

Electronic Supplementary Information

Nitrogen-free commercial carbon cloth with rich defects for electrocatalytic ammonia synthesis under ambient conditions

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Experimental section

Preparation of CC-X samples. All of the chemical reagents were analytical grade (AR) and were used without further purification. The commercial carbon cloth (CC, HCP330) was purchased from Shanghai HESEN company, which was composed of the interwoven carbon fibers and fabricated at high temperature (1500~1800 °C) in Ar atmosphere. Firstly, the commercial carbon cloth (CC) was rinsed adequately with ethanol and water for several times, then thermally treated at different temperatures (250, 350 and 450 °C) in a muffle under air atmosphere for 2 h with a heating rate of 5 °C min⁻¹. After that, the as-fabricated CC samples were collected and denoted as CC-X, in where X represents the temperature of 250, 350 and 450 °C, respectively.

Characterization. The crystalline phase and structure of the obtained samples were characterized by X-ray diffraction (XRD, X'Pert Pro Super, Philips Co., the Netherlands) with Cu K α radiation (1.5478 Å). The morphology and precise structure of the samples were characterized by field emission scanning electron

microscopy (FESEM, Quanta 200FEG) and transmission electron microscopy (TEM, JEOL 2010) with an energy dispersive X-ray spectrometer (EDS Oxford, Link ISIS). X-ray photoelectron spectroscopy (XPS) analysis of the samples was performed on an ESCALAB 250(Thermo, America) equipped with Al $K\alpha_{1,2}$ monochromatized radiation at 1486.6 eV X-ray source. Raman spectra of the samples were recorded on a Renishaw inVia Raman microspectrometer. N_2 adsorption–desorption isotherms of the samples were carried out on Autosorb-iQ-Cx (Quantachrome, United States). Temperature-programmed desorption (N_2 -TPD) of N_2 experiments were conducted on a Quantachrome ChemBET Pulsar TPR/TPD. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer apparatus (Pyris 1) at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ from room temperature to $700\text{ }^\circ\text{C}$ in a flowing air.

Electrochemical measurements. All electrochemical measurements were performed on a CHI 760E electrochemical workstation (CH Instrumental Corporation, Shanghai, China). All experiments were performed in a sealed single-compartment reactor with a configuration composed of the thermally treated carbon cloth (CC, $1\times 1\text{ cm}^2$) working electrode, Ag/AgCl reference electrode and pristine CC ($1\times 1\text{ cm}^2$) counter electrode. The polarization curves were measured with a scan rate of 5.0 mV s^{-1} at room temperature and all polarization curves were obtained at the steady-state ones after several cycles. The electrochemical impedance spectroscopy (EIS) measurements were performed by applying an AC voltage with 10 mV amplitude in a frequency range from 100,000 to 1 Hz and recorded at -0.3 V (vs. RHE). For N_2 reduction reaction (NRR) experiments, the potentiostatic test was conducted for 1 h

under the N_2 -saturated 0.1 M Na_2SO_4 +0.02 M H_2SO_4 solution (20 mL) by continuously supplying N_2 into the electrolyte under ambient conditions.

Determination of ammonia. Concentration of the produced ammonia was spectrophotometrically detected by the indophenol blue method. In detail, 5 mL of sample was taken, and then diluted with 5 mL of deionized water. Subsequently, 100 μ L of oxidizing solution (sodium hypochlorite ($pCl=4\sim 4.9$) and 0.75 M sodium hydroxide), 500 μ L of colouring solution (0.4 M sodium salicylate and 0.32 M sodium hydroxide) and 100 μ L of catalyst solution (0.1g $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ diluted to 10 mL with deionized water) were added respectively to the measured sample solution. After the placement of 1 h in room temperature, the absorbance measurements were performed at wavelength of 697 nm. The obtained calibration curve (Fig. S4) was used to calculate the ammonia concentration.

Determination of hydrazine. The hydrazine present in the electrolyte was estimated by the method of Watt and Chrisp. A mixture of para-(dimethylamino) benzaldehyde (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. In detail, 5 mL of sample with 0.1 M HCl solution was taken, and then 5 mL of the prepared color reagent was added to the above sample solution. Subsequently, the absorbance measurements were performed after the placement of 20 min at wavelength of 455 nm. The obtained calibration curve (Fig. S5) was used to calculate the $N_2H_4\cdot H_2O$ concentration.

