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Supporting Information

Facile, Cost-Effective Plasma Synthesis of Self-Supportive FeS_x on Fe Foam for Efficient Electrochemical Reduction of N₂ under Ambient Conditions

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Analysis of ammonia by the indophenol blue method¹: A 2.5 mL aliquot of the test solution was taken from the electrochemical cell and diluted to 25 mL using 0.1 M KOH solution. To this solution was added 2 mL of a 1 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate, followed by the addition of 1 mL of 0.05 M NaClO and 0.2 mL of 1 wt% Na[Fe(NO)(CN)₅] (sodium nitroferricyanide) aqueous solution. After 2 h, the absorption spectrum of the mixed solution was measured by using a UV-visible spectrophotometer (Shimadzu UV-2450). The concentration of the formed indophenol blue was determined by using the absorbance at a wavelength of 697.5 nm² and the corresponding absolute calibration curve was obtained by using the ammonium chloride (NH₄Cl) aqueous solutions with a series of known concentrations as the standards. To obtain the calibration curve, each NH₄Cl standard solution was diluted to 25 mL using 0.1 M KOH, and to this solution was added 2 mL of the 1 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate, followed by the addition of 1 mL of 0.05 M NaClO and 0.2 mL of 1 wt% Na[Fe(NO)(CN)₅] (sodium nitroferricyanide) aqueous solution. After 2 h, the absorption spectrum was measured by using the UV-visible spectrophotometer (Shimadzu UV-2450). Note that all the measurements for the NRR products and the calibration standards were taken together, in parallel, to avoid any potential interference from ambient. All the measurements were taken for three times to check the reproducibility, and the data variation was within 0.2%. It is worth noting that the NH₃ concentration in the test solution was reasonably high (~2 mM at -0.30 V), and thus the NH₃ quantification by this method was reasonably accurate.

Analysis of ammonia by the Nessler's reagent method: A 1.25 mL aliquot of the test solution was taken from the electrochemical cell and diluted to 25 mL using 0.1 M KOH solution. To this solution was added 1 mL of 0.2 M potassium sodium tartrate ($KNaC_4H_4O_6$) solution and 1 mL of the Nessler's reagent. After 20 min, the absorption spectrum of the mixed solution was measured by using a UVvisible spectrophotometer (Shimadzu UV-2450). The absorbance at a wavelength of 425 nm was used to calculate the ammonia concentration, and the corresponding absolute calibration curve was obtained by using the ammonium chloride (NH_4CI) aqueous solutions with a series of known concentrations as the standards. To obtain the calibration curve, each NH₄Cl standard solution was diluted to 25 mL using 0.1 M KOH, and to this solution was added 1 mL of 0.2 M potassium sodium tartrate ($KNaC_4H_4O_6$) solution and 1 mL of the Nessler's reagent. After 20 min, the absorption spectrum was measured by using the UV-visible spectrophotometer (Shimadzu UV-2450). Note that all the measurements for the NRR products and the calibration standards were taken together, in parallel, to avoid any potential interference from ambient. All the measurements were taken for three times to check the reproducibility, and the data variation was within 0.25%. It is worth noting that the NH₃ concentration in the test solution was reasonably high (~2 mM at -0.30 V), and thus the NH₃ quantification by this method was reasonably accurate.

Analysis of ammonia by the ion chromatograms method: A 10 mL aliquot of the test solution was taken from the electrochemical cell and diluted to 20 mL using 0.1 M HCl solution. The obtained solution was analyzed by an ion chromatography system (Dionex Aquion, Thermo Fisher, USA) with the software Chromeleon 7.2 SR4. The corresponding absolute calibration curve was obtained by using the ammonium chloride (NH₄Cl) aqueous solutions with a series of known concentrations as the standards. Note that all the measurements for the NRR products and the calibration standards were taken together, to avoid any potential interference from ambient. It is worth noting that the NH₃ concentration in the test solution was reasonably high (2 mM at -0.30 V), and thus the NH₃ quantification by this method was reasonably accurate.

