Supporting Information

Highly Efficient Electrochemical N\textsubscript{2} Reduction over Strongly-Coupled CeO\textsubscript{2}-Mo\textsubscript{2}C Nanocomposites Anchored by Reduced Graphene Oxide

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Experimental Section

Chemicals.
Ammonium molybdate [(NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O] and Cerium nitrate hexahydrate [Ce(NO$_3$)$_3$·6H$_2$O] were purchased from Aladdin Chemical Co. Ltd. Sodium sulfate (Na$_2$SO$_4$) was purchased from Sinopharm Chemical Reagent Co., Ltd. Hydrogen peroxide solution (H$_2$O$_2$, 30wt% in H$_2$O) was acquired from XiLong Scientific Co., Ltd. Graphene oxide (GO) was purchased from Shenzhen Suiheng Technology Co., Ltd. Ethyl alcohol (C$_2$H$_5$OH) was acquired from Tianjin Fuyu Fine Chemical Co., Ltd. Hydrazine monohydrate (N$_2$H$_4$·H$_2$O, ≥50%) obtained from Beijing Yili Fine Chemicals Co., Ltd. Salicylic acid (C$_7$H$_6$O$_3$), sodium citrate dehydrate (C$_6$H$_5$Na$_3$O$_7$·2H$_2$O), sodium hydroxide (NaOH), hypochlorite solution (NaClO, 6-14%), sodium nitroferricyanidedihydrate (C$_5$FeN$_6$Na$_2$O·2H$_2$O), p-dimethylaminobenzaldehyde (C$_9$H$_11$NO) and ammonium chloride (NH$_4$Cl) obtained from Macklin. 212 Nafion membrane and nafion solution were acquired from DuPont. All chemicals were analytical grade and used without further purification.

Characterization.
The morphologies of samples were characterized by field emission scanning electron microscope (FEI, Qunta250, USA) and transmission electron microscope (FEI, TECNAI G2) accelerating voltage of 20 kV. X-ray diffraction (XRD) pattern was carried out using a Bruker D8 Focus powder X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) was analyzed by ESCALAB-MKII 250 photoelectron spectrometer with Kα radiation. Inductively coupled plasma optical emission spectroscopy (ICP-OES) data were obtained from a Varian Liberty 200 spectrophotometer. SHIMADZU UV-3600 spectrometer was used to measure the UV-Vis absorption spectra. All electrochemical tests were implemented using CHI 660E electrochemistry workstation (CH Instruments, Inc., Shanghai).

Synthesis of CeO$_2$/Mo$_2$C@rGO catalyst.
The CeO$_2$/Mo$_2$C@rGO was prepared by a thermal reduction treatment, in detail, GO (50 mg), (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (25 mg, 0.02 mmol) and Ce (NO$_3$)$_3$·6H$_2$O (0.92 mg,
0.002 mmol) were dispersed in 20 mL ethanol to generate a homogeneous suspension under constant stirring. After the above suspension was dried at 60 °C with constant stirring, a claybank mixture of GO, (NH₄)₆Mo₇O₂₄·4H₂O and Ce (NO₃)₃·6H₂O was obtained. The resultant claybank mixture was then annealed at 800 °C for 3 h under an N₂ atmosphere. After cooling to room temperature, the product of CeO₂/Mo₂C@rGO was obtained. To investigate the effect of the doped Ce, the CeO₂/Mo₂C@rGO-L and CeO₂/Mo₂C@rGO-H were also synthesized using the same procedure as above by controlling with the amounts of Ce (NO₃)₃·6H₂O (0.46 mg and 1.84 mg).

**Synthesis of Mo₂C@rGO catalyst.**

The synthesis of Mo₂C@rGO was the same as that of above preparing CeO₂/Mo₂C@rGO, except that there was no Ce (NO₃)₃·6H₂O added.

**Synthesis of CeO₂@rGO catalyst.**

The synthesis of CeO₂@rGO was the same as that of above preparing CeO₂/Mo₂C@rGO, except that there was no (NH₄)₆Mo₇O₂₄·4H₂O added.

**Synthesis of CeO₂ and rGO catalysts.**

Ce (NO₃)₃·6H₂O (20 mg) or GO (50 mg) was directly annealed using the same method as above CeO₂/Mo₂C@rGO to prepare CeO₂ and rGO catalyst, respectively.

**NRR cathode preparation.**

Typically, 5 mg of catalyst and 40 μL Nafion solution (DuPont, 5 wt%) were dissolved in 960 μL mixed water/ethanol solution (v/v = 1 : 1) by sonicating for 1 h to form a homogeneous ink. 20 μL of the above catalyst ink was then dropped onto a carbon paper with an area of 1 x 1 cm² which was next dried at 60 °C for 1 h. The loading mass of catalyst is 0.1 mg cm⁻².