Calculations of NH_3 production rate and Faradaic efficiency.

The equation of NH_3 production rate:

$$R(\text{NH}_3)(\text{mol cm}^{-2} \text{ s}^{-1}) = \frac{\chi(\text{ppm}) \times 10^{-3} (\text{g mg}^{-1}) \times V(\text{L})}{M_{\text{r}_{\text{NH}_4^+-\text{N}}} (\text{g mol}^{-1}) \times t(\text{s}) \times S(\text{cm}^{-2})}$$

where $R(\text{NH}_3)$ is the ammonia production rate in $\text{mol cm}^{-2} \text{ s}^{-1}$; χ (ppm) is the produced ammonia concentration; V (L) is the electrolyte solution volume; $M_{\text{r}_{\text{NH}_4^+-\text{N}}}$ = 14 (g mol^{-1}); t (s) is the reaction time; S is the geometric area of the cathodic electrode in cm^2 , and in this work two sides of the carbon cloth electrode are electrocatalytically active for the NRR, thus the NH_3 production rate is calculated by dividing the total geometric area of two sides of the carbon cloth electrode.

The equation of Faradaic efficiency:

$$FE(\text{NH}_3)(\%) = \frac{3 \times R(\text{NH}_3)(\text{mol cm}^{-2} \text{ s}^{-1}) \times S(\text{cm}^{-2}) \times F}{Q} \times 100\%$$

where F is the Faradaic constant (96485.34); Q is the total charge during the NRR.

Supplementary Tables and Figures

Table S1. Elemental composition analysis of the pristine CC and CC-X samples by XPS technique.

Sample	C (at.%)	O (at.%)
Pristine CC	98.49	1.51
CC-250	98.67	1.33
CC-350	97.77	2.23
CC-450	98.99	1.01

Table S2. The comparable results of our work and other recently reported carbon-based NRR electrocatalysts.

References	Catalyst	System /Conditions	NH ₃ Production Rate	Faradaic Efficiency (%)	Detection method
Angew. Chem. Int. Ed. 2017, 56, 2699.	Fe ₂ O ₃ -CNTs	KHCO ₃	2.2×10 ⁻³ g _{NH₃} m ⁻² h ⁻¹ (-2.0V vs. Ag/AgCl)	0.15	Indophenol method
Adv. Mater. 2017, 29, 1604799.	Au nanorods	0.1 M KOH	1.648 g h ⁻¹ cm ⁻² (-0.2 V vs. RHE)	3.87	Nessler's reagent
ACS Catal. 2018, 8, 1186.	N doped porous carbon	0.05 M H ₂ SO ₄	1.40 mmol g ⁻¹ h ⁻¹ (-0.9 V vs. RHE)	1.5	Nessler's reagent
Nano Energy 2018, 48, 217.	ZIF-derived carbon	0.1 M KOH	3.4×10 ⁻⁶ mol cm ⁻² h ⁻¹ (-0.3V vs. RHE)	10.2	Indophenol method
Nat. Commun. 2018, 9, 1795.	Pd/C	0.1 M PBS	4.5 μg mg ⁻¹ _{Pd} h ⁻¹ (0.1V vs. RHE)	8.2	Indophenol method
Adv. Mater. 2018, 1800191.	MoS ₂ /CC	0.1 M Na ₂ SO ₄	8.08×10 ⁻¹¹ mol s ⁻¹ cm ⁻¹ (-0.2 V vs. RHE)	1.17	Indophenol method
Sci. Adv. 2018, 4: e1700336.	N doped carbon nanospikes	0.25 M LiClO ₄	97.18 ± 7.13 mg h ⁻¹ cm ⁻² (-1.19 V vs. RHE)	11.56 ± 0.85	Indophenol method
Chem. Commun. 2018, 54, 5323.	VN/CC	0.1 M HCl	2.48×10 ⁻¹⁰ mol s ⁻¹ cm ⁻¹ (-0.3 V vs. RHE)	3.58	Indophenol method
J. Mater. Chem. A 2018, 6, 7762.	N doped porous carbon	0.1 M HCl	15.7 μg h ⁻¹ mg ⁻¹ (-0.3 V vs. RHE)	1.45	Indophenol method
Angew. Chem. Int. Ed. 2018, 57, 1.	N doped porous carbon	1.0 M HCl	0.08 g h ⁻¹ m ⁻² (-0.3 V vs. RHE)	5.2	Indophenol method
ACS Energy Lett. 2018, 3, 1219.	α-Fe@Fe ₃ O ₄	[C ₄ mpyr][eFAP]-FPEE mix	2.35 × 10 ⁻¹¹ mol s ⁻¹ cm ⁻² (-0.6 V vs. NHE)	32	Indophenol method
Energy Environ. Sci. 2017, 10, 2516.	Fe electrode/FTO	[P _{6,6,6,14}][eFAP]	14 mg h ⁻¹ m ⁻² (-0.8 V vs. NHE)	60	Indophenol method
This work	CC-450	0.1 M Na₂SO₄+ 0.02 M H₂SO₄	2.59×10⁻¹⁰ mol s⁻¹ cm⁻¹ or 9.3×10⁻⁷ mol cm⁻² h⁻¹ or 15.8 μg cm⁻¹ h⁻¹ (-0.3 V vs. RHE)	6.92	Indophenol method