Analysis of ammonia by nuclear magnetic resonance (NMR) with ¹⁵N labelling³: The NRR experiments were performed using either ¹⁵N₂ (99% isotopic purity, Wuhan Newradar Special Gas Co. Ltd.) for

isotopic labelling or normal ¹⁴N₂ for comparison. Each NRR experiment was conducted at -0.30 V vs. RHE for 1 h. A 5 mL aliquot of the test solution was taken from the electrochemical cell, into which 1.1 mL of 0.5 M H₂SO₄ was added to adjust the solution pH = 1. A 500 µL aliquot of the resultant solution was added into an NMR tube, and 10 vol. % D₂O was added for the lock signal and internal standard. The ammonia concentration was quantified by measuring the ¹H NMR spectra (Bruker, Ultrashield Plus 400 MHz) for ¹⁴NH₄⁺ or ¹⁵NH₄⁺. The corresponding absolute calibration curves were obtained by using the ¹⁵NH₄Cl (98.5% isotopic purity, Shanghai Engineering Research Center of Stable Isotope) and ¹⁴NH₄Cl (dissolved in 0.05 M H₂SO₄) aqueous solutions with a series of known concentrations as the standards.

Analysis of hydrazine by the Watt-Chrisp spectrophotometric method⁴: The color reagent for this method consisted of 5.99 g of *p*-dimethylaminobenzaldehyde, 30 mL of concentrated HCl (36%), and 300 mL of ethanol. A 2.5 mL aliquot of the test solution was taken from the electrochemical cell and diluted to 25 mL using 0.1 M HCl solution. To this solution was added 5 mL of the color reagent. The mixed solution was stirred for 10 min at room temperature, and then the absorption spectrum was measured using a UV-visible spectrophotometer (Shimadzu UV-2450). The absorbance at a wavelength of 455 nm was used to calculate the hydrazine concentration, and the corresponding absolute calibration curve was obtained by using the hydrazine (N₂H₄) aqueous solutions with a series of known concentrations as the standards. To obtain the calibration curve, each N₂H₄ standard solution was diluted to 25 mL using 0.1 M HCl, and to this solution was measured by using the UV-visible spectrophotometer (Shimadzu UV-2450). Note that all the measurements for the NRR products and the calibration standards were taken together, in parallel, to avoid any potential interference from ambient. All the measurements were taken for three times to check the reproducibility, and the data variation was within 0.35%.

Faradaic efficiency: The Faradaic efficiencies (FE) were separately calculated for ammonia and hydrazine. Assuming that three electrons were needed to produce one NH_3 molecule and four electrons were needed to produce one N_2H_4 molecule, the Faradaic efficiencies can be calculated as the following:

$$FE(NH_3) = 3F \times c_{NH3} \times V / Q$$

and
$$FE(N_2H_4) = 4F \times c_{N2H4} \times V / Q,$$

where *F* is the Faraday constant, *Q* is the total charge passed through the electrode, *V* is the volume of electrolyte, and c_{NH3} and c_{N2H4} are the measured molar concentrations of NH₃ and N₂H₄, respectively.

EIS measurements were performed in the frequency range from 0.1 Hz to 10 kHz. The bias potentials were set to be -0.14, -0.22, -0.30, -0.38 and -0.42 V vs. RHE, and the ac amplitude was set to be 5 mV. The EIS data were fitted using ZView software.

DFT Calculation: The density functional theory (DFT) calculation was carried out using the Vienna ab initio simulation package (VASP).⁵ The Perdue-Burke-Ernzerhof (PBE) version of generalized gradient approximation (GGA)⁶ was used to describe the exchange-correlation interactions. The projector-augmented wave (PAW) method was used to model the core-valence electron interactions.⁷ A DFT-D3 correction with Becke-Jonson damping was adopted to account for van der Waals interactions. The energy cutoff of the plane-wave basis set was 400 eV. For structural relaxations, the energy and force convergence criteria were 10^{-4} eV and 0.02 eV/Å, respectively. The reciprocal space was sampled with 5×5×1 Monkhorst-pack grids. Previous study suggested that the tetragonal mackinawite FeS and corresponding surface structures were non-magnetic,⁸ and thus no spin-polarization was included in the calculation.

