

Supporting Information

Electron Distribution Tuning of Fluorine-Doped Carbon for Ammonia

Electrosynthesis

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Experimental

Chemicals and materials. Carbon black (BP2000, Tianjin Aweixin Chemical Technology Co., Ltd), polytetrafluoroethylene preparation (Aladdin, P111312, aqueous dispersion, 60 wt%), sodium hydroxide (Macklin, S835850, $\geq 98\%$), salicylic acid (Macklin, S817529, 99.5%), potassium sodium tartrate tetrahydrate (Macklin, P816438, 99.5%), sodium nitroferricyanide(III) dehydrate (Macklin, S817931, 99.98% metals basis), sodium hypochlorite solution (Macklin, S828471, available chlorine 4.0%), ammonium chloride (Macklin, A801305, 99.8%), hydrazine monohydrate (Alfa Aesar, A14005, 98+%), hydrochloric acid (Sinopharm Chemical Reagent Co., Ltd, 10011018, 36.0~38.0%), sulfuric acid (Sinopharm Chemical Reagent Co., Ltd, 10021618,

95.0~98.0%), ethyl alcohol (Sinopharm Chemical Reagent Co., Ltd, 10009218, $\geq 99.7\%$), 4-(dimethylamino) benzaldehyde (Sigma Aldrich, 156477, 99%), Nafion solution (Alfa Aesar, 42117, 5% w/w), 211 Nafion membrane (Alfa Aesar, 42180), Nessler Reagent (Aladdin, C1921001).

Synthesis of fluorine-doped carbon. 0.2 g of carbon black (BP2000) and 6.67 g of polytetrafluoroethylene (PTFE) preparation (60 wt %) were mixed in 5 mL of ethanol and 10 mL of deionized (DI) water. The mixture was stirred and sonicated for 1 h to fully distribute PTFE, then dried and annealed 950 °C under Ar atmosphere for 1 h at a heating rate of 5 °C min⁻¹. After annealing, the cooled sample was immersed in a 0.6 M hydrochloric acid (HCl) for 24 h, during which the hydrochloric acid solution was changed for three times in order to remove impurities. Finally, the sample was rinsed with DI water, and then dried at 70 °C.

Electrochemical measurements. The electrochemical tests were conducted in 0.05 M H₂SO₄ solution using an Autolab electrochemical workstation (CH Instruments Inc., USA) with a three-electrode setup. A platinum foil and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. All potentials were referred to the RHE by adding a value of $(0.2046 + 0.05917 \times \text{pH})$ V. For the working electrode, 2 mg of the sample was dispersed in 1 mL of ethanol and 0.12 mL of 5 wt% Nafion aqueous solution. The mixed solution was sonicated for 30 min to form a homogeneous ink. 120 μL of the ink was drop-casted onto carbon paper with an area of 0.5 cm², followed by drying under room temperature. Before electrolysis, the electrolyte was bubbled with high-purity N₂ gas (99.99%) for 30 min to saturate in the solution. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were carried out in a

voltage window from -1.0 to 0 V vs. RHE at the scan rate of 1 and 120 mV s^{-1} , respectively. All the polarization curves were the steady-state ones after several CV cycles. The current density was normalized to the geometrical area.

Quantification of ammonia. The indophenol blue method was used to accurately measure the concentration of ammonia. 1.474 g of sodium hydroxide (NaOH) solid was dissolved in 100 mL of DI water, followed by adding 5 g of salicylic acid and 5 g of sodium potassium tartrate. The prepared solution was a color reagent. 0.1 g of sodium nitroprusside was dissolved in 10 mL of DI water to form a sodium nitroprusside solution. 1.5 g of sodium hydroxide was added into 50 mL of sodium hypochlorite solution. In the color test, 8 mL of the electrolyte (after the N_2RR test) was added into a 10 -mL colorimetric tube, with the following solutions: including 1 mL of color reagent, 500 μL of NaOH solution (4 M), 100 μL of sodium nitroprusside solution, and 100 μL of sodium hypochlorite solution, and 300 μL of DI water. The mixed solution was set aside for 1 h, before the UV-Vis measurements performed at 660 nm.

