**MnO-carbon nanofibers composite material toward electro-chemical N\textsubscript{2} fixation at ambient conditions**

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### Electronic Supplementary Information

#### 1. Materials

Polyvinyl Alcohol (PVA, AR), Mw = 67000, supplied by Aladdin Co. Ltd; Manganese acetate (Mn(OAc)\textsubscript{2}·4H\textsubscript{2}O, AR) was obtained from Tianjin Fuchen Chemical Co. Ltd; Nafion 117 solution (5 wt%), obtained from Sigma-Aldrich Co. Ltd; Sodium sulfate anhydrous (Na\textsubscript{2}SO\textsubscript{4}, AR), sodium hydroxide (NaOH, AR), sodium hypochlorite solution (NaClO, content of active chlorine > 5.5%), supplied by Chengdu Kelong Co. Ltd; Sodium salicylate (AR), ammonium chloride and sodium nitroferricyanide (Na\textsubscript{2}[Fe(CN)\textsubscript{5}NO].2H\textsubscript{2}O, AR), para-(dimethylamino) benzaldehyde (p-C\textsubscript{9}H\textsubscript{11}NO), Hydrazine dihydrochloride (N\textsubscript{2}H\textsubscript{4}.2HCl) obtained from Aladdin Co. Ltd; Ultrapure water (18.2 MΩ.cm) was utilized to prepare all solutions. All reagents were used as received without further purification; N\textsubscript{2} gas (99.99%), Ar gas (99.99%).

#### 2. Preparation of PVA/manganese acetate composite gels

1.3 g PVA powder was dissolved 8 ml ultrapure and heated at 80°C with stirring for 2 h, then cooling to room temperature and stirring for 12 h. The PVA solution was dropped slowly into manganese acetate solution (0.5 g Mn(OAc)\textsubscript{2}·4H\textsubscript{2}O and 0.8 g H\textsubscript{2}O), and proceeded in a water bath at 50°C for 5 h. Thus, a viscous gel of PVA/manganese acetate composite was obtained.\textsuperscript{1}

In addition, 1.3 g PVA powder was used to make a viscous gel without Mn(OAc)\textsubscript{2} at the same procedure.

#### 3. Preparation of nanofibers

The solution was injected into a syringe, which was fixed in a syringe pump. The size of the needle for the electrospinning experiment was 22 G, and the needle was connected to a high-voltage power supply. The flow rate of the syringe pump was fixed at 0.6 mL/h, and the distance between the needle and sample collector was 16 cm with an applied voltage of 20 kV. The as-electrospun Mn(OAc)\textsubscript{2}-PVA nanowires were dried at 80 °C for 12 h in air. Then, the nanowires...
were annealed at 700 °C in Ar gas for 2 h to remove the polymer matrix with a heating rate of 30 °C/h. At a contrast, the dried Mn(OAc)$_2$-PVA nanowires were annealed at 700 °C in air for 2h. The product is Mn$_2$O$_3$.

PVA viscous gel was used to make nanowires by electrostatic spinning method. After drying at 80 °C for 12 h in air, the nanowires were annealed at 700 °C in Ar gas for 2 h. The product is carbon fiber.

4. Cathode preparation

Typically, 5 mg sample and 10 μL of Nafion 117 solution (5 wt%) were dispersed in 0.5 ml solution ($V_{\text{alcohol}}: V_{\text{pure water}}=1:1$) by sonicating for 1 h to form a homogeneous ink. Then, a certain amount of the dispersion was loaded onto a glassy carbon electrode with diameter of 3 mm and dried in N$_2$ atmosphere at 40 °C for 1 h.

Mn$_2$O$_3$ and carbon nanofibrer were as comparisons.

5. Characterizations

X-ray diffraction (XRD) patterns were performed using a RigakuD/MAX 2550 diffractometer (SHIMADZU, Japan) with Cu Kα radiation ($\lambda = 1.5418$ Å) at 40 kV and 40 mA. Samples were analyzed over a range of 10–80° using a step scan mode with a step rate of 5 °/min. Scanning electron microscopy (SEM) image was collected on a MERLIN Compact scanning electron microscope at an accelerating voltage of 20 kV. The elemental mapping was carried out on a field-emission scanning electron microscope (FESEM, Hitachi S4800) equipped with an energy dispersive X-ray spectrometer (EDX). Transmission electron microscopy (TEM) image was made on a Zeiss Libra 200FE transmission electron microscope. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. Absorbance of samples were detected by spectrophotometer (SHIMADZU UV-1800) at wavelength range from 800 nm to 500 nm with a light path of 1 cm.