The lattice parameters of the tetragonal FeS structure were first obtained by calculating the energy-volume relations. The obtained *a* and *c* values were 3.582 and 4.927Å, respectively. These values are in good agreement with previous theoretical and experimental values.⁸⁻⁹ Based on the optimized lattice constants, low-Miller index FeS surfaces were created. A vacuum region of 15 Å along the *c*-axis was added to avoid the interactions between the surface slab and its periodic image. The bottom layers of the slabs were fixed during relaxation.

The adsorption energy is defined as $E_{ad} = E_{slab+NxHy} - E_{slab} - xE_N - yE_H$, where $E_{slab+NxHy}$, E_{slab} , E_N , and E_H are the energy of the slab-adsorbates system, the energy of the clean slab, and the energies of N and H atoms, respectively. In this calculation, the energies of N and H were calculated as the per-atom energies of the gaseous dinitrogen (N₂) and dihydrogen (H₂) molecules, respectively. The free energies were calculated by considering the vibrational modes of the adsorbates within the harmonic oscillator approximation, which is given by $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where ΔZPE and ΔS are the changes of the zero-point energy and entropy, and T is the temperature (298.15K). These calculations were performed using the thermochemistry module of the ASE package,¹⁰ treating adsorbates within the harmonic oscillator approximation.



Figure S1. (a) High-resolution cross-sectional TEM image of the as-synthesized FeS_x/Fe foam electrode. (b,c) Fast Fourier transform (FFT) analysis of the yellow-boxed areas in the TEM image (a). The FFT patterns can be indexed to be the (b) marcasite FeS_2 and (c) pyrite FeS_2 . (d) XRD of the as-synthesized FeS_x/Fe foam electrode, which shows a mixed pyrite (P) and marcasite (M) FeS_2 .



Figure S2. Representative chronoamperogram for the measurement of the polarization curves in N₂ and Ar. The applied potential was stepwise increased from -0.14 to -0.42 V (vs. RHE) and the potential was held constant in each step for 120 s to allow the current to reach a steady state. The values of the steady-state current in each step were used to generate the polarization curves.



Figure S3. (a) Ion chromatograms of the standard NH₄Cl solutions with a series of known concentrations and (b) the corresponding calibration curve.



Figure S4. Photographs and the measured absorption spectra of the indophenol blue method for the analysis of ammonia.



Figure S5. Photographs and the measured absorption spectra of the Nessler's reagent method for the analysis of ammonia.



Figure S6. Absolute calibrations of (a,b) the indophenol blue and (c,d) Nessler's reagent methods for the analysis of ammonia and (e,f) the Watt-Chrisp method for the analysis of hydrazine. Absorption spectra of the (a,c) NH_4Cl and (e) N_2H_4 standard solutions with series of known concentrations and (b,d,f) the corresponding absolute calibration curves.

Table S1. Comparison of the ion chromatography, indophenol blue, and Nessler's reagent methods for the analysis of NH_3 . The numbers listed in the table are the NH_3 generation rates obtained from the above three methods, and all the numbers are in the unit of 10^{-10} mol s⁻¹ cm⁻².

| Potential | Ar (0 V) | -0.14 V | –0.22 V | –0.30 V | –0.38 V | -0.42 V |
|--------------------|----------|---------|---------|---------|---------|---------|
| Ion Chromatography | 0.0035 | 0.12 | 1.10 | 4.45 | 3.84 | 1.51 |
| Indophenol blue | 0.0023 | 0.11 | 1.03 | 4.21 | 3.61 | 1.43 |
| Nessler's reagent | 0.0014 | 0.11 | 1.07 | 4.29 | 3.73 | 1.47 |



Figure S7. Photographs and the measured absorption spectra of the Watt-Chrisp method for the analysis of hydrazine.