Quantification of hydrazine. The amount of hydrazine was measured based on the condensation of hydrazine with 4-(dimethylamino) benzaldehyde. 5.99 g of p-dimethylbenzaldehyde was dissolved in 30 mL of hydrochloric acid($36.0\sim38.0\%$) and 300 mL of ethanol, as a color reagent. For the color test, 5 mL of the test solution and 5 mL of the color reagent were added into a 10 -mL colorimetric tube, and set aside for 20 min. Then, the UV-Vis measurements were performed at 458 nm.

Faradaic efficiency. Faradaic efficiency of the ammonia production was calculated using the following equation: $\text{FE}_{\text{NH}_3} = 3F \times m_{\text{NH}_3} / (17 \times Q)$, where F is the Faraday constant, m_{NH_3} is

the measured NH₃ mass, and Q is the quantity of applied electricity.

Calculation details. In our work, DFT calculations were performed as implemented in the Vienna *ab initio* simulation package (VASP).^{S1, S2} The projector augmented wave (PAW) method was adopted to describe interactions between ions and electrons.^{S3} The generalized gradient approximation (GGA) in the form of Perdew, Burke, and Ernzerhof (PBE) was used to describe electron exchange and correlation.^{S4} The plane-wave basis set along with a kinetic cut-off energy was 520 eV. The Brillouin zones were sampled with $2 \times 2 \times 1$ Monkhorst-Pack meshes. The structures were fully relaxed until the maximum force on each atom was less than -0.02 eV/Å and 10^{-5} eV. A vacuum space of at least 20 Å was inserted along the z direction to avoid any interactions between the periodically repeated images. The *van der Waals* interaction was considered using the DFT-D3 scheme.

The Gibbs free energy (ΔG) was defined as follow:

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S \quad (1)$$

ΔE is the reaction energy from the density functional theory calculations. ΔE_{ZPE} and ΔS are the zero point energy difference and the entropy difference between the products and the reactants at room temperature, respectively. The entropies of the free molecules were taken from the NIST database.

Supplementary Figures and Tables

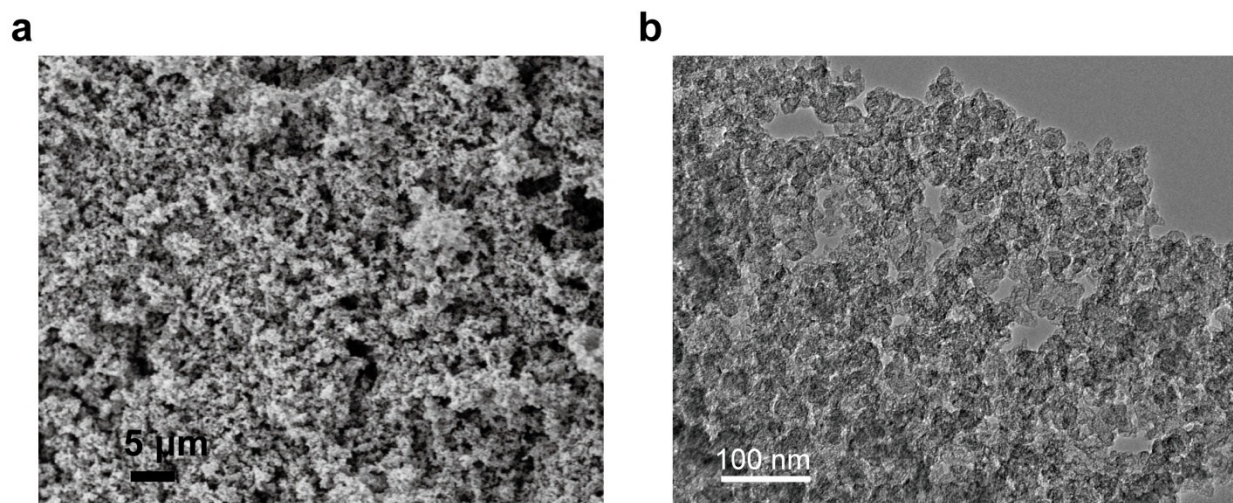


Figure S1. (a) SEM image of undoped carbon. (b) TEM image of undoped carbon.

