Supplementary Material

Fe_3C/Fe Nanoparticles Embedded in N-Doped Carbon as Catalysts for Electrocatalytic Nitrogen Reduction to Ammonia

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Experimental section：

Determination of NH_3: The ammonia concentration was determined by the indophenol blue method. Chromogenic agent A: 2 g NaOH was dissolved in 50 mL deionized water, then 5% (mass fraction) salicylic acid and 5% (mass fraction) sodium citrate were added. Chromogenic agent B: 1.8 g sodium hypochlorite solution was weighed and added to 50 mL deionized water to obtain 0.05 M NaClO solution. Chromogenic agent C: 0.1 g sodium nitroprusside was added to 9.9 mL deionized water to obtain 1 wt% sodium nitroprusside solution. 2 mL electrolyzed solution, 2 mL chromogenic agent A, 1 mL chromogenic agent B, and 0.2 mL chromogenic agent C were mixed in the dark for 2 h. An appropriate amount of the solution was

placed in a colorimetric tube for testing, and the absorbance at a wavelength of 655 nm was recorded. The standard working curve of ammonia concentration was established by gradually diluting NH_4Cl solution. The absorbances of NH_4^+ with the concentration of 0.00, 0.02, 0.04, 0.08, 0.16, 0.32, and 0.64 μg mL^{-1} were recorded respectively, and the relationship between absorbance and ammonia concentration was obtained by linear fitting (Figures S1 and S2).

Determination of N_2H_4: The detection method for the possible by-product N_2H_4 is based on the Watt-Chrisp method. First, 2 g p-dimethylaminobenzaldehyde (p-$C_9H_{11}NO$) was mixed with 10 mL concentrated hydrochloric acid, then 100 mL ethanol solution was added and mixed uniformly as the chromogenic agent. 3 mL electrolyzed solution was added to 3 mL chromogenic agent and stood for 15 min. The absorbance at a wavelength of 455 nm was recorded. The absorbance of N_2H_4 with a concentration of 0.0, 0.2, 0.4, 0.6, and 0.8 μg mL^{-1} were recorded respectively, and the relationship between absorbance and N_2H_4 concentration was obtained by linear fitting (Figures S3 and S4).

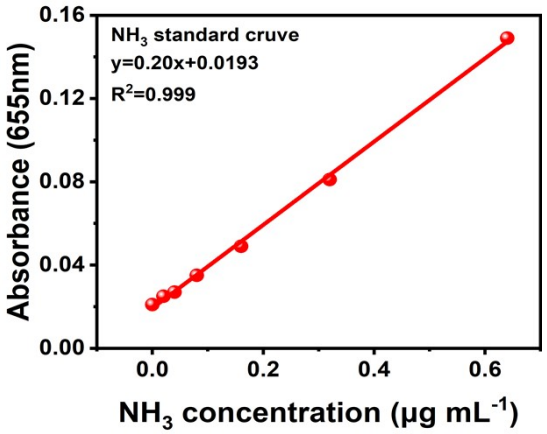

Figure S1. Calibration curve for determining NH_3。

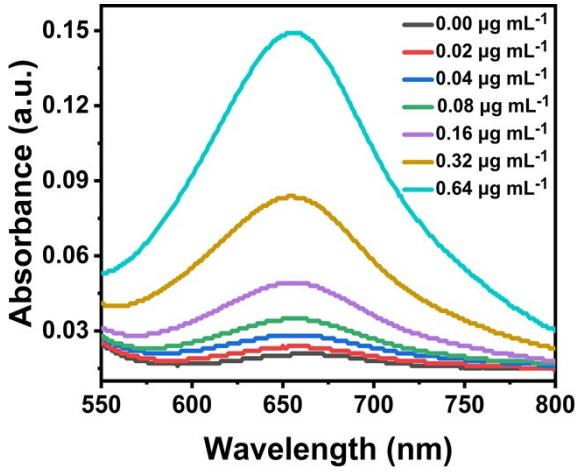

Figure S2. UV-Vis absorption spectra of standard NH_3 solutions in 0.1 M KOH electrolyte solution.