Table S2. Rates and the Faradaic efficiencies (FE) for the electrochemical productions of NH_3 and N_2H_4 .

| Potential | NH ₃ | | N ₂ H ₄ | | |
|-----------|--|-------------------|--|--------------------|-------------------------------------|
| | Production rate (mol s ⁻¹ cm ⁻²) | FE _{NH3} | Production rate (mol s ⁻¹ cm ⁻²) | FE _{N2H4} | Δ <i>J</i> / J _{N2} |
| -0.14 V | 0.12×10 ⁻¹⁰ | 12.2% | 0.29×10^{-11} | 1.9% | 13.9% |
| -0.22 V | 1.10×10 ⁻¹⁰ | 16.7% | 1.58×10 ⁻¹¹ | 1.6% | 18.4% |
| -0.30 V | 4.45×10 ⁻¹⁰ | 18.9% | 4.67×10 ⁻¹¹ | 1.3% | 19.7% |
| -0.38 V | 3.84×10 ⁻¹⁰ | 6.8% | 4.20×10 ⁻¹¹ | 0.5% | 7.3% |
| -0.42 V | 1.51×10 ⁻¹⁰ | 1.7% | 1.07×10 ⁻¹¹ | 0.08% | 1.9% |



Figure S8. Quantifying the ammonia production by NMR with ¹⁵N labelling. (a) ¹H NMR spectra of the solutions containing ¹⁴NH₄⁺ and ¹⁵NH₄⁺ produced by the NRR from ¹⁴N₂ and ¹⁵N₂, respectively (at –0.30 V vs. RHE for 1 h). No ammonia signals were detected for the solutions subjected to continuously ¹⁴N₂, ¹⁵N₂, or Ar bubbling under open circuit potential (OCP) for 1 h. (b) Absolute calibrations of the NMR method for the analysis of ammonia, and the integrated peak areas for ¹⁴NH₄⁺ and ¹⁵NH₄⁺ were extracted from ¹H NMR spectra shown in (c) and (d). ¹H NMR spectra of the (c) ¹⁴NH₄Cl and (d) ¹⁵NH₄Cl standard solutions with series of known concentrations.

Using the calibrations curves shown in (b), the NH₃ production rates were calculated, based on the ¹H NMR spectra shown in (a), to be 4.13×10^{-10} mol s⁻¹ cm⁻² (for ¹⁵N₂) and 4.11×10^{-10} mol s⁻¹ cm⁻² (for ¹⁴N₂).

Table S3. Comparison of the FeS_x/Fe with various other electrocatalysts for the electrochemical production of NH₃ from N₂ under ambient conditions.