6. Electrochemical NRR measurements:

The experiments have been carried out in an electrochemical cell. The reduction of nitrogen (99.99%) was performed in a two-compartment cell, which was separated by Nafion 211 membrane. Before NRR tests, the Nafion membrane was pretreated by heating in H$_2$O$_2$ 5%
aqueous solution at 80 °C for 1 h and ultrapure water at 80 °C for another 1 h, respectively.

The electrochemical experiments were carried out with an electrochemical workstation using a three-electrode configuration with prepared electrodes, graphite rod and Ag/AgCl electrode as working electrode, counter electrode and reference electrode, respectively. In this work, all potentials were converted to RHE scale via calibration. And the presented current density was normalized to the geometric surface area. All the polarization curves were the steady-state ones after several cycles.

For \( \text{N}_2 \) reduction experiments, NRR test was conducted in \( \text{N}_2 \) saturated 0.1 M \( \text{Na}_2\text{SO}_4 \) solution (40 mL) (\( \text{Na}_2\text{SO}_4 \) electrolyte was purged with \( \text{N}_2 \) for 30 min before the measurement). Pure \( \text{N}_2 \) (99.99 % purity) was continuously fed to the cathodic compartment using properly positioned spargers so that the whole cathode was hit by the gas bubbles. For comparison, NRR tests in Ar saturated 0.1 M \( \text{Na}_2\text{SO}_4 \) solution and bare GCE were also conducted in this work.

The NRR tests were tested in 0.1 M \( \text{Na}_2\text{SO}_4 \) aqueous solution at different potentials such as -1.1 V, -1.15 V, -1.2 V, -1.25 V and -1.3 V vs. RHE. The NRR performance of catalyst with different loading amounts of 25, 37.5, 50, 62.5, 75 \( \mu \text{g} \) were detected.

6. Determination of NRR production:

The concentration of ammonia was measured using a colorimetric assay adapted from the standard methods. Spectrophotometry measurement with salicylic acid.\(^2,^3\)

Regents used: (a) coloring solution: sodium salicylate (0.4 M) and sodium hydroxide (0.32 M); (b) oxidation solution: sodium hypochlorite (concentration of active chlorine = 4-4.9 wt%) and sodium hydroxide (0.75 M); (c) catalyst solution: 0.1 g \( \text{Na}_2\text{[Fe(CN)]}_5\text{NO}\).2H\( \text{H}_2\)O diluted to 10 mL with deionized water; (d) standard ammonium solution: \( \text{NH}_4^+ \) concentration=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 \( \mu \text{g} \text{mL}^{-1} \).

Procedure: 4 mL of sample was taken. Then 50 \( \mu \text{L} \) of oxidizing solution, 500 \( \mu \text{L} \) of coloring solution and 50 \( \mu \text{L} \) of catalyst solution were added respectively to the sample solution. Absorbance measurements were performed after 1 h at \( \lambda=655 \text{ nm} \). The calibration curve below was used to calculate the ammonia concentration. Comparing the curves in the same conditions, these give similar value on different calibration sets

Calibration curves were prepared from \( \text{Na}_2\text{SO}_4 \) solution (0.1 M, 50 \( \mu \text{L} \)) mixed with kit
reaction buffer and the appropriate amount of ammonium chloride and incubated in the dark at room temperature. The background was corrected by subtracting the value derived from value of blank control without NH$_4$Cl from all readings.

7. Calculation of Faradaic Efficiency (FE) and yield of NH$_3$

The FE for N$_2$ reduction was defined as the amount of electric charge used for synthesizing NH$_3$ divided the total charge passed through the electrodes during the electrolysis. The total amount of NH$_3$ produced was measured using colorimetric methods. Assuming three electrons were needed to produce one NH$_3$ molecule,

$$FE = \frac{3F \cdot C_{NH_3} \cdot V}{M_{NH_3} \times 10^6 \cdot Q} \times 100\%$$

the FE could be calculated as follows:

the yield of NH$_3$ ($\mu$g h$^{-1}$ mg$^{-1}$) was calculated using the following equation:

$$\vartheta_{NH_3} = \frac{C_{NH_3} \cdot V}{t \cdot m_{cat}}$$

$C_{NH_3}$ ($\mu$g mL$^{-1}$) is the measured NH$_3$ concentration, $V$ (mL) is the volume of Na$_2$SO$_4$ solution for NH$_3$ collection, $M_{NH_3}$ (g mol$^{-1}$) is the molecular weight of NH$_3$, F (C mol$^{-1}$) is the Faraday constant, $t$ (h) is the reduction time and $m_{cat}$ (mg) is the catalyst mass.

