Supporting Information for

Efficient electrocatalytic nitrogen reduction to ammonia with aqueous silver nanodots

Wenyi Li¹², Ke Li¹, Yixing Ye¹, Shengbo Zhang¹, Yanyan Liu¹², Guozhong Wang¹, Changhao Liang*¹
Haimin Zhang*¹ & Huijun Zhao³

¹ Key Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials, Anhui
² University of Science and Technology of China, Hefei 230026, China.
³ Centre for Clean Environment and Energy, Griffith University, Gold Coast Campus, QLD 4222, Australia.

* These authors contributed equally: Wenyi Li, Ke Li and Yixing Ye. Correspondence and requests for materials should be addressed to C.L. (email: chliang@issp.ac.cn) or to H.Z. (email: zhanghm@issp.ac.cn).
Supplementary Table 1. The comparable results of our work and other recently reported NRR electrocatalysts.

| Catalyst          | System /Conditions | NH₃ Yield Rate | FE (%)     | Detection method | Ref. |
|-------------------|--------------------|----------------|------------|------------------|------|
| AgNDs 0.1 M Na₂SO₄ (PH =10.5) Ti mesh in three-electrode system | 600.4±23.0 μg h⁻¹ mg⁻¹ Ag ( -0.25 V vs. RHE) | Ti plate in two-electrode system | 804.5±30.6 μg h⁻¹ mg⁻¹ Ag ( -1.8 V cell voltage) | Ov-TiO₂/Ti in three-electrode system | 1.27 ± 0.03 μg mL⁻¹ ( -0.25 V vs. RHE) |
|                  |                    |                |            | Indophenol method | This work |
| NiO NDs/G 0.1 M Na₂SO₄ | 18.6 μg h⁻¹ mg⁻¹ | 7.8           | Indophenol method | 1 |
| CuO/RGO 0.1 M Na₂SO₄ | 1.8×10⁻¹⁰ mol s⁻¹ cm² | 3.9           | Indophenol method | 2 |
| CoO QD/RGO 0.1 M Na₂SO₄ | 21.5 μg h⁻¹ mg⁻¹ | 8.3           | Indophenol method | 3 |
| ZnO QDs/RGO 0.1 M Na₂SO₄ | 17.7 μg h⁻¹ mg⁻¹ | 6.4           | Indophenol method | 4 |
| SnO₂ QDs/RGO 0.1 M Na₂SO₄ | 25.6 μg h⁻¹ mg⁻¹ | 7.1           | Indophenol method | 5 |
| Mo₂C/C 0.5 M Li₂SO₄ (PH =2) | 11.3 μg h⁻¹ mg⁻¹ Mo₂C⁻¹ | 7.8           | Nessler method | 6 |
| Ag nanosheet 0.1 M HCl | 4.62×10⁻¹¹ mol s⁻¹ cm² | 4.8           | Indophenol method | 7 |
| SA-Ag/NC 0.1 M HCl | 270.9 μg h⁻¹ mg⁻¹ Ag⁻¹ | 21.9           | Indophenol method | 8 |
| AgTPs 0.5 M K₂SO₄ (pH=3.5) | 58.5 μg h⁻¹ Ag⁻¹ | 25           | Nessler and Indophenol method | 9 |
| BD-Ag/AF 0.1 M Na₂SO₄ | 2.07×10⁻¹¹ mol s⁻¹ cm² | 9.61           | Indophenol method | 10 |
| Catalyst                  | Solution | Reaction Rate | Current Density | Potential vs. RHE | Method         | REF |
|---------------------------|----------|---------------|-----------------|-------------------|----------------|-----|
| Ag\textsubscript{3}Cu BPNs| 0.1 M Na\textsubscript{2}SO\textsubscript{4} | 24.59 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. | (0.5 V vs. RHE)  | 13.28             | Indophenol method | 11  |
| Ag-Au@ZIF EtOH in THF     | LiCF\textsubscript{3}SO\textsubscript{3} 1% | 10 pmol cm\textsuperscript{-2} s\textsuperscript{-1} | (-2.9 V vs. Ag/AgCl) | 18±4              | Indophenol method | 12  |