| Electrocatalyst | Electrolyte | Temperature | Potential (V vs. RHE) | NH₃ production rate (mol s ⁻¹ cm ⁻²) | NH₃ Faradaic efficiency | Reference |
|--|---------------------------------------|-------------|--------------------------|---|-------------------------------|---|
| FeS _x /Fe | 0.1 M KOH | 21°C | -0.30 | 4.13×10 ⁻¹⁰ | 17.6% | This Work |
| Ru-SA/N-C | 0.05 M H ₂ SO ₄ | 25°C | -0.20 | 5.03×10 ⁻¹⁰ | 29.6% | <i>Adv. Mater.</i> 2018, 30, 1803498 |
| NCM-Au NP | 0.1 M HCl | 25°C | -0.20 | 5.85×10 ⁻¹⁰ | 22.0% | Angew. Chem. 2018, 130, 1 |
| Single-Site Au/NC | 0.1 M HCl | 20°C | -0.20 | 3.79×10 ⁻¹¹ | 12.3% | Small Methods, 2018, 1800202 |
| Polymeric carbon nitride | Diluted HCl | 20°C | -0.20 | 1.32×10 ⁻¹⁰ | 11.6% | Angew.Chem. Int.Ed. 2018, 57, 10246 |
| Bi nanosheet | $0.1 \text{ M Na}_2 \text{SO}_4$ | 25°C | -0.80 | 4.15×10 ⁻¹¹ | 10.4% | ACS Catal., 2019, 9, 2902 |
| MOF-derived N- carbon | 0.1 M KOH | 24°C | -0.30 | 9.40×10 ⁻¹⁰ | 10.2% | Nano Energy, 2018, 48, 217 |
| S-rich MoS_2 | 0.1 M Li ₂ SO ₄ | 25°C | -0.20 | 4.38×10 ⁻¹⁰ | 9.8% | Adv. Energy Mater., 2019, 1803935 |
| Fe-N/CNT | 0.1 M KOH | 25°C | -0.20 | 11.38×10 ⁻¹⁰ | 9.2% | ACS Catal., 2019, 9, 336 |
| O-Fe ₂ O ₃ /CNT | 0.1 M KOH | 25°C | -0.11 | 2.36×10 ⁻¹¹ | 8.3% | Chem. Eur. J. 2018, 24, 1 |
| CoO quantum dots | 0.5 M H ₂ SO ₄ | 25°C | -0.60 | 12.88×10 ⁻¹⁰ | 8.3% | J. Mater. Chem. A., 2019, 7, 4389 |
| MnO | 0.1 M Na ₂ SO ₄ | 25°C | -0.39 | 1.11×10 ⁻¹¹ | 8.0% | <i>Adv. Sci.,</i> 2018, 54, 13010 |
| Boron nitride | 0.1 M Na ₂ SO ₄ | 25°C | -0.70 | 14.80×10 ⁻¹⁰ | 5.5% | Nanoscale, 2019, 11, 4231 |
| Pd _{0.2} Cu _{0.8} /RGO | 0.1 M KOH | 25°C | -0.20 | 2.10×10 ⁻¹¹ | 4.5% | Adv. Energy Mater. 2018, 1800124 |
| Fe ₃ O ₄ /Ti | 0.1 M Na ₂ SO ₄ | 25°C | -0.40 | 5.60×10 ⁻¹¹ | 2.6% | Nanoscale, 2018, 10, 14386 |
| VN/Ti | 0.1 M HCI | 25°C | -0.50 | 8.40×10 ⁻¹¹ | 2.3% | ACS Sustainable Chem. Eng. 2018, 6, 9545 |
| γ - Fe ₂ O ₃ | 0.1 М КОН | < 65°C | 0.0 | 1.21×10 ⁻¹¹ | 1.9% | ACS Sustainable Chem. Eng. 2017, 5, 10986 |
| MoS ₂ | 0.1 M Na ₂ SO ₄ | 25°C | -0.50 | 8.08×10 ⁻¹¹ | 1.2% | <i>Adv. Mater.</i> 2018, <i>30,</i> 1800191 |
| a-Au/CeO _x –RGO | 0.1 M HCI | 25°C | -0.20 | 2.71×10 ⁻¹¹ | 10.1% | <i>Adv. Mater.</i> 2017, <i>29,</i> 1700001 |
| Au subnanoclusters/ TiO ₂ | 0.1 M HCI | 25°C | -0.20 | 3.50×10 ⁻¹¹ | 8.1% | Adv. Mater. 2017, 29, 1606550 |
| THH Au NRs | 0.1 M KOH | 25°C | -0.20 | 2.70×10 ⁻¹¹ | 3.8% | <i>Adv. Mater.</i> 2017, <i>29,</i> 1604799 |
| PEBCD/C | 0.5 M Li ₂ SO ₄ | 25°C | -0.50 | 2.60×10 ⁻¹¹ | 2.8% | J. Am. Chem. Soc. 2017, 139, 9771 |



Figure S9. Nyquist (a,c,e,g) and Bode (b,d,f,h) plots of the EIS measurements in N_2 - and Ar-saturated solutions at different potentials (vs. RHE).