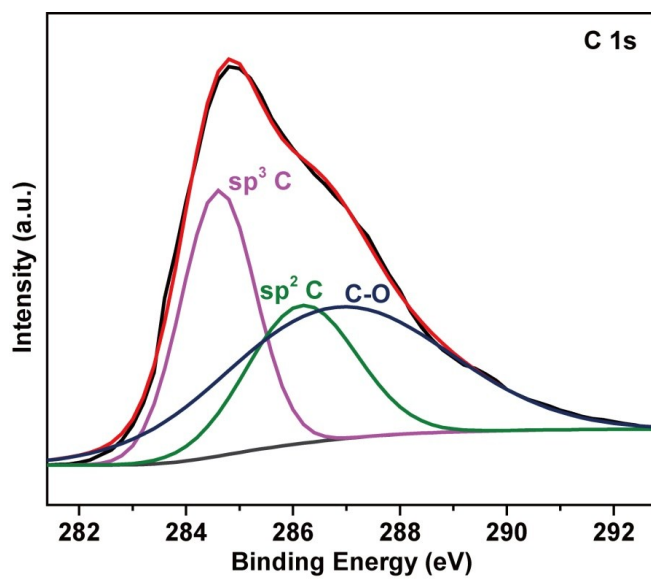


Figure S2. C 1s XPS spectra of undoped carbon.

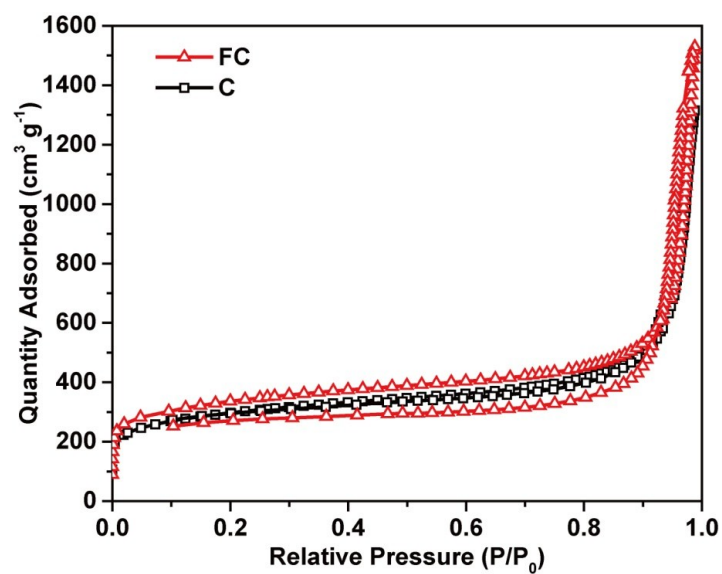


Figure S3. BET surface area of FC and undoped carbon (C).

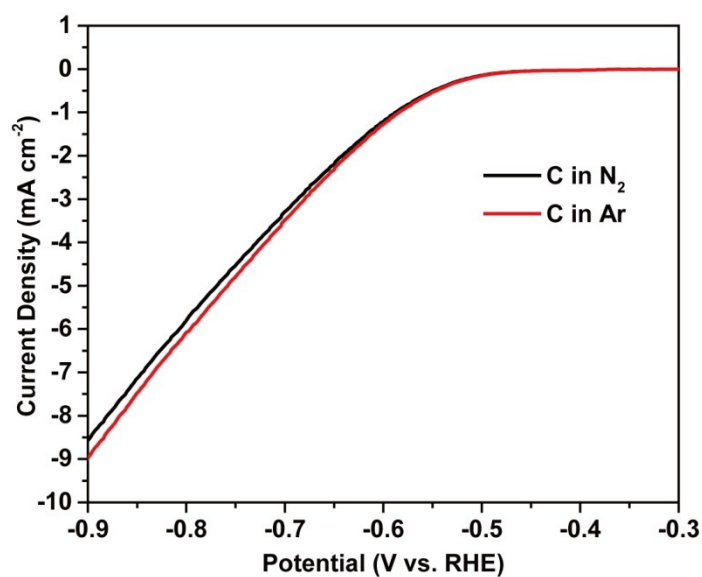


Figure S4. LSV curves of undoped carbon (C) in N₂-saturated and Ar-saturated solutions.