**Single-Atom Electrocatalysts**

| Catalyst                  | Solution | Reaction Rate | Current Density | Potential vs. RHE | Method         | REF |
|---------------------------|----------|---------------|-----------------|-------------------|----------------|-----|
| SA-Ag/NC                  | 0.1 M HCl | 270.9 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. | 69.4 mg h\textsuperscript{-1} mg\textsuperscript{-1} Ag | 21.9 (-0.65 V vs. RHE) | Indophenol method | 8   |
| AuSAs-NDPCs               | 0.1 M HCl | 2.32 μg h\textsuperscript{-1} cm\textsuperscript{-2} | (3.87 μg h\textsuperscript{-1} mg\textsuperscript{-1}) | 12.3 (-0.2 V vs. RHE) | Indophenol method | 13  |
| Au\textsubscript{1}/C\textsubscript{3}N\textsubscript{4} | 0.005 M H\textsubscript{2}SO\textsubscript{4} | 1.305 μg h\textsuperscript{-1} Au | (-0.1 V vs. RHE) | 11.1 (-0.1 V vs. RHE) | Indophenol method | 14  |
| Ru SAs/N-C                | 0.05 M H\textsubscript{2}SO\textsubscript{4} | 120.9 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. | (-0.2 V vs. RHE) | 29.6 (-0.21 V vs. RHE) | Indophenol method | 15  |
| Ru@ZrO\textsubscript{2}/NC | 0.1 M HCl | 3.665 mgNH\textsubscript{3} h\textsuperscript{-1} mg\textsuperscript{-1} cat. | (3665 μg h\textsuperscript{-1} mg Ru\textsuperscript{-1}) | 21 (-0.11 V vs. RHE) | Indophenol method | 16  |
| FeSA-N-C                  | 0.1 M KOH | 7.48 μg h\textsuperscript{-1} mg\textsuperscript{-1} | (0 V vs. RHE) | 56.55 (-0.1 V vs. RHE) | Indophenol method | 17  |
| SA-Mo/NPC                 | 0.1 M KOH | 34.0 ± 3.6 μgH\textsubscript{2}SO\textsubscript{4} h\textsuperscript{-1} mg\textsuperscript{-1} cat. | (-0.3 V vs. RHE) | 14.6 ±1.6 (-0.3 V vs. RHE) | Nessler method | 18  |
| ISAS-Fe/NC                | 0.1 M PBS | 62.9 ± 2.7 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. | (-0.4 V vs. RHE) | 18.6 ±0.8 (-0.45 V vs. RHE) | Indophenol method | 19  |
| Fe-(O-C\textsubscript{2})\textsubscript{4} | 0.1 M KOH | 32.1 μg h\textsuperscript{-1} mg\textsuperscript{-1} | (-0.1 V vs. RHE) | 29.3 (-0.1 V vs. RHE) | Indophenol method | 20  |