Table S4 Fitted parameters of the experimental EIS data shown in Figures 3 and S5. The equivalent circuit used for fitting is shown in Figure 3c. The equivalent double-layer capacitance (C_{dl}) is calculated from $T = C_{dl}^{\varphi} (R_s^{-1} + R_{ct}^{-1})^{1-\varphi}$, where T and φ are the fitted parameters of the CPE element.

| | Potential | -0.14 V | –0.22 V | –0.30 V | –0.38 V | -0.42 V |
|--------------------|--|---------------|---------------|---------------|---------------|---------------|
| in Ar | <i>R</i> _s (Ω cm ²) | 11.69 (±0.06) | 11.67 (±0.06) | 11.66 (±0.04) | 11.72 (±0.05) | 11.60 (±0.02) |
| | CPE-T | 0.89 (±0.01) | 0.95 (±0.01) | 1.23 (±0.02) | 1.02 (±0.03) | 1.08 (±0.03) |
| | CPE-φ | 0.71 (±0.01) | 0.73 (±0.01) | 0.80 (±0.01) | 0.73 (±0.01) | 0.72 (±0.03) |
| | $R_{\rm ct}$ (Ω cm ²) | 270.2 (±9.9) | 154.0 (±3.1) | 74.82 (±0.36) | 17.37 (±0.11) | 7.18 (±0.06) |
| | C _{dl} (mF/cm ²) | 2.30 (±0.04) | 2.21 (±0.10) | 2.30 (±0.02) | 2.04 (±0.21) | 1.98 (±0.30) |
| in N2 | $R_{\rm s}$ (Ω cm ²) | 11.63 (±0.06) | 11.79 (±0.05) | 11.86 (±0.04) | 11.63 (±0.04) | 11.50 (±0.02) |
| | CPE-T | 1.02 (±0.02) | 1.10 (±0.01) | 4.26 (±0.06) | 5.43 (±0.21) | 7.28 (±0.25) |
| | CPE-φ | 0.73 (±0.02) | 0.75 (±0.01) | 0.81 (±0.01) | 0.75 (±0.01) | 0.74 (±0.01) |
| | R _{ct} (Ω cm ²) | 231 (±11) | 124.0 (±2.3) | 59.26 (±0.52) | 15.52 (±0.17) | 6.78 (±0.05) |
| | C _{dl} (mF/cm ²) | 2.50 (±0.03) | 2.42 (±0.11) | 2.11 (±0.23) | 1.90 (±0.41) | 2.20 (±0.12) |
| F | R _{HER} (Ω cm²) | 270.2 (±9.9) | 154.0 (±3.1) | 74.82 (±0.36) | 17.37 (±0.11) | 7.18 (±0.06) |
| F | R _{NRR} (Ω cm²) | 1599 (±18) | 637 (±10) | 285.0 (±7.3) | 145.7 (±2.9) | 121.7 (±1.3) |
| $R_{\rm NRR}^{-1}$ | $(R_{\rm NRR}^{-1} + R_{\rm HER}^{-1})$ | 14.4% (±0.6%) | 19.5% (±0.2%) | 20.8% (±0.1%) | 10.7% (±0.1%) | 5.2% (±0.1%) |



Figure S10. (a,d) SEM images and (b,c,e,f) the corresponding EDS elemental maps of the FeS_x/Fe foam electrode (a–c) before and (d–f) after 20 h of potentiostatic NRR at –0.30 V (vs. RHE). All scale bars represent 50 μ m.



Figure S11. Crystallinity analysis of the the FeS_x/Fe foam electrode after 20 h of potentiostatic NRR at -0.30 V (vs. RHE). (a) High resolution cross-sectional TEM image. (b) Fast Fourier transform (FFT) analysis of the yellow-boxed area in the TEM image (a), and the FFT pattern can be indexed to be the mackinawite FeS structure. (d) XRD of the post-NRR FeS_x/Fe foam electrode, showing the peaks of the mackinawite FeS.