**Electrochemical measurements.**

The electrocatalytic NRR was implemented in an H-type cell, which was separated by a Nafion 212 membrane. Before the NRR experiments, this Nafion 212 membrane was pretreated by H₂O₂ (5%) aqueous solution and deionized water at 80 °C for 1h, respectively. The electrocatalytic NRR measurements were carried out in a CHI 660e electrochemical workstation in a standard three-electrode system. The carbon paper
coated with catalysts used as working electrode, and an Ag/AgCl (saturated 3 M KCl electrolyte) and Pt foil were used as reference electrode and counter electrode, respectively. The potentials used in this work were translated to reversible hydrogen electrode (RHE) using the following formula: \( E (\text{vs. RHE}) = E (\text{vs. Ag/AgCl}) + 0.197 + 0.059 \times \text{pH} \). Prior to NRR tests, pure \( \text{N}_2 \) or \( \text{Ar} \) was fed into electrolyte of 0.1 M \( \text{Na}_2\text{SO}_4 \) solution (40 mL) for 0.5 h. Then chronoamperometry tests were conducted at different potentials for 1h with continuous gas feeding.

**Determination of the produced ammonia.**
The produced ammonia was determined by indophenol blue method\(^ {15} \). In detail, 2 mL tested 0.1 M \( \text{Na}_2\text{SO}_4 \) electrolyte was mixed with 2 mL NaOH solution (1.0 M) containing salicylic acid (5 wt%) and sodium citrate (5 wt%). Then, 1 mL of 0.05 M NaClO solution and 0.2 mL of 1 wt% \( \text{C}_5\text{FeN}_6\text{Na}_2\text{O} \) (sodium nitroferricyanide) solution were sequentially added into above mixture solution. After standing for 2h at room temperature, the UV-Vis absorption spectrum of resultant solution was recorded at 655nm using an UV-vis spectrophotometer. Additionally, the concentration-absorbance calibration curve was calibrated using standard ammonia chloride with various concentrations, and the fitting curve \( y = 0.3228x + 0.0175, R^2=0.999 \) shown in Figure S11.

**Determination of the produced hydrazine.**
The possibly produced hydrazine in the electrolyte was determined by Watt and Chrisp method\(^ {16} \). First, a mixture solution of 5.99 g p-dimethylaminobenzaldehyde, 30 mL HCl and 300 mL ethanol was prepared to use as the color reagent. Typically, 5 mL of tested 0.1 M \( \text{Na}_2\text{SO}_4 \) electrolyte was mixed with 5 mL of above color reagent. After standing for 20 min at room temperature, the UV-Vis absorption spectrum of resultant solution was recorded at 455nm using an UV-vis spectrophotometer. The concentration-absorbance calibration curve was also calibrated using standard hydrazine solutions with different concentrations, and the fitting curve \( y = 0.586x + 0.003, R^2=0.999 \) shown in Figure S12.

**Calculations of \( \text{NH}_3 \) yield and FE.**
The \( \text{NH}_3 \) yield and Faradaic efficiency were calculated using the following equation:
Yield rate (NH$_3$) = \( \frac{C(NH3) \times V}{m(\text{cat.}) \times t} \)

\[
\text{FE} = \frac{3 \times F \times C(NH3) \times V}{17 \times Q} \times 100\%
\]

where C(NH$_3$) refers to the NH$_3$ concentration; V represents to volume of reaction electrolyte; m(cat.) is the catalyst loading; t is the reaction time; F represents to the Faraday constant and Q is the total charge of applied electricity.

**15N Isotopic Labeling Experiment.**

15N$_2$ (Sigma-Aldrich, enrichment of 99%) was used as feed gas to perform isotopic labeling experiments. Before electrolysis, ultrapure argon (99.999%) was purged through the electrolyte of 0.1M Na$_2$SO$_4$ for 30 min to remove excess 14N$_2$. During the electrolysis process, 15N$_2$ was continuously fed into the electrolyte and electrolyzed at -0.3V vs RHE for 1h. After electrolysis, 10 mL reaction solution in cathodic chamber was concentrated to 1 mL at 80 ℃ and the pH was adjusted to 2. Then 30 μL of the above solution was dissolved in 600 μL dimethyl sulfoxide-D6, followed by the addition of 10 μL maleic acid solution (20 mM, internal standard), and then the above mixture was subjected to 1H NMR spectroscopy measurement. 14N$_2$ labeling experiment and 1H NMR measurement were conducted with the same method. 1H NMR calibration curves for calculating the amount of NH$_3$ were plotted using different concentrations of (14NH$_4$)$_2$SO$_4$ and (15NH$_4$)$_2$SO$_4$ solution.

