** NH$_3$ yield was calculated using the following equation:

$$\text{NH}_3\text{ yield} = [\text{NH}_4^+] \times \frac{V}{(\text{m}_{\text{cat.}} \times t)}$$

FE was calculated according to following equation:

$$\text{FE} = 3 \times F \times [\text{NH}_4^+] \times \frac{V}{(18 \times Q)}$$

Where $[\text{NH}_4^+]$ is the measured NH$_4^+$ concentration; V is the volume of the cathodic reaction electrolyte; t is the potential applied time; $m_{\text{cat.}}$ is the loaded quality of catalyst; F is the Faraday constant; and Q is the quantity of charge in Coulombs.
Fig. S1. XRD pattern of S.
Fig. S2. EDX spectrum of SDG.
Fig. S3. (a) UV-Vis absorption spectra of indophenol assays with NH$_4^+$ concentrations after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of NH$_4^+$ concentrations.
**Fig. S4.** (a) UV-Vis absorption spectra of various $\text{N}_2\text{H}_4$ concentrations after incubated for 10 min at room temperature. (b) Calibration curve used for calculation of $\text{N}_2\text{H}_4$ concentrations.
Fig. S5. (a) Time-dependent current density curves for SDG/CP at different potentials in 0.1 M Na$_2$SO$_4$. (b) NH$_3$ yields and FEs for SDG/CP at a series of potential.
Fig. S6. (a) UV-Vis curves of indophenol assays with NH$_4^+$ ions in 0.1 M HCl after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of NH$_3$ concentrations in 0.1 M HCl.
Fig. S7. NH₃ yields and FE of SDG/CP in 0.1 M HCl and 0.1 M LiClO₄ at -0.85 V.
Fig. S8. (a) Ion chromatogram for the standard NH$_4^+$ samples and (b) corresponding calibration curve. (c) Ion chromatogram for the electrolytes at a series of potentials after electrolysis for 2 h. (d) NH$_3$ yields and FEs for SDG/CP at corresponding potentials.
Fig. S9. UV-Vis absorption spectra of electrolytes stained with para-(dimethylamino)benzaldehyde indicator before and after 2 h electrolysis.
Fig. S10. Nyquist plots of SDG/CP (red curve) and S/CP (black curve).
Fig. S11. $^1$H NMR spectra of $^{15}$NH$_4^+$ standard sample and the product obtained after electrolysis at $-0.85$ V under $^{15}$N$_2$ atmosphere on the SDG/CP.
Fig. S12. NH₃ yields and FEs after charging at −0.85 V for 2 and 24 h.
Fig. S13. TEM image of SDG after stability test.
Fig. S14. XPS spectra of SDG after NRR test in the (a) SDG, (b) C 1s, (c) O 1s and (d) S 2p regions.
**Table S1.** Comparison of the electrocatalytic NRR performance of SDG with other NRR electrocatalysts under ambient reaction conditions in aqueous media.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>NH$_3$ yield</th>
<th>FE(%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDG</td>
<td>0.5 M LiClO$_4$</td>
<td>28.56 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>7.07</td>
<td>This work</td>
</tr>
<tr>
<td>PEBCD/C</td>
<td>0.5 M Li$_2$SO$_4$</td>
<td>1.58 µg h$^{-1}$ cm$^{-2}$</td>
<td>2.85</td>
<td>4</td>
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<tr>
<td>β-FeOOH nanorod</td>
<td>0.5 M LiClO$_4$</td>
<td>23.32 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>6.7</td>
<td>5</td>
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<tr>
<td>CNS</td>
<td>0.25 M LiClO$_4$</td>
<td>97.18 µg h$^{-1}$ cm$^{-2}$</td>
<td>11.56</td>
<td>6</td>
</tr>
<tr>
<td>MoS$_2$/CC</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>$8.8 \times 10^{-11}$ mol s$^{-1}$ cm$^{-2}$</td>
<td>1.17</td>
<td>7</td>
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<tr>
<td>Fe$_3$O$_4$/Ti</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>$5.6 \times 10^{-10}$ mol s$^{-1}$ cm$^{-2}$</td>
<td>2.6</td>
<td>8</td>
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<tr>
<td>Mn$_3$O$_4$ nanocube</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>11.6 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>3.0</td>
<td>9</td>
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<tr>
<td>TiO$_2$-rGO</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>15.13 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>3.3</td>
<td>10</td>
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<tr>
<td>B-TiO$_2$</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>14.4 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>3.4</td>
<td>11</td>
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<tr>
<td>C-TiO$_2$</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>16.22 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>1.84</td>
<td>12</td>
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<td>VO$_2$ hollow microsphere</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>14.85 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>3.97</td>
<td>13</td>
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<tr>
<td>hollow Cr$_2$O$_3$ microspheres</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>25.3 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>6.78</td>
<td>14</td>
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<tr>
<td>Fe$_2$O$_3$ nanorods</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>15.9 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>0.94</td>
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<tr>
<td>MnO</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>$1.11 \times 10^{-10}$ mol s$^{-1}$ cm$^{-2}$</td>
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<tr>
<td>Mn$_3$O$_4$ nanocube</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>11.6 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>3.0</td>
<td>17</td>
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<tr>
<td>N-doped porous carbon</td>
<td>0.05 M H$_2$SO$_4$</td>
<td>1.40 mmol g$^{-1}$ h$^{-1}$</td>
<td>1.42</td>
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<td>polymeric carbon nitride</td>
<td>0.1 M HCl</td>
<td>8.09 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>11.59</td>
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<tr>
<td>B$_4$C nanosheet</td>
<td>0.1 M HCl</td>
<td>26.57 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>15.95</td>
<td>20</td>
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<tr>
<td>Black P nanosheet</td>
<td>0.01 M HCl</td>
<td>31.37 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>5.07</td>
<td>21</td>
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References