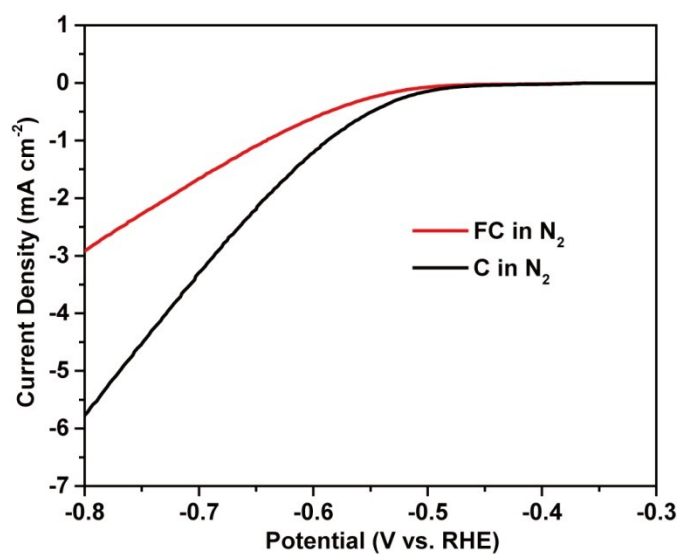


Figure S5. LSV curves of FC and undoped carbon (C) in N₂-saturated solutions.

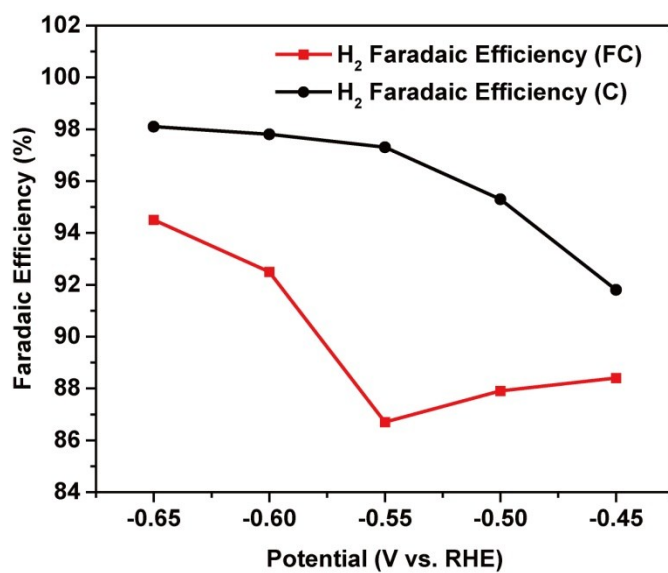


Figure S6. FE_{H₂} of FC and C at different potential.