**Metal Electrocatatysts**

| Catalyst                  | Solution | Reaction Rate | Current Density | Potential vs. RHE | Method         | REF |
|---------------------------|----------|---------------|-----------------|-------------------|----------------|-----|
| FePc/C                    | 0.1 M Na\textsubscript{2}SO\textsubscript{4} | 137.95 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. | (-0.3 V vs. RHE) | 14.17 (-0.2 V vs. RHE) | Indophenol method | 21  |
| Rh\textsubscript{2}Sb RNRs/C| 0.5 M Na\textsubscript{2}SO\textsubscript{4} | 228.85 ± 12.96 μg h\textsuperscript{-1} mg\textsuperscript{-1} Ru | (-0.45 V vs. RHE) | 6.32 ±0.28 (-0.30 V vs. RHE) | Indophenol method | 22  |
| Bi\textsubscript{4}O\textsubscript{11}/CeO\textsubscript{2} | 0.1 M HCl (pH = 1) | 23.21 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. | (-0.2 V vs. RHE) | 10.16 (-0.2 V vs. RHE) | Indophenol method | 23  |
| MXene (T\textsubscript{i}3C\textsubscript{2}Tx) | 0.5 M Li\textsubscript{2}SO\textsubscript{4}+ 0.1 M HCl (pH=2) | 4.72 μg h\textsuperscript{-1} cm\textsuperscript{-2} | (2.68 μg h\textsuperscript{-1} mg\textsuperscript{-1}) | 5.78 (-0.1 V vs. RHE) | Nessler method | 24  |
| TiO\textsubscript{2}/T\textsubscript{i}3C\textsubscript{2}Tx | 0.1 M HCl | 32.17 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. | (-0.45 V vs. RHE) | 16.07 (-0.45 V vs. RHE) | Indophenol method | 25  |
| C-T\textsubscript{i}3O\textsubscript{y}/C | 0.1 M LiClO\textsubscript{4} | 14.8 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. | (-0.4 V vs. RHE) | 17.8 (-0.4 V vs. RHE) | Indophenol method | 26  |
| Electrode Material | Electrolyte | Current Density | Overpotential | Method | Reference |
|--------------------|-------------|----------------|---------------|--------|-----------|
| Zr-TiO₂            | 0.1 M KOH   | 8.90 µg h⁻¹ cm⁻² \( (8.9 \mu g h^{-1} mg^{-1}) \) \(-0.45 \text{ V vs. RHE} \) | 17.3 | Indophenol method | 27 |
| OVs-rich MoO₂      | 0.1 M HCl   | 12.20 µg h⁻¹ mg⁻¹ \(-0.15 \text{ V vs. RHE} \) | 8.2 | Indophenol method | 28 |
| Nb₂O₅/CP          | 0.1 M HCl   | 43.6 µg h⁻¹ \( \text{g cm}^{-2} \) \(-0.55 \text{ V vs. RHE} \) | 9.26 | Indophenol method | 29 |
| Cu-CeO₂-3.9       | 0.1 M Na₂SO₄ (pH = 6.3) | \(5.3 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2} \) \( (13.3 \mu g h^{-1} mg^{-1}) \) \(-0.1 \text{ V vs. RHE} \) | 19.1 | Indophenol method | 30 |
| Mn₂O₄             | 0.1 M Na₂SO₄ | 11.6 µg h⁻¹ \( \text{g cm}^{-2} \) \(-0.8 \text{ V vs. RHE} \) | 3 | Indophenol method | 31 |
| Fe/Fe₃O₄         | 0.1 M PBS (pH = 7.2) | \(~0.19 \mu g cm^{-2} h^{-1} \) \(~0.19 \mu g h^{-1} \) \(-0.3 \text{ V vs. RHE} \) | 8.29 | Indophenol method | 32 |
| Ti/C              | 0.1 M HCl   | 14.1 µg h⁻¹ \( \text{g cm}^{-2} \) \(-0.5 \text{ V vs. RHE} \) | 5.8 | Indophenol method | 33 |
| MoS₂              | 0.1 M Na₂SO₄ | \(8.08 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2} \) \(-0.6 \text{ V vs. RHE} \) | 1.17 | Indophenol method | 34 |
| FeS@MoS₂/CFC      | 0.1 M Na₂SO₄ | 8.45 µg cm² h⁻¹ \( (6.34 \mu g h^{-1} mg^{-1}) \) \(-0.3 \text{ V vs. RHE} \) | 2.96 | Nessler method | 35 |
| CoS₂/NS-G         | 0.05 M H₂SO₄ | 25.0 µg h⁻¹ \( \text{g cm}^{-2} \) \(-0.2 \text{ V vs. RHE} \) | 25.9 | Indophenol method | 36 |
| LaF₃              | 0.5 M LiClO₄ | 55.9 µg h⁻¹ \( \text{g cm}^{-2} \) \(-0.45 \text{ V vs. RHE} \) | 16 | Indophenol method | 37 |
| PdRu              | 0.1 M HCl   | 34.2 µg h⁻¹ \( \text{g cm}^{-2} \) \(-0.2 \text{ V vs. RHE} \) | 2.4 | Indophenol method | 38 |
| Pd₃Cu₁           | 1 M KOH     | 39.9 µg h⁻¹ \( \text{g cm}^{-2} \) \(-0.25 \text{ V vs. RHE} \) | 1.56 | Nessler method | 39 |
| PdCuIr           | 0.1 M Na₂SO₄ | 13.43 µg h⁻¹ \( \text{g cm}^{-2} \) \(-0.3 \text{ V vs. RHE} \) | 5.29 | Indophenol method | 40 |