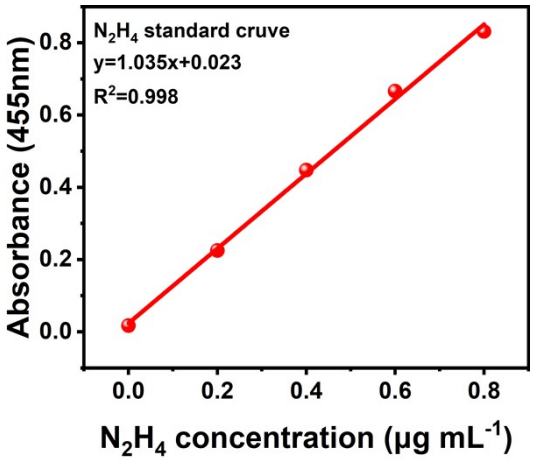

Figure S3. Calibration curve for determining N_2H_4.

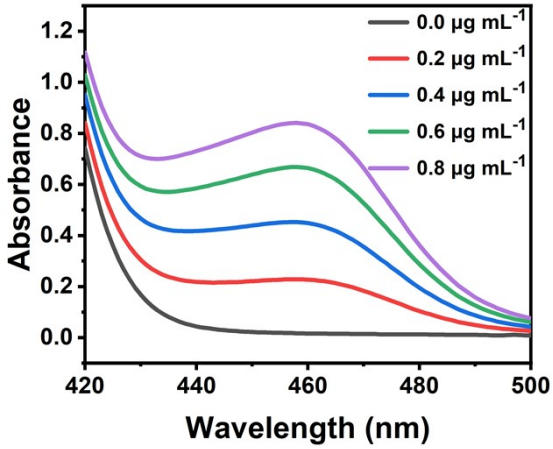

Figure S4. UV-Vis absorption spectra of standard N_2H_4 solutions in 0.1 M KOH electrolyte solution.

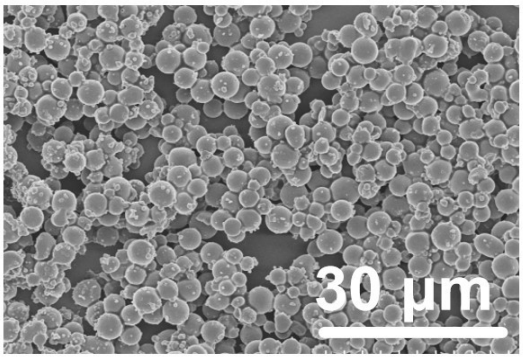

Figure S5. SEM image of the precursor of NC before calcination.

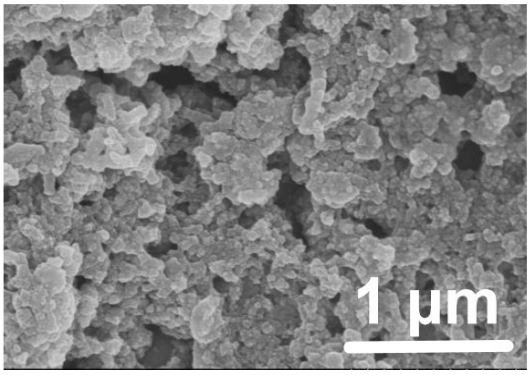

Figure S6. SEM image of the precursor of Fe_3C/Fe@NC before calcination.

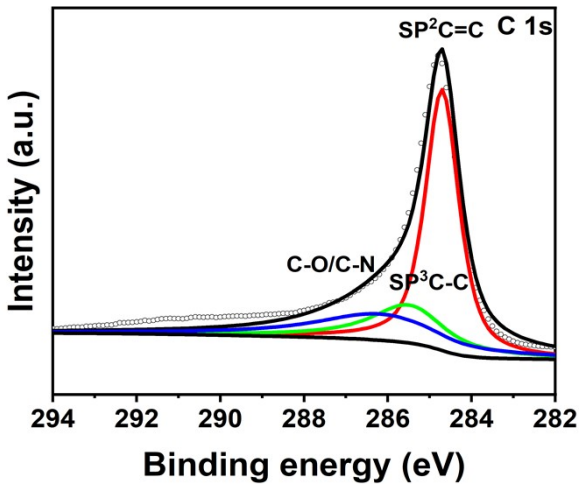

Figure S7. High-resolution XPS spectrum of C1s.