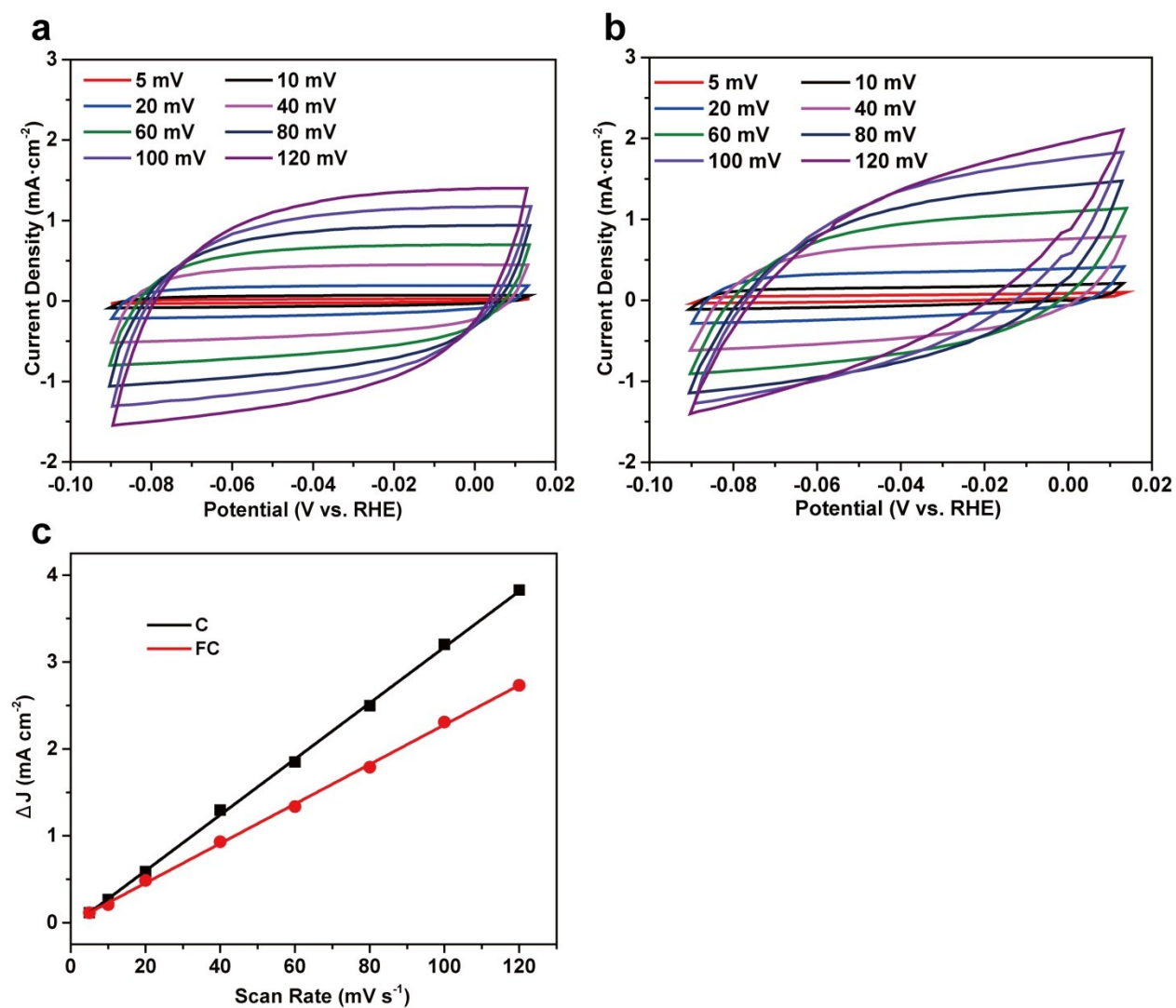


Figure S7. Cyclic voltammetry curves at different scan rates of (a) undoped carbon and (b) FC. (c) Charging current density differences ($\Delta J = J_a - J_c$) plot against scan rates to calculate C_{dl} , which was used to represent the ECSAs.