**Metal-Free Electrocatalysts**

| Electrode Material | Electrolyte | Current Density | Overpotential | Method | Reference |
|--------------------|-------------|----------------|---------------|--------|-----------|
| CC-450            | 0.1 M Na₂SO₄ + 0.02 M H₂SO₄ | \(15.8 \mu g \text{ cm}^{-2} \text{ h}^{-1} \) \(-0.3 \text{ V vs. RHE} \) | 6.92 | Indophenol method | 41 |
| S-CNS             | 0.1 M Na₂SO₄ | 19.07 µg h⁻¹ \( \text{g cm}^{-2} \) \(-0.3 \text{ V vs. RHE} \) | 7.47 | Indophenol method | 42 |
| d-FG              | 0.1 M Na₂SO₄ | 9.3 µg h⁻¹ \( \text{g cm}^{-2} \) \(-0.7 \text{ V vs. RHE} \) | 4.2 | Indophenol method | 43 |
| Sample      | Solution     | Activity (µg h\(^{-1}\) mg\(^{-1}\)) | Current Density (µg h\(^{-1}\) mg\(^{-1}\) cat) | Potentials (V vs. RHE) | Method          |
|-------------|--------------|---------------------------------------|-------------------------------------------------|------------------------|-----------------|
| FL-BP NSs   | 0.01 M HCl   | 31.37                                  | 5.07                                            | -0.7 V (-0.6 V)        | Indophenol      |
| BG          | 0.05 M H\(_2\)SO\(_4\) | 9.8                                   | 10.8                                            | -0.5 V                 | Indophenol      |
| BCN         | 0.1 M HCl    | 7.75                                  | 13.79                                           | -0.3 V                 | Indophenol      |
| NPC         | 0.05 M H\(_2\)SO\(_4\) | 1.40 mmol g\(^{-1}\) h\(^{-1}\)       | 1.42                                            | -0.9 V                 | Nessler         |
| VN NPs      | 0.05 M H\(_2\)SO\(_4\) | 3.3 × 10\(^{-10}\) mol s\(^{-1}\) cm\(^{-2}\) | 6.0                                             | -0.1 V                 | Nessler         |
| MBN         | 0.1 M Na\(_2\)SO\(_4\) | 18.2                                 | 5.5                                             | -0.7 V                 | Indophenol      |
| PCN         | 0.1 M HCl    | 8.09                                 | 11.05                                           | -0.2 V                 | Indophenol      |
| B\(_4\)C/CPE| 0.1 M HCl    | 26.57                                 | 15.95                                           | -0.75 V                | Indophenol      |
Supplementary Figure 1. Schematic illustration of two NRR electrocatalytic systems. a The non-loading electrocatalysis process using AgNDs catalyst uniformly dispersed in 0.1 M Na$_2$SO$_4$ solution (pH=10.5). b The traditional catalyst-loading electrocatalysis process in 0.1 M Na$_2$SO$_4$ solution (pH=10.5).
Supplementary Figure 2. TEM characterizations. TEM images of the as-synthesized Ag nanodots by the laser-ablation technique and inset of the corresponding nanodot size distribution curve.
Supplementary Figure 3. XPS characterizations of the AgNDs. a Surface survey XPS spectrum of the AgNDs. b High-resolution O 1s XPS spectrum of the AgNDs.
Supplementary Figure 4. Photograph of electrochemical NRR experimental setup.

This experimental set up was established following a similar protocol as the previously reported works to remove the possible interferences of NH$_3$ and NO$_x$ in the feeding gases.$^{20,52}$ Cu-Fe-Al unit was employed to purify the feeding gases. The Cu-Fe-Al catalyst (Supplementary Figure 5) was synthesized according to the reported methods.$^{53-55}$ Before each experiment, the Cu-Fe-Al catalyst was thermally treated at 300°C for 2 h under 5% H$_2$/Ar stream. The treated Cu-Fe-Al catalyst was covered with a stainless-steel vessel which filled up with the mixed ethanol and liquid nitrogen. For complete elimination of NO interference, a CrO$_3$ catalyst packed column (Dongguan Zhongtian Electronic Technology Co. LTD, China) was also employed in this work. Utilizing this purification system, any NO passed through this purification unit will be converted to water soluble NO$_2$, and then removed by the H$_2$SO$_4$ and distilled water before reaching the electrochemical cell.
Supplementary Figure 5. SEM image and photograph (inset) of the Cu-Fe-Al catalyst.
Supplementary Figure 6. Determination of ammonia. UV-Vis absorption spectra of the indophenol blue indicator with various concentrations of NH$_4^+$-N (0, 0.1, 0.2, 0.4, 0.8, 1.0 μg mL$^{-1}$) after incubating for 1 h at room temperature, a in 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5) and b in 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5) with AgNDs incorporation. c The calibration curve used for calculation of NH$_4^+$-N concentration (red sphere: in 0.1 M Na$_2$SO$_4$ electrolyte; green sphere: in 0.1 M Na$_2$SO$_4$ electrolyte with AgNDs incorporation). The error bars correspond to the standard deviations of three independent measurements.

The above results indicate that the influence of AgNDs introduction in 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5) is ignorable for the detection of NH$_3$ product by the indophenol blue method.
Supplementary Figure 7. Determination of hydrazine. UV-Vis absorption spectra with various concentrations of N$_2$H$_4$·H$_2$O (0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 μg mL$^{-1}$) after incubated for 20 min at room temperature, a in 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5) and b in 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5) with AgNDs incorporation. c The calibration curve used for calculation of N$_2$H$_4$·H$_2$O concentrations (Magenta sphere: in 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5); green sphere: in 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5) with AgNDs incorporation. The error bars correspond to the standard deviations of three independent measurements. d UV-Vis absorption spectra of samples after NRR measurement at -0.25 V vs. RHE in 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5) with AgNDs incorporation.