8. Determination concentration of N$_2$H$_4$

The concentration of N$_2$H$_4$ was determined by the method of spectrophotometry. 4, 5 4.0 g C$_9$H$_{11}$NO was dissolved in 20 ml HCl ($\rho$=1.19 g/mL) and 200 mL ethanol and used as a color reagent. 0.328 g N$_2$H$_4$.2HCl was used to prepare reference solution with concentration of N$_2$H$_4$.H$_2$O 1 $\mu$g/mL. Then it was diluted to prepare a series of reference solutions and their calibration concentrations are 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.7 $\mu$g/mL. 5 mL color reagent was added into each solution under stirring for 20 min at room temperature, which was used to determine the absorption spectrum. The calibration curve was made based on the absorbance at 458 nm. Equation of working curve is $y$=0.6464$x$-0.0084, $R^2$=0.9997. The yields of N$_2$H$_4$ after NRR reaction was determined with the same procedures.
Fig. S1. EDX spectrum of MnO-CNFs

Scheme S1 Schematic diagram of the experiment process
Fig S2. Linear sweep voltammetric curves in an N₂ saturated (red line) solution and Ar saturated solution (black line)

Fig. S3. Absolute calibration of colorimetric assay using ammonium chloride solutions of known concentration as standards. (a) UV-Vis curves of colorimetric assay with NH₄⁺ ions after incubated for an hour at room temperature; (b) calibration curve used for estimation of NH₃ by NH₄⁺ ion concentration. The absorbance at 655 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance.
Fig S4 (a) UV-Vis spectra of reference solutions with various concentrations of 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7 μg/mL; (b) Calibration curve for calculation of N₂H₄ concentrations. The absorbance at 458 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance.

Fig. S5 Production of NH₃ with different electrodes after 2h electrolysis at potential of -1.25 V under ambient conditions.
Fig. S6 UV-Vis absorption spectra of electrolytes with p-C9H11NO indicator before and after 2h NRR reaction.

Fig. S7. Time-dependent current density curve of MnO-CNFs in NRR.
Table S1 Comparison of the NH₃ yield and Faradaic Efficiency of MnO-CNFs with other reported NRR electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Temperature</th>
<th>NH₃ yield rate (μg h⁻¹ mg⁻¹cat)</th>
<th>Faradaic Efficiency (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO-CNFs</td>
<td>0.1 M Na₂SO₄</td>
<td>25 °C</td>
<td>35.9</td>
<td>1.52</td>
<td>This work</td>
</tr>
<tr>
<td>Fe₂O₃ nanorods</td>
<td>0.1 M Na₂SO₄</td>
<td>25 °C</td>
<td>15.9</td>
<td>0.94</td>
<td>6</td>
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<tr>
<td>Mo nanofilm</td>
<td>0.01 M H₂SO₄</td>
<td>25 °C</td>
<td>1.89</td>
<td>0.72</td>
<td>7</td>
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<tr>
<td>Au nanorods</td>
<td>0.1 M KOH</td>
<td>25 °C</td>
<td>6.042</td>
<td>4.0</td>
<td>8</td>
</tr>
<tr>
<td>MoS₂/CC</td>
<td>0.1 M Na₂SO₄</td>
<td>25 °C</td>
<td>4.94</td>
<td>1.17</td>
<td>9</td>
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<tr>
<td>α-Au/CeOₓ-RGO</td>
<td>0.1 M HCl</td>
<td>25 °C</td>
<td>8.3</td>
<td>10.1</td>
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<td>hollow Cr₂O₃ microspheres</td>
<td>0.1 M Na₂SO₄</td>
<td>25 °C</td>
<td>25.3</td>
<td>6.78</td>
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<tr>
<td>TiO₂-rGO</td>
<td>0.1 M Na₂SO₄</td>
<td>25 °C</td>
<td>15.13</td>
<td>3.3</td>
<td>12</td>
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<td>Mn₃O₄ nanocube</td>
<td>0.1 M Na₂SO₄</td>
<td>25 °C</td>
<td>11.6</td>
<td>3.0</td>
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<td>MoO₃</td>
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<td>29.43</td>
<td>1.9</td>
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<td>25 °C</td>
<td>23.2</td>
<td>10.16</td>
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<tr>
<td>γ-Fe₂O₃</td>
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<td>25 °C</td>
<td>0.212</td>
<td>1.9</td>
<td>16</td>
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</table>
Reference