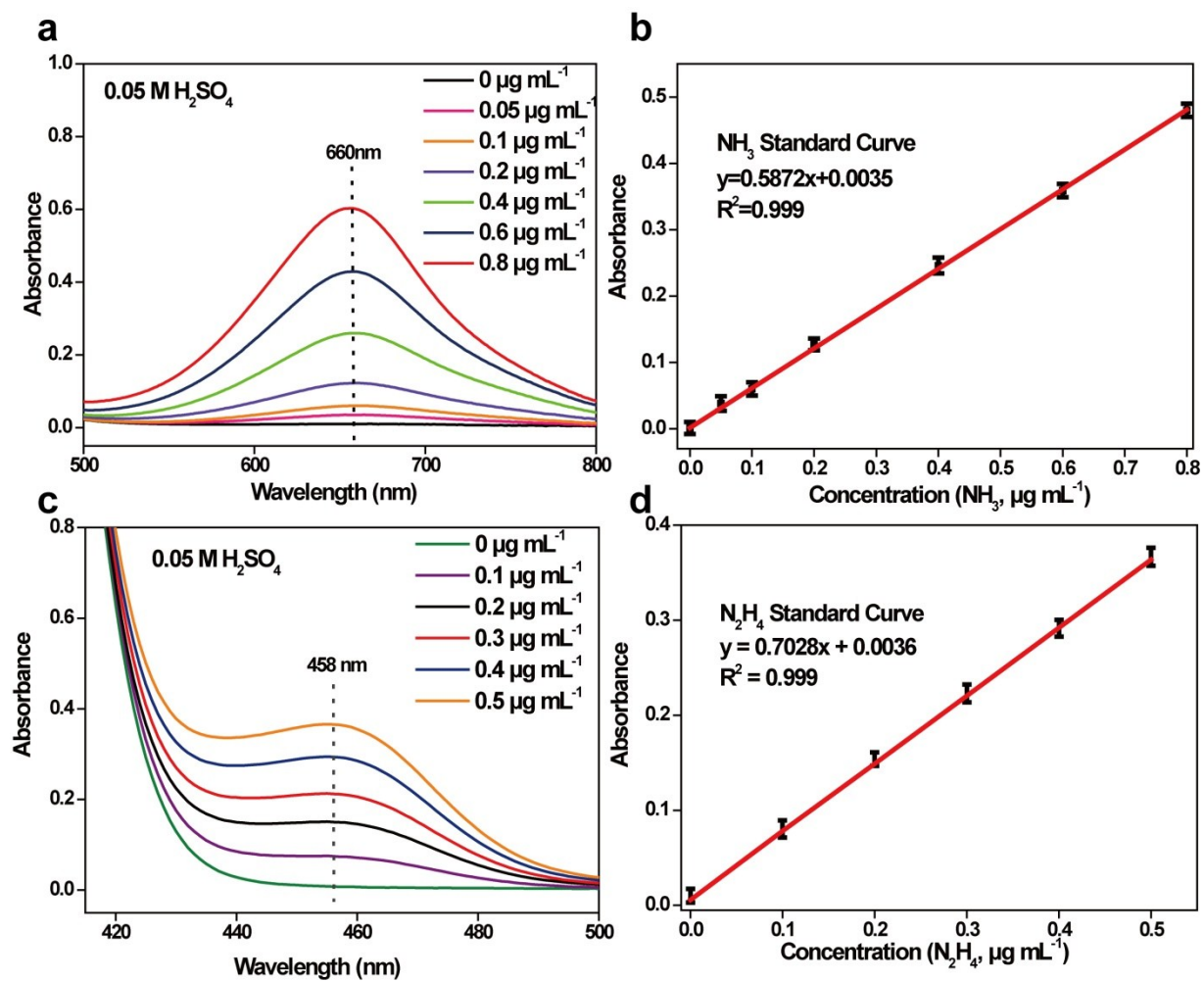


Figure S8. (a) UV-Vis spectra and (b) the calibration of colorimetric NH_3 assay. (c) UV-Vis spectra curves and (d) the calibration of colorimetric N_2H_4 assay.

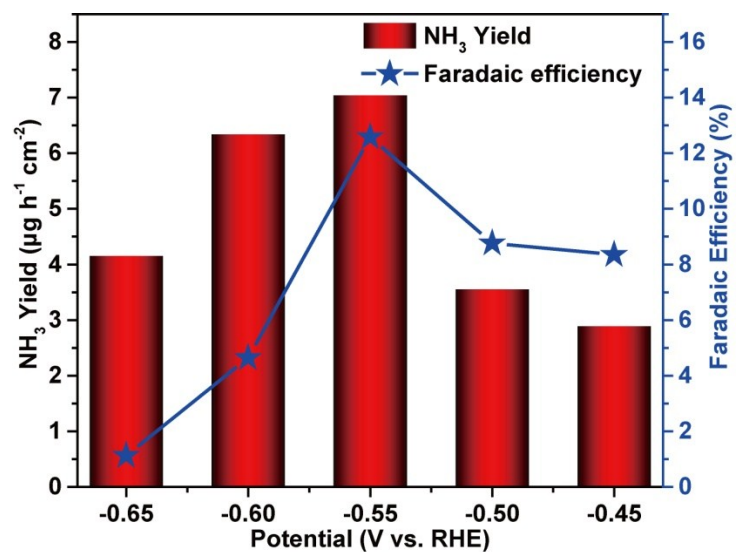


Figure S9. NH_3 Yield and FE of FC quantified by Nessler Reagent.