The above results indicate that the influence of AgNDs introduction in 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5) is ignorable for the detection of N$_2$H$_4$·H$_2$O by the Watt and Chrisp method.
Supplementary Figure 8. The characterizations of the NH₃ yield of AgNDs catalyst on the applied potential. UV-Vis absorption spectra of the collected samples from a cathodic compartment and b anodic compartment after NRR for 1 h in N₂-saturated 0.1 M Na₂SO₄ electrolyte (pH=10.5) at different potentials. c Total NH₃ yield using AgNDs in N₂-saturated 0.1 M Na₂SO₄ electrolyte (pH=10.5) at different potentials. d Time-dependent current curves of AgNDs at different potentials in N₂-saturated 0.1 M Na₂SO₄ electrolyte (pH=10.5).
Supplementary Figure 9. The quantification of the produced H₂. a The time-dependent current curve of NRR measurement at -0.25 V vs. RHE in 0.1 M Na₂SO₄ electrolyte (pH=10.5) with AgNDs incorporation. b Chromatograms of H₂ standards (100, 200, 400, 600, 800, 1000 μL). c The calibration curve used for calculation of H₂ volume. d The chromatogram of the yielded H₂ after 1 h NRR measurement at -0.25 V vs. RHE in 0.1 M Na₂SO₄ electrolyte (pH=10.5) with AgNDs incorporation. e The UV-Vis absorption spectra of yielded NH₃ after 1 h NRR measurement at -0.25 V vs. RHE in 0.1 M Na₂SO₄ electrolyte (pH=10.5) with AgNDs incorporation.
Supplementary Figure 10. Durability test. a Durability test of AgNDs catalyst at -0.25 V (vs. RHE) for 5 h NRR and the corresponding b $R_{RNH3}$ and c NH$_3$ yield measured every 1 h during 5 h NRR. The error bars correspond to the standard deviations of three independent measurements.
Supplementary Figure 11. *In-situ* time-dependence Raman spectra of AgNDs during durability measurement of NRR.
Supplementary Figure 12. TEM characterizations after 5 h NRR measurement. TEM and HRTEM images (inset of corresponding FFT patterns) of AgNDs after 5 h NRR measurement.
Supplementary Figure 13. XPS characterizations of the AgNDs after 5 h NRR measurement. a Surface survey XPS spectrum, b High-resolution N 1s XPS spectrum, c High-resolution Ag 3d XPS spectrum, d High-resolution O 1s XPS spectrum of the AgNDs before and after 5 h NRR measurement.
Supplementary Figure 14. Reproducibility test. TEM and HRTEM images (insets of corresponding FFT patterns) of a 1st batch and b 2nd batch of AgNDs. c NH₃ yield rate of two batches of AgNDs at -0.25 V (vs. RHE) in N₂-saturated 0.1 M Na₂SO₄ electrolyte (pH=10.5) for 1 h NRR in the non-loading electrocatalysis system. The error bars correspond to the standard deviations of three independent measurements. d The corresponding time-dependent current curves. e The corresponding UV-Vis absorption spectra of the collected solution samples.
Supplementary Figure 15. NH$_3$ quantification of the control experiments. a NH$_3$ yield under different control experiment conditions. The error bars correspond to the standard deviations of three independent measurements. UV-Vis absorption spectra of the corresponding collected solution samples from b cathodic compartment and c anodic compartment.
Supplementary Figure 16. Chromatograms of the standard solution (5.0 ppm NO$_2^-$ and 5.0 ppm NO$_3^-$) and the collected samples under various conditions.
Supplementary Figure 17. Isotopic labelling quantification experiments. a, c $^1$H NMR spectra of the $^{15}$NH$_4^+$ and $^{14}$NH$_4^+$ standards with different concentrations. b, d Corresponding $^{15}$NH$_4^+$ and $^{14}$NH$_4^+$ calibration curves constructed by plotting the integrated $^1$H NMR signal (7.00 ppm for $^{15}$NH$_4^+$ and 6.97 ppm for $^{14}$NH$_4^+$) against the standard concentration.
Supplementary Figure 18. TEM image of the as-synthesized Ag$_2$ONPs. (Inset of the corresponding Ag$_2$O nanoparticles size distribution curve and HRTEM image).
Supplementary Figure 19. TEM image of the as-synthesized AgNPs. (Inset of the corresponding Ag nanoparticles size distribution curve and HRTEM image).
Supplementary Figure 20. Contrast experiments. NH$_3$ yield rate and faradaic efficiency of Ag$_2$ONPs/CC, AgNPs/CC and AgNDs/CC at -0.25 V (vs. RHE) in N$_2$-saturated 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5) for 1 h NRR. The error bars correspond to the standard deviations of three independent measurements.
Supplementary Figure 21. Contrast experiments. NH$_3$ yield rate and faradaic efficiency of AgNDs catalyst using Ti mesh and carbon cloth (CC) as the current collectors in the non-loading electrocatalysis system. The error bars correspond to the standard deviations of three independent measurements.
Supplementary Figure 22. The influence of AgNDs concentration on the NH$_3$ yield. a NH$_3$ yield and b NH$_3$ yield rate of different concentrations of AgNDs at -0.25 V (vs. RHE) in N$_2$-saturated 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5) for 1 h NRR in the non-loading electrocatalysis system. The error bars correspond to the standard deviations of three independent measurements.
Supplementary Figure 23. The characterizations of the NH₃ yield of AgNDs catalyst in Ti plate-based two-electrode configured flow-type electrochemical reactor. UV-Vis absorption spectra of the collected samples from a cathodic compartment and b anodic compartment after NRR for 1 h in N₂-saturated 0.1 M Na₂SO₄ electrolyte (pH=10.5) at different cell voltages. c Time-dependent current curves of AgNDs at different cell voltages in N₂-saturated 0.1 M Na₂SO₄ electrolyte (pH=10.5).
Supplementary Figure 24. XRD patterns of the pristine Ti mesh and O$_x$-TiO$_2$/Ti mesh.
Supplementary Figure 25. SEM characterizations. SEM images of a-c pristine Ti mesh and d-f TiO$_2$/Ti mesh with different magnifications.
Supplementary Figure 26. TEM characterizations. a TEM and b corresponding HRTEM images of O$_x$-TiO$_2$/Ti mesh.
Supplementary Figure 27. EPR spectra of O$_v$-TiO$_2$/Ti mesh.
Supplementary Figure 28. The characterizations of the NH$_3$ yield of AgNDs catalyst using O$_x$-TiO$_2$/Ti current collector. UV-Vis absorption spectra of the collected samples from a cathodic compartment and b anodic compartment after NRR for 1 h at different potentials using O$_x$-TiO$_2$/Ti current collector and AgNDs in N$_2$-saturated 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5). c Time-dependent current curves of AgNDs at different potentials in N$_2$-saturated 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5) using O$_x$-TiO$_2$/Ti current collector.
Supplementary Figure 29. Contrast experiments. Comparison of NH$_3$ yield and FE for O$_x$-TiO$_2$/Ti with and without AgNDs incorporation in N$_2$-saturated 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5) at -0.25 V vs. RHE. The error bars correspond to the standard deviations of three independent measurements.
Supplementary Figure 30. Durability test. Time-dependent current curve of O$_x$-TiO$_2$/Ti with AgNDs incorporation in N$_2$-saturated 0.1 M Na$_2$SO$_4$ electrolyte (pH=10.5) at -0.25 V vs. RHE for 5 h NRR.
Supplementary Figure 31. The optimized geometric structure model of Ag(111) plane.
Supplementary Figure 32. Top view and side view of relaxed N\textsubscript{2} adsorption configurations on Ag(111) plane. (Ag: cyan, N: dark blue)
Supplementary References