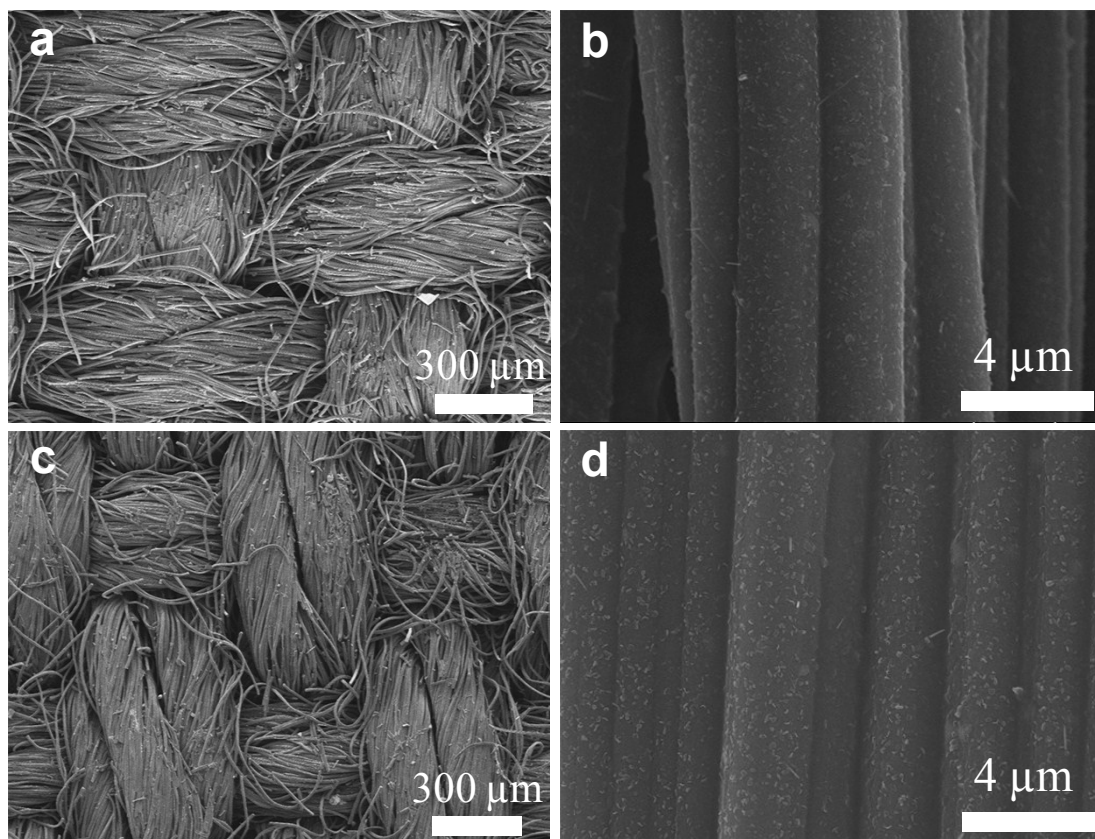


Fig. S1 Low- and high-magnification SEM images of (a), (b) the pristine CC and (c), (d) the thermally treated CC-450.