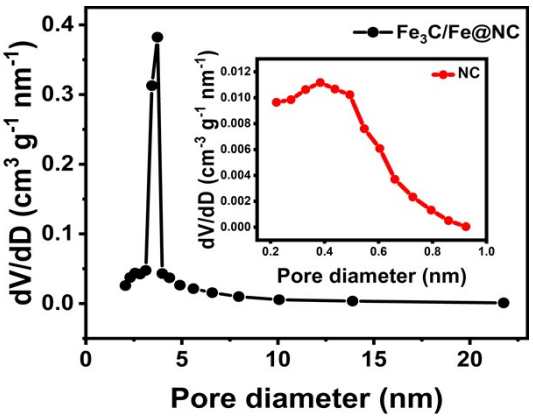

Figure S8. Pore size distribution of Fe_3C/Fe@NC and NC.

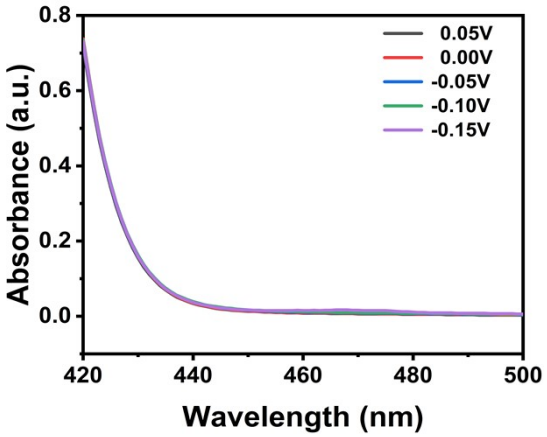

Figure S9. UV-vis absorption spectra of N_2H_4 at different voltages.

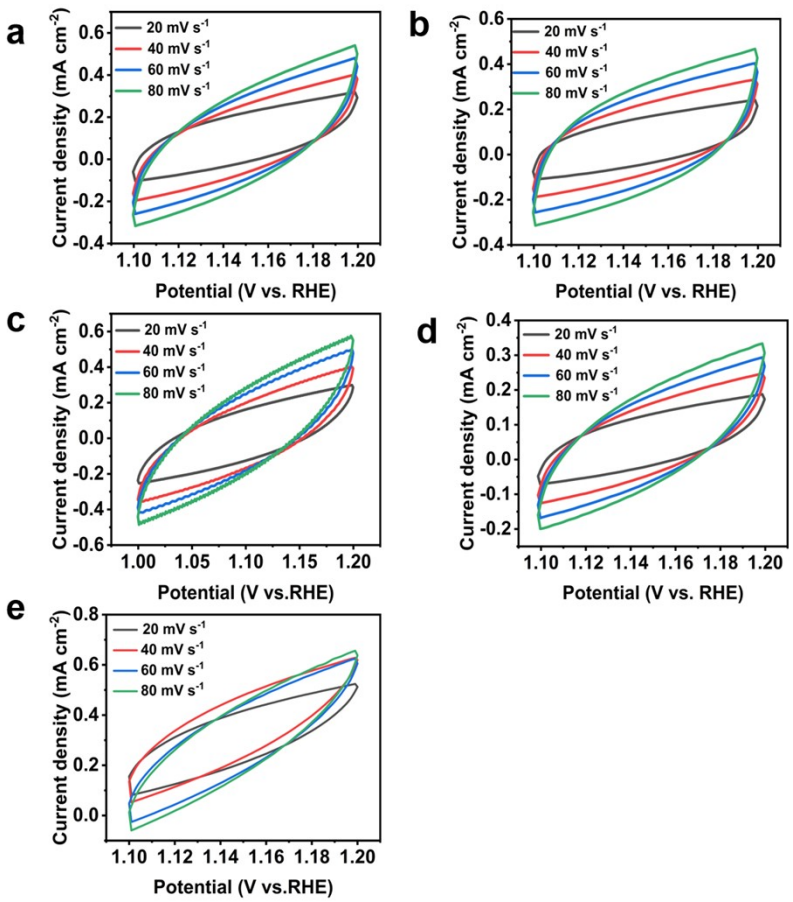

Figure S10. CV of (a) Fe_3C/Fe@NC, (b) NC, (c) Fe_3C, (d) C and (e) FeNPs at different scan rates.