1. Chu, K. et al. NiO nanodots on graphene for efficient electrochemical N\textsubscript{2} reduction to NH\textsubscript{3}. *ACS Appl. Energy Mater.* 2, 2288-2295 (2019).

2. Wang, F. et al. CuO/Graphene nanocomposite for nitrogen reduction reaction. *ChemCatChem* 11, 1441-1447 (2019).

3. Chu, K. et al. Efficient electrocatalytic N\textsubscript{2} reduction on CoO quantum dots. *J. Mater. Chem. A* 7, 4389-4394 (2019).

4. Liu, Y. P. et al. ZnO quantum dots coupled with graphene toward electrocatalytic N\textsubscript{2} reduction: experimental and DFT investigations. *Chem. Eur. J.* 25, 11933-11939 (2019).

5. Chu, K. et al. Electronically coupled SnO\textsubscript{2} quantum dots and graphene for efficient nitrogen reduction reaction. *ACS Appl. Mater. Interfaces* 11, 31806-31815 (2019).

6. Cheng, H. et al. Molybdenum carbide nanodots enable efficient electrocatalytic nitrogen fixation under ambient conditions. *Adv. Mater.* 30, 1803694 (2018).

7. Sun, X. et al. Ag nanosheets for efficient electrocatalytic N\textsubscript{2} fixation to NH\textsubscript{3} under ambient conditions. *Chem. Commun.* 54, 11427-11430 (2018).

8. Chen, Y. et al. Highly productive electrosynthesis of ammonia by admolecule-targeting single Ag sites. *ACS Nano* 14, 6938-6946 (2020).

9. Gao, W. Y. et al. Morphology-dependent electrocatalytic nitrogen reduction on Ag triangular nanoplates. *Chem. Commun.* 55, 10705-10708 (2019).