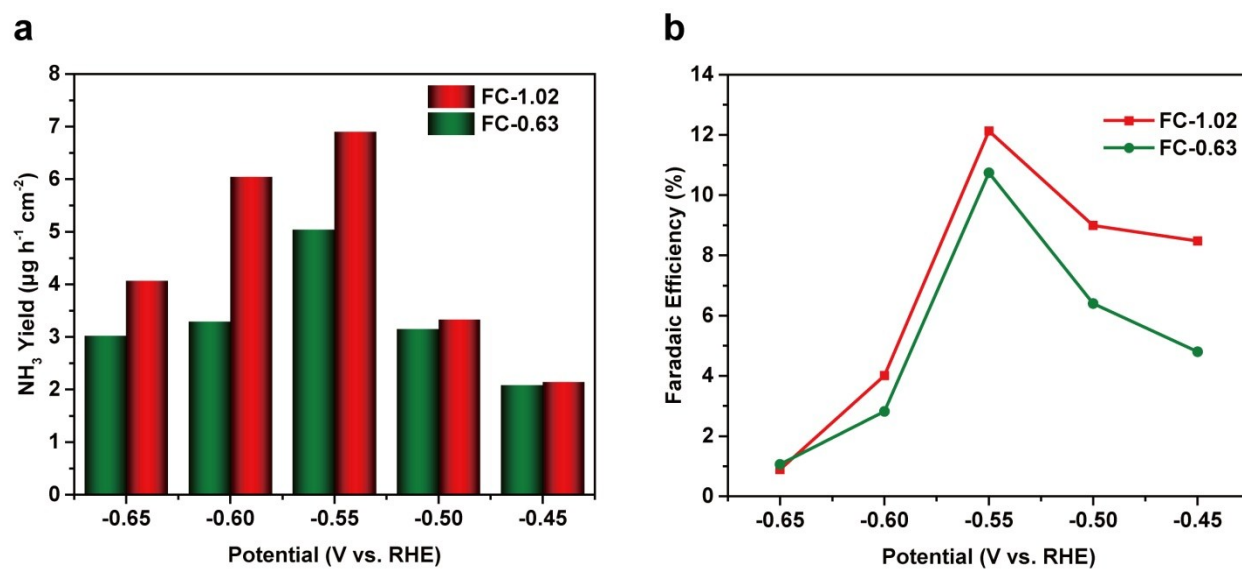


Figure S10. (a) NH_3 Yield of FC-1.02 and FC-0.63. (b) FE_{NH_3} of FC-1.02 and FC-0.63.

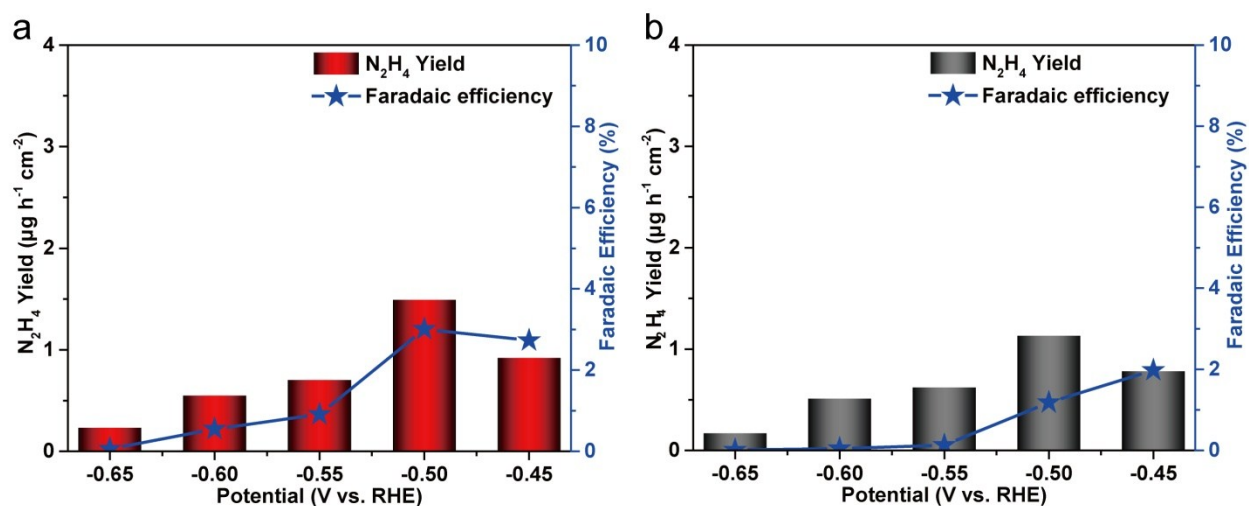


Figure S11. The N_2H_4 production rates (left y-axis) and $\text{FE}_{\text{N}_2\text{H}_4}$ (right y-axis) of (a) FC and (b) undoped carbon at different applied potentials.