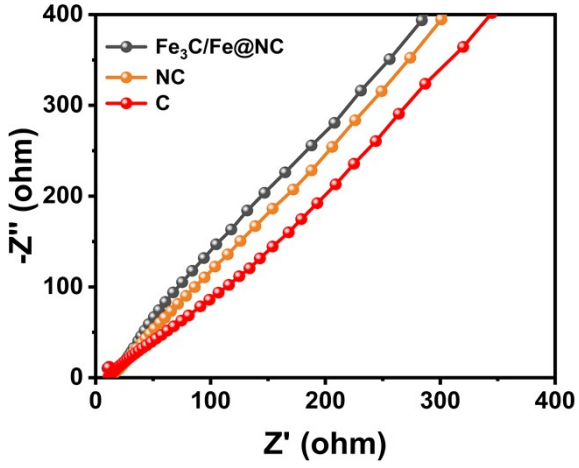

Figure S11. The impedance spectrum of Fe_3C/Fe@NC, NC and C.

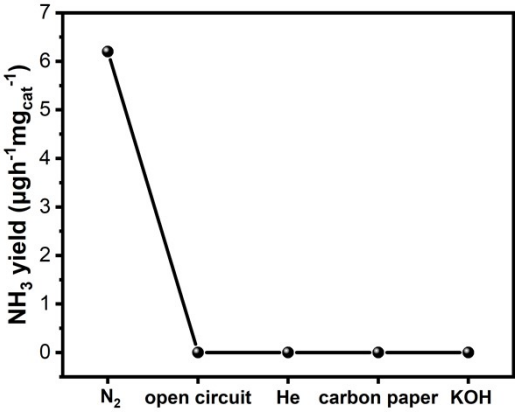

Figure S12. Ammonia production rate under different control conditions.

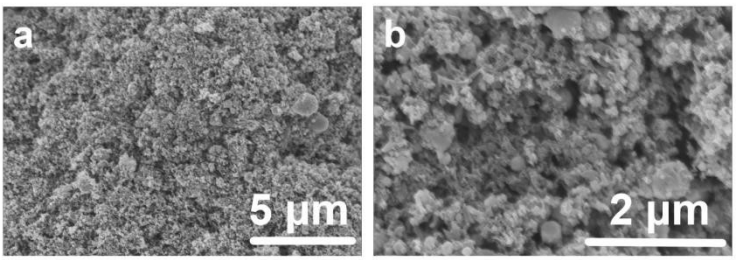

Figure S13. (a and b) SEM images of Fe_3/Fe@NC after the cycling test.

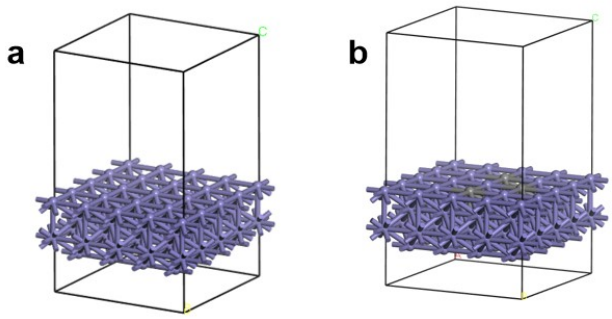

Figure S14. The constructed heterostructure models of (a) Fe and (b) Fe_3C/Fe.

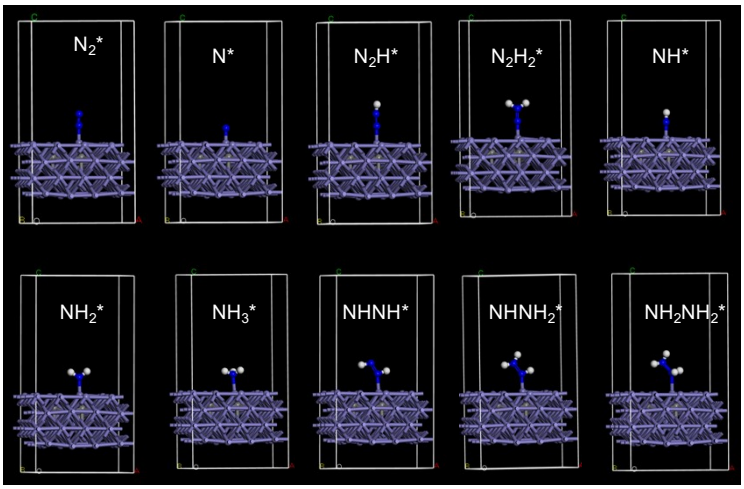

Figure S15. The constructed heterostructure models of various nitrogen-containing species supported on Fe_3C/Fe.