**DFT calculations.**

The density functional theory (DFT) computations were conducted by the Vienna ab-initio simulation package (VASP) using the projector augmented wave (PAW) method.\textsuperscript{17} The exchange-correlation potential was described by the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).\textsuperscript{18} The energy cutoff for plane wave expansions was set to 450 eV, and the 2×2×1 Monkhorst-Pack grid k-points were selected to sample the Brillouin zone integration. The vacuum space is adopted 15 Å above the surfaces to avoid periodic interactions. The structural optimization was completed for energy and force convergence set at
$1.0 \times 10^{-4}$ eV and 0.02 eV Å$^{-1}$, respectively.

**Fig. S1.** EDX spectra of the as-prepared Mo$_2$C@rGO and CeO$_2$/Mo$_2$C@rGO.
Fig. S2. Nitrogen adsorption-desorption isotherms of the as-prepared CeO$_2$/Mo$_2$C@rGO.
Fig. S3. (a) HRTEM image; (b) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image; (c-d) Corresponding element mappings of the as-prepared Mo$_2$C@rGO.
Fig. S4. (a) SEM image and (b) XRD pattern of the prepared CeO$_2$@rGO.
Fig. S5. (a) SEM image and (b) XRD pattern of the prepared CeO₂.
Fig. S6. (a) SEM image and (b) XRD pattern of the prepared rGO.
Fig. S7. (a) SEM image and (b) XRD pattern of the prepared CeO$_2$/Mo$_2$C@rGO-L.
Fig. S8. (a) SEM image and (b) XRD pattern of the prepared CeO$_2$/Mo$_2$C@rGO-H.
Fig. S9. EPR spectra of CeO$_2$/Mo$_2$C@rGO, CeO$_2$@rGO and CeO$_2$. 
Fig. S10. XPS survey pattern of the CeO$_2$/Mo$_2$C@rGO.
Fig. S11. (a) UV-Vis absorption spectra of various NH$_3$ concentrations after being incubated for 2 h under ambient conditions. (b) Calibration curve used for calculation of NH$_3$ concentrations.
Fig. S12. (a) UV-Vis absorption spectra of various N$_2$H$_4$·H$_2$O concentrations after being incubated for 10 min under ambient conditions. (b) Calibration curve used for calculation of N$_2$H$_4$·H$_2$O concentrations.
Fig. S13. UV-vis absorption spectra of the electrolytes for 10% CeO$_2$/Mo$_2$C@rGO at each given potentials.
Fig. S14. (a) UV-vis absorption spectra of electrolyte stained with indophenol indicator at different potentials for Mo$_2$C@rGO. (b) Corresponding calculated NH$_3$ yield rates and Faradaic efficiencies at each given potentials.
Fig. S15. (a) UV-vis absorption spectra of electrolyte stained with indophenol indicator for CeO$_2$@rGO at different potentials. (b) Corresponding calculated NH$_3$ yield rates and Faradaic efficiencies at each given potentials.
Fig. S16. (a) UV-vis absorption spectra of electrolyte stained with indophenol indicator for CeO₂ at different potentials. (b) Corresponding calculated NH₃ yield rates and Faradaic efficiencies at each given potentials.
Fig. S17. (a) UV-vis absorption spectra of electrolyte stained with indophenol indicator for rGO at different potentials. (b) Corresponding calculated NH$_3$ yield rates and Faradaic efficiencies at each given potentials.
Fig. S18. (a) UV-vis absorption spectra of electrolyte stained with indophenol indicator for CeO$_2$/Mo$_2$C@rGO-L at different potentials. (b) Corresponding calculated NH$_3$ yield rates and Faradaic efficiencies at each given potentials.
Fig. S19. (a) UV-vis absorption spectra of electrolyte stained with indophenol indicator for CeO$_2$/Mo$_2$C@rGO-H at different potentials. (b) Corresponding calculated NH$_3$ yield rates and Faradaic efficiencies at each given potentials.
Fig. S20. The comparison of NRR performance for the CeO$_2$/Mo$_2$C@rGO doped with different concentrations of Ce.
Fig. S21. (a) UV-vis absorption spectra of electrolyte stained with indophenol indicator for 2 h under different conditions. (b) Corresponding calculated NH$_3$ yield rates and FEs at a potential of -0.3 V for different electrodes.