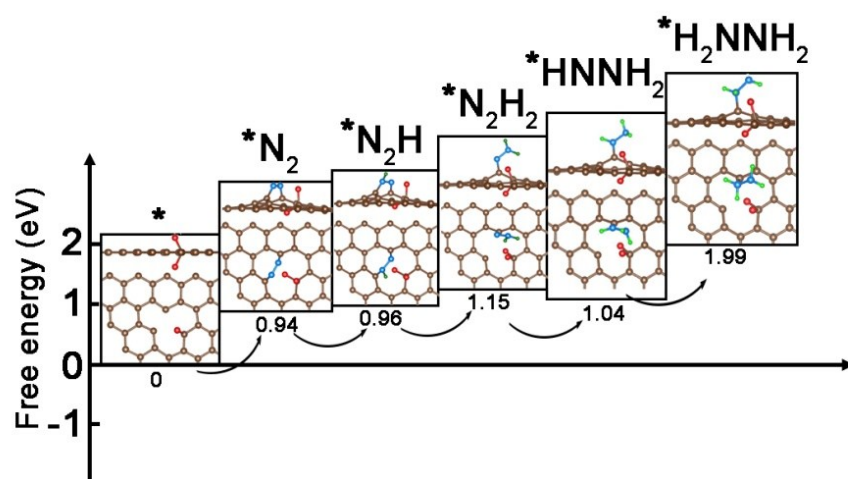


Figure S12. Free energy diagram for N_2H_4 synthesis on the FC catalytic surface.

Table S1. XPS elemental concentrations (F 1s, C 1s, O 1s).

Sample	Element content (atom%)		
	F 1s	C 1s	O 1s
FC	1.02	83.53	15.45
C	0	89.52	10.48

Table S2. The NH₃ yield rates and Faradaic efficiencies (%) of control tests.

Controlled conditions	NH ₃ yield rate	Faradaic efficiency
	($\mu\text{g h}^{-1} \text{cm}^{-2}$)	(%)
FC in N ₂ with open circuit	0.07	--
FC in Ar at -0.55 V	0.09	0.23
Carbon paper in N ₂ at -0.55 V	0.07	0.14

Table S3 Summary of the representative reports on electrochemical N₂ reduction in aqueous solution at low temperature and ambient pressure.

Temp.	Catalyst	Electrolyte	Yield	FE (%)	Potential	Ref.
25 °C	FC	0.05 M H ₂ SO ₄	6.9 µg h ⁻¹ cm ⁻²	12.1	-0.55V vs. RHE	This work
25 °C	^a PEBCD	0.5 M Li ₂ SO ₄	1.58 µg h ⁻¹ cm ⁻²	2.85	-0.5 V vs. RHE	Red. ^{S5}
25 °C	C-ZIF	0.1 M KOH	57.8 µg h ⁻¹ cm ⁻²	10.2	-0.3 V vs. RHE	Ref. ^{S6}
25 °C	^b NCMs	0.1 M HCl	8 µg h ⁻¹ cm ⁻²	5.2	-0.3 V vs. RHE	Ref. ^{S7}
25 °C	^c PCN	0.1 M HCl	8.09 µg h ⁻¹ mg ⁻¹	11.59	-0.2 V vs. RHE	Ref. ^{S8}
^d RT	^e CNSs	0.25 M LiClO ₄	97.2µg h ⁻¹ cm ⁻²	11.6	-1.19 V vs. RHE	Ref. ⁸
RT	Pd/C	0.1 M ^e PBS	4.5 µg h ⁻¹ cm ⁻²	8.2	0.1 V vs. RHE	Ref. ^{S9}
RT	B ₄ C	0.1 M HCl	26.57µg h ⁻¹ mg ⁻¹	15.95	-0.75 V vs. RHE	Ref. ^{S10}

Note:

a:poly(N-ethyl-benzene-1,2,4,5-tetracarboxylicdiimide)

b: NCMs, nitrogen-doped nanoporous graphitic carbon membranes.

c: PCN, polymeric carbon nitride.

d: Room temperature.

e: CNSs, N-doped carbon nanospikes.

Supplemental References

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