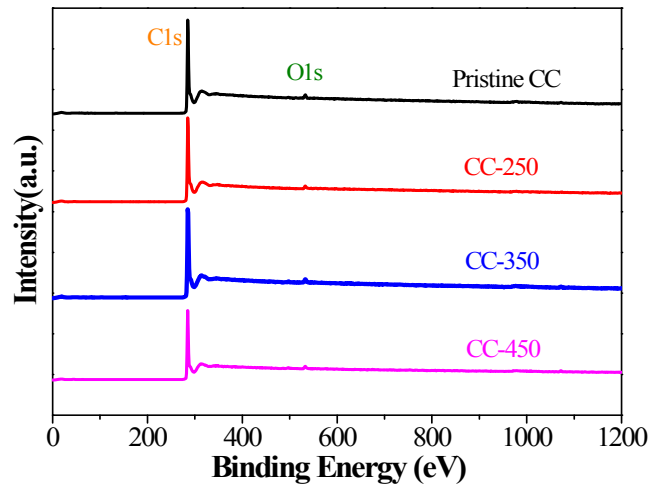


Fig. S2 The surface survey XPS spectra of the pristine CC and CC-X samples.

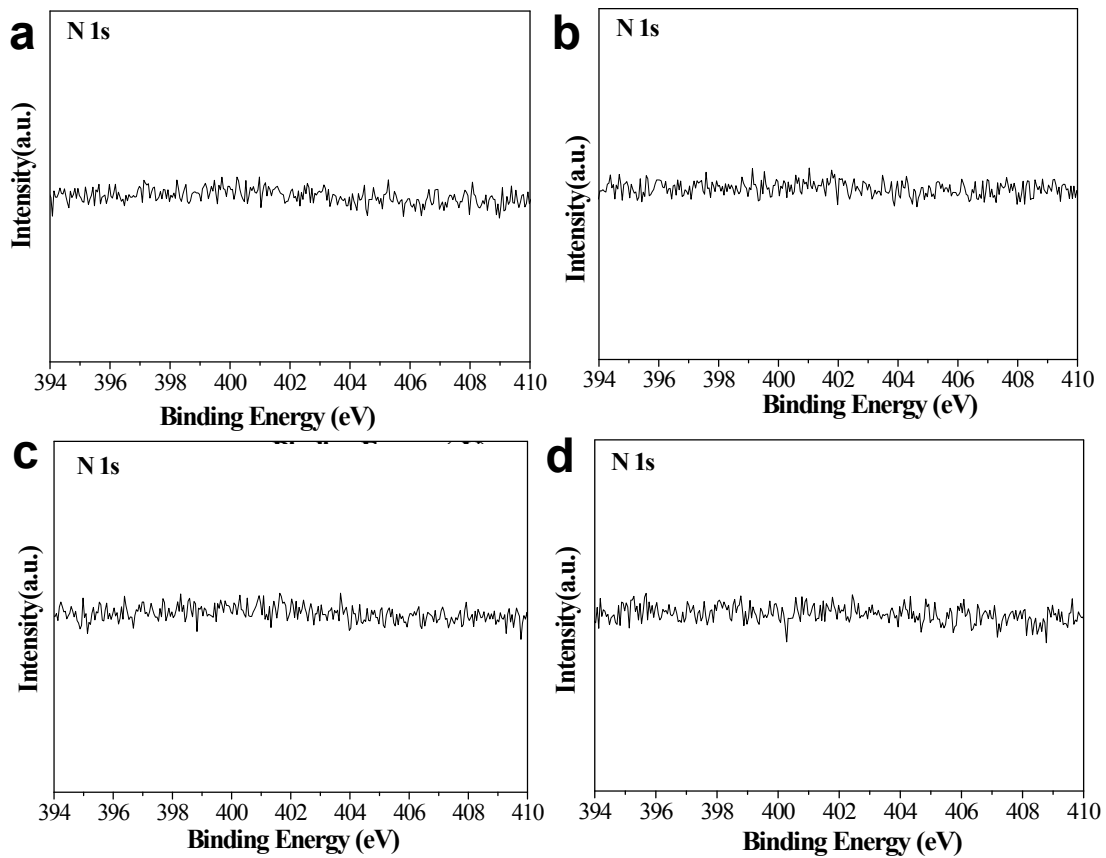


Fig. S3 The high-resolution N 1s XPS spectra of (a) the pristine CC; (b) CC-250; (c) CC-350; (d) CC-450 samples before the NRR.