Figure S12. Raman spectra of the FeS_x layer on Fe foam before (green) and after (blue) the NRR. The Raman spectra of (red) the solvothermally-synthesized¹¹ mackinawite FeS, (purple) ALD-synthesized¹² FeS₂ (mixed pyrite-marcasite), and (black) ALD-synthesized FeS (mackinawite)¹³ are also shown for comparison. The initial FeS_x showed three Raman peaks at 316, 333, and 369 cm⁻¹, which could be assigned to the A_g mode of the marcasite-structure FeS₂¹⁴ and the E_g and A_g modes of the pyrite-structure FeS₂,¹⁵ respectively, resembling the case of using the H₂S plasma for the ALD of FeS₂.¹² The post-NRR FeS_x showed two Raman peaks at 212 and 270 cm⁻¹, which could be assigned to the asymmetric stretching modes of the mackinawite-structure FeS,¹⁶⁻¹⁷ resembling the spectra of the solvothermally-synthesized mackinawite FeS and the ALD-synthesized mackinawite FeS.¹³ In addition, it is worth noting that, elemental S (S₈ or S₆) should typically have multiple intense Raman peaks in 400~500 cm⁻¹ and below 300 cm⁻¹,¹⁸ but our spectra did not contain these features, which indicates that the plasma-sulfurized FeS_x surface layer was free of elemental S impurity.



Figure S13. XPS O 1s spectra of the FeS_x/Fe foam electrode (a) before and (b) after 20 h of potentiostatic NRR at -0.30 V (vs. RHE). (b) The peak components at 529.6 eV (FeOOH) and 531.1 eV (FeOOH) correspond to the two types of the oxygen atoms (underlined) in FeOOH.¹⁹ The other peak component at 535.8 eV corresponds to SO_x²⁻.²⁰



Figure S14. Comparison of the NRR performance for the plasma-synthesized FeS_x and ALD-prepared mackinawite FeS. (b) The measured NH₃ production rates and (b) the corresponding electrochemical polarization curves (in N₂- and Ar-saturated solutions). Both the results are normalized by their actual surface areas, which were obtained by the cyclic voltammetry performed in a non-Faradaic regime to obtain the double-layer capacitances (C_{dl}) of the electrodes (c-f). The voltage scan rate was varied from 5 to 60 mV/s, and C_{dl} was extracted from the slope of the linear fit in the plot of current density versus scan rate. Accordingly, the C_{dl} for the plasma-synthesized FeS_x/Fe and ALD-FeS/Fe electrodes were found to be 2.08 and 1.35 mF/cm², respectively. Assuming a smooth flat surface has a C_{dl} value of 60 μ F/cm²,²¹⁻²² the roughness factors of the plasma-FeS_x/Fe and ALD-FeS/Fe electrodes were 34.67 and 22.5, respectively.

Note that the ALD of the mackinawite FeS on Fe foam was carried out using a process previously developed in our group.^{13, 17} In brief, the deposition was performed at 120 °C in a home-built tubular reactor using bis(N,N'-diisopropylacetamidinato)iron(II) and H₂S (3% diluted in Ar) as the precursors for iron and sulfur, respectively. The deposition consisted of a total of 500 ALD cycles, which afforded a ~13 nm thick FeS film conformally covering the surface of the porous Fe foam.



Figure S15. Elementary reaction steps of the NRR process based on the DFT calculation.



Figure S16. (a) Cyclic voltammetry experiment for the Fe_2O_3/Fe electrode was performed in a non-Faradaic regime, with various voltage scan rates from 5 to 60 mV/s. (b) Plot of the current density versus the scan rate, in which the C_{dl} of the Fe_2O_3/Fe electrode was extracted to be 2.29 mF/cm².

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