10. Ji, L. et al. Nanostructured bromide-derived Ag film: an efficient electrocatalyst for N\textsubscript{2} reduction to NH\textsubscript{3} under ambient conditions. *Inorg. Chem.* 57, 14692-14697 (2018).

11. Yu, H., *et al.* Bimetallic Ag\textsubscript{3}Cu porous networks for ambient electrolysis of nitrogen to ammonia. *J. Mater. Chem. A* 7, 12526-12531 (2019).

12. Lee, H.K., *et al.* Favoring the unfavored: Selective electrochemical nitrogen fixation using a reticular chemistry approach. *Sci. Adv.* 4, eaar3208 (2018).

13. Qin, Q., Heil, T., Antonietti, M. & Oschatz, M. Single-site gold catalysts on hierarchical N-doped porous noble carbon for enhanced electrochemical reduction of nitrogen. *Small Methods* 2, 1800202 (2018).

14. Wang, X., *et al.* Atomically dispersed Au\textsubscript{1} catalyst towards efficient electrochemical synthesis of ammonia. *Sci. Bull.* 63, 1246-1253 (2018).

15. Geng, Z., *et al.* Achieving a record-high yield rate of 120.9 μg\textsubscript{NH3} mg\textsuperscript{-1} h\textsuperscript{-1} for N\textsubscript{2} electrochemical reduction over Ru single-atom Catalysts. *Adv. Mater.* 30, 1803498 (2018).

16. Tao, H., *et al.* Nitrogen fixation by Ru single-atom electrocatalytic reduction. *Chem* 5, 204-214 (2019).

17. Wang, M., *et al.* Over 56.55% faradaic efficiency of ambient ammonia synthesis enabled by positively shifting the reaction potential. *Nat. Commun.* 10, 341 (2019).

18. Han, L., *et al.* Atomically dispersed molybdenum catalysts for efficient ambient nitrogen fixation. *Angew. Chem., Int. Ed.* 58, 2321-2325 (2019).

19. Lü, F., *et al.* Nitrogen-coordinated single Fe sites for efficient electrocatalytic N\textsubscript{2} fixation in neutral media. *Nano Energy* 61, 420-427 (2019).

20. Zhang, S., *et al.* Electrocatalytically Active Fe-(O-C\textsubscript{2})\textsubscript{4} single-atom sites for efficient reduction of nitrogen to ammonia. *Angew. Chem., Int. Ed.* 59, 13423-13429 (2020).

21. He, C., *et al.* Identification of FeN\textsubscript{4} as an efficient active site for electrochemical N\textsubscript{2} Reduction. *ACS Catal.* 7311-7317 (2019).

22. Zhang, N., *et al.* Surface-regulated rhodium–antimony nanorods for nitrogen fixation. *Angew. Chem., Int. Ed.* 59, 8066-8071 (2020).
23. Lv, C., et al. An amorphous noble-metal-free electrocatalyst that enables nitrogen fixation under ambient conditions. *Angew. Chem., Int. Ed.* 57, 6073-6076 (2018).

24. Luo, Y., et al. Efficient electrocatalytic N2 fixation with MXene under ambient conditions. *Joule* 3, 279-289 (2019).

25. Fang, Y., et al. High-performance electrocatalytic conversion of N2 to NH3 using oxygen-vacancy-rich TiO2 in situ grown on Ti3C2Tx MXene. *Adv. Energy Mater.* 0, 1803406 (2019).

26. Qin, Q., et al. Enhanced electrocatalytic N2 reduction via partial anion substitution in titanium oxide-carbon composites. *Angew. Chem., Int. Ed.* 58, 13101-13106 (2019).

27. Cao, N., et al. Doping strain induced bi-Ti3+ pairs for efficient N2 activation and electrocatalytic fixation. *Nat. Commun.* 10, 2877 (2019).

28. Zhang, G., Ji, Q. & Zhang, K. Triggering surface oxygen vacancies on atomic layered molybdenum dioxide for a low energy consumption path toward nitrogen fixation. *Nano Energy* 59, 10-16 (2019).

29. Han, J., et al. Ambient N2 fixation to NH3 at ambient conditions: using Nb2O5 nanofiber as a high-performance electrocatalyst. *Nano Energy* 52, 264-270 (2018).

30. Zhang, S., et al. Cu doping in CeO2 to form multiple oxygen vacancies for dramatically enhanced ambient N2 reduction performance. *Chem. Commun.* 55, 2952-2955 (2019).

31. Wu, X., et al. Mn3O4 Nanocube: An efficient electrocatalyst toward artificial N2 fixation to NH3. *Small Methods* 14, 1803111 (2018).

32. Hu, L., et al. Ambient electrochemical ammonia synthesis with high selectivity on Fe/Fe oxide Catalyst. *ACS Catal.* 8, 9312-9319 (2018).