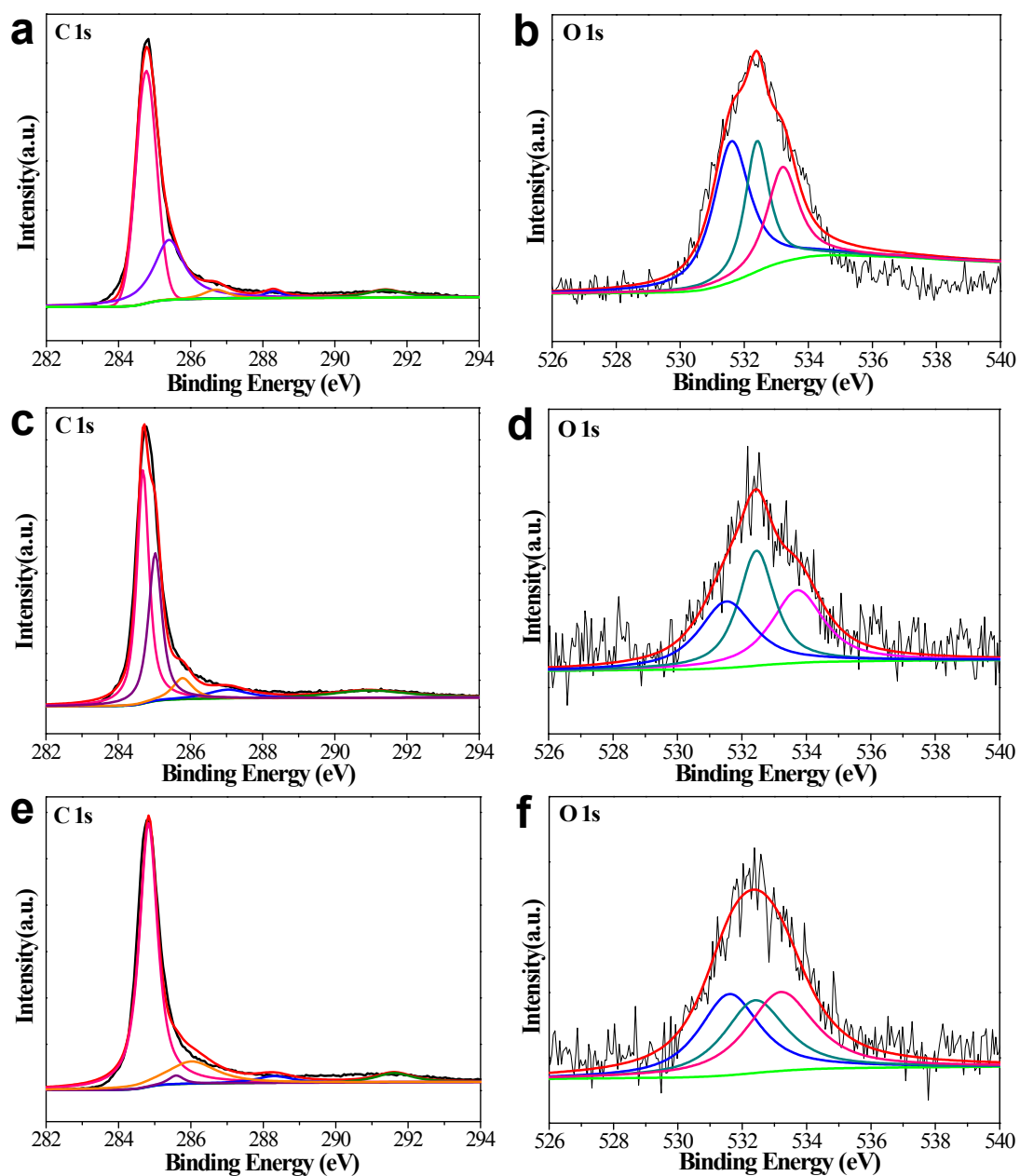


Fig. S4 The high-resolution C 1s and O 1s XPS spectra of (a),(b) pristine CC; (c), (d) CC-250; (e), (f) CC-350.