Fig. S22. (a, b) 1H NMR spectra of $^{14}\text{NH}_4^+$ with a series of concentrations and the corresponding calibration curve. (c, d) 1H NMR spectra of $^{15}\text{NH}_4^+$ with a series of concentrations and the corresponding calibration curve.
Fig. S23. (a) UV-Vis spectra of the electrolyte estimated by the method of Watt and Chrisp after NRR process for CeO$_2$/Mo$_2$C@rGO. (b) Corresponding calculated N$_2$H$_4$·H$_2$O concentration.
Fig. S24. XRD pattern for CeO$_2$/Mo$_2$C@rGO after 20 h stability test.
**Fig. S25.** Morphology of CeO$_2$/Mo$_2$C@rGO after 20 h stability test. (a) SEM image; (b) HRTEM image; (c) Corresponding line-scanning intensity profiles from b; (d) Elemental mapping images of CeO$_2$/Mo$_2$C@rGO after 20 h stability test.
Fig. S26. XPS spectra in (a) Mo 3d, (b) C 1s, (c) Ce 3d and (d) O 1s regions of CeO$_2$/Mo$_2$C@rGO after 20 h stability test.
Fig. S27. CV curves of (a) CeO$_2$/Mo$_2$C@rGO, (b) Mo$_2$C@rGO, (c) CeO$_2$@rGO, (d) CeO$_2$ and (e) rGO at 100-200 mV s$^{-1}$ in the range of 0.1 and 0.2 V vs. RHE. (f) Calculated corresponding C$_{dl}$ values of the above samples.
Table S1. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of different samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ce content (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂/Mo₂C@rGO</td>
<td>1.1</td>
</tr>
<tr>
<td>CeO₂/Mo₂C@rGO-L</td>
<td>0.61</td>
</tr>
<tr>
<td>CeO₂/Mo₂C@rGO-H</td>
<td>2.2</td>
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Table S2. Comparison of NRR performances with reported graphene-based catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Potential (V vs. RHE)</th>
<th>NH$_3$ yield ($\mu$g h$^{-1}$ mg$^{-1}$)</th>
<th>FE (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$/Mo$_2$C@rGO</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>-0.3</td>
<td>22.3</td>
<td>12.7</td>
<td>This work</td>
</tr>
<tr>
<td>IrTe 4 PNRs</td>
<td>0.1 M HCl</td>
<td>-0.2</td>
<td>8.3</td>
<td>10.10</td>
<td>[1]</td>
</tr>
<tr>
<td>a-Au/CeO$_x$-rGO</td>
<td>0.1 M HCl</td>
<td>-0.2</td>
<td>8.3</td>
<td>10.10</td>
<td>[1]</td>
</tr>
<tr>
<td>Pd$<em>{0.2}$Cu$</em>{0.8}$/rGO</td>
<td>0.1 M KOH</td>
<td>-0.2</td>
<td>2.8</td>
<td>4.5</td>
<td>[2]</td>
</tr>
<tr>
<td>NiO/graphene</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>-0.7</td>
<td>18.6</td>
<td>7.8</td>
<td>[3]</td>
</tr>
<tr>
<td>F-doped graphene</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>-0.7</td>
<td>9.3</td>
<td>4.2</td>
<td>[4]</td>
</tr>
<tr>
<td>O-doped graphene</td>
<td>0.1 M HCl</td>
<td>-0.55</td>
<td>21.3</td>
<td>12.6 (-0.45 V)</td>
<td>[5]</td>
</tr>
<tr>
<td>MoP@rGO</td>
<td>0.1 M Li$_2$SO$_4$</td>
<td>-0.6</td>
<td>7.5</td>
<td>9.1</td>
<td>[6]</td>
</tr>
<tr>
<td>CeO$_2$-rGO</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>-0.7</td>
<td>16.98</td>
<td>4.78</td>
<td>[7]</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-rGO</td>
<td>0.5 M LiClO$_4$</td>
<td>-0.5</td>
<td>22.13</td>
<td>5.89 (-0.4 V)</td>
<td>[8]</td>
</tr>
<tr>
<td>ZnO@rGO</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>-0.65</td>
<td>17.7</td>
<td>6.4</td>
<td>[9]</td>
</tr>
<tr>
<td>mVOx@rGO</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>-0.35</td>
<td>18.84</td>
<td>16.97</td>
<td>[10]</td>
</tr>
<tr>
<td>In$_2$O$_3$/rGO</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>-0.7</td>
<td>18.4</td>
<td>8.1</td>
<td>[11]</td>
</tr>
<tr>
<td>Tannic acid-rGO</td>
<td>0.5 M LiClO$_4$</td>
<td>-0.75</td>
<td>17.02</td>
<td>4.83</td>
<td>[12]</td>
</tr>
<tr>
<td>N,S co-doped graphene</td>
<td>0.1 M HCl</td>
<td>-0.6</td>
<td>7.7</td>
<td>5.8</td>
<td>[13]</td>
</tr>
<tr>
<td>MoS$_2$ nanodots/rGO</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>-0.75</td>
<td>16.41</td>
<td>27.93</td>
<td>[14]</td>
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Supplementary references