33. Yu, G., et al. Electrospun TiC/C nanofibers for ambient electrocatalytic N2 reduction. *J. Mater. Chem. A* 7, 19657-19661 (2019).

34. Zhang, L., et al. Electrochemical ammonia synthesis via nitrogen reduction reaction on a MoS2 catalyst: theoretical and experimental studies. *Adv. Mater.* 30, 1800191 (2018).

35. Guo, Y. et al. Boosting nitrogen reduction reaction by bio-inspired FeMoS containing hybrid electrocatalyst over a wide pH range. *Nano Energy* 62, 282-288 (2019).

36. Chen, P., et al. Interfacial engineering of cobalt sulfide/graphene hybrids for highly efficient ammonia electrolysis. *Pnas* 201817881 (2019).

37. Li, P., et al. Ambient electrocatalytic N2 reduction to NH3 by metal fluorides. *J. Mater. Chem. A* 7, 17761-17765 (2019).

38. Wang, H., et al. Direct fabrication of bi-metallic PdRu nanorod assemblies for electrochemical ammonia synthesis. *Nanoscale* 11, 5499-5505 (2019).

39. Pang, F., et al. Bimodal nanoporous Pd3Cu1 alloy with restrained hydrogen evolution for stable and high yield electrochemical nitrogen reduction. *Nano Energy* 58, 834-841 (2019).

40. Kumar, R.D., et al. Trimetallic PdCuIr with long-spined sea-urchin-like morphology for ambient electroreduction of nitrogen to ammonia. *J. Mater. Chem. A* 7, 3190-3196 (2019).

41. Li, W., et al. Nitrogen-free commercial carbon cloth with rich defects for electrocatalytic ammonia synthesis under ambient conditions. *Chem. Commun.* 54, 11188-11191 (2018).

42. Xia, L., et al. S-doped carbon nanospheres: An efficient electrocatalyst toward artificial N2 fixation to NH3. *Small Methods* 3, 1800251 (2019).

43. Zhao, J., et al. Defect-rich fluorographene nanosheets for artificial N2 fixation under ambient conditions. *Chem. Commun.* 55, 4266-4269 (2019).

44. Zhang, L., Ding, L.X., Chen, G. F., Yang, X. & Wang, H. Ammonia synthesis under ambient conditions: selective electroreduction of dinitrogen to ammonia on black phosphorus nanosheets. *Angew. Chem., Int. Ed.* 58, 2612-2616 (2019).

45. Yu, X., et al. Boron-doped graphene for electrocatalytic N2 reduction. *Joule* 2, 1610-1622 (2018).
46. Chen, C., et al. B N pairs enriched defective carbon nanosheets for ammonia synthesis with high efficiency. Small Methods 15, 1805029 (2019).

47. Liu, Y., et al. Facile ammonia synthesis from electrocatalytic N₂ reduction under ambient conditions on N-doped porous carbon. ACS Catal. 8, 1186-1191 (2018).

48. Yang, X., et al. Mechanistic Insights into electrochemical nitrogen reduction reaction on vanadium Nitride nanoparticles. J. Am. Chem. Soc. 140, 13387-13391 (2018).

49. Zhao, J., et al. High-performance N₂-to-NH₃ fixation by a metal-free electrocatalyst. Nanoscale 11, 4231-4235 (2019).

50. Lv, C., et al. Defect engineering metal-free polymeric carbon nitride electrocatalyst for effective nitrogen fixation under ambient conditions. Angew. Chem., Int. Ed. 57, 10246-10250 (2018).

51. Qiu, W., et al. High-performance artificial nitrogen fixation at ambient conditions using a metal-free electrocatalyst. Nat. Commun. 9, 3485 (2018).

52. Andersen, S.Z., et al. A rigorous electrochemical ammonia synthesis protocol with quantitative isotope measurements. Nature 570, 504-508 (2019).

53. Ma, L., et al. In situ DRIFTS and temperature-programmed technology study on NH₃-SCR of NOₓ over Cu-SSZ-13 and Cu-SAPO-34 catalysts. Appl. Catal. B Environ. 156-157, 428-437 (2014).

54. Ma, L., et al. Characterization of commercial Cu-SSZ-13 and Cu-SAPO-34 catalysts with hydrothermal treatment for NH₃-SCR of NOₓ in diesel exhaust. Chem. Eng. J. 225, 323-330 (2013).

55. Ye, Q., Wang, L. & Yang, R.T. Activity, propene poisoning resistance and hydrothermal stability of copper exchanged chabazite-like zeolite catalysts for SCR of NO with ammonia in comparison to Cu/ZSM-5. Appl. Catal. A Gen. 427-428, 24-34 (2012).