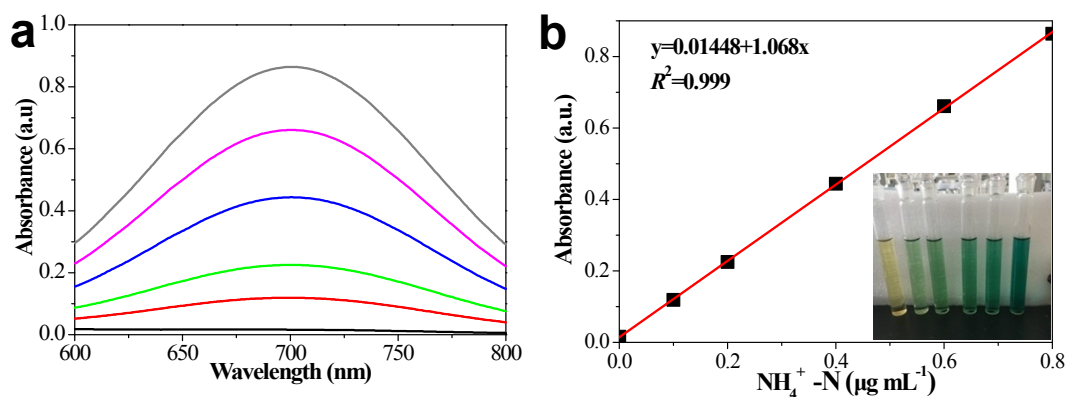


Fig. S5 (a) UV-Vis absorption spectra of various $\text{NH}_4^+\text{-N}$ concentrations (0, 0.1, 0.2, 0.4, 0.6 and 0.8 $\mu\text{g mL}^{-1}$) after incubated for 1 h at room temperature. (b) The calibration curve used for calculation of $\text{NH}_4^+\text{-N}$ concentration; the inset in (b) of the corresponding photographs of different concentrations of $\text{NH}_4^+\text{-N}$ solutions.

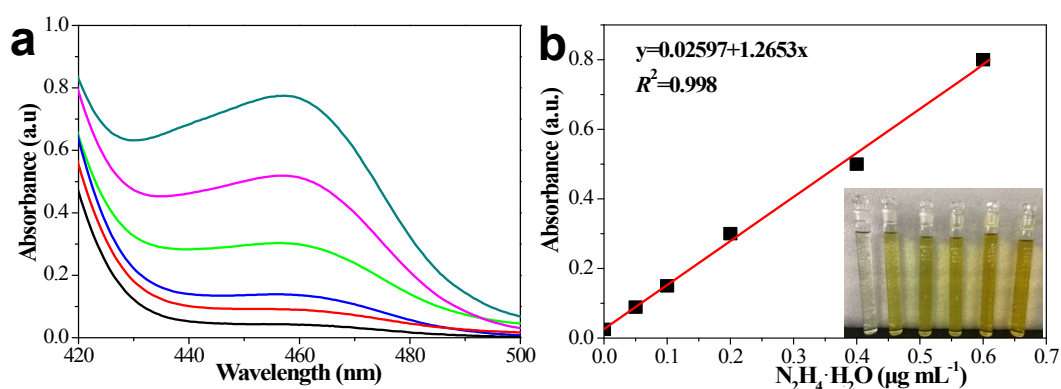


Fig. S6 (a) UV-Vis absorption spectra of various $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ concentrations (0, 0.5, 1, 2, 4 and 6 $\mu\text{g mL}^{-1}$) after incubated for 20 min at room temperature. (b) The calibration curve used for calculation of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ concentrations. The inset in (b) of the corresponding photographs of different concentrations of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ solutions.

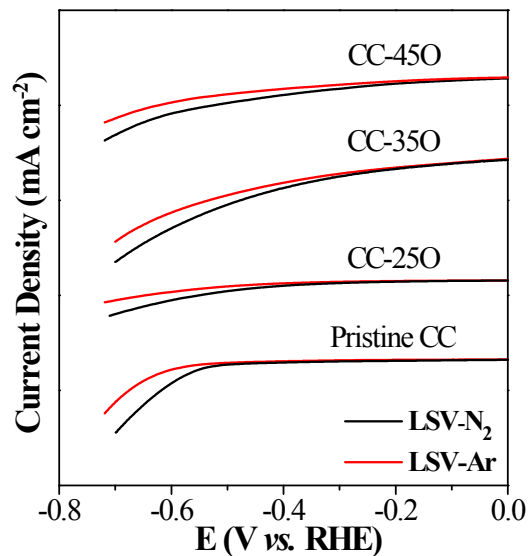


Fig. S7 Linear sweep voltammogram (LSV) curves of the pristine CC and thermally treated CC electrocatalysts in Ar- or N₂-saturated 0.1 M Na₂SO₄+0.02 M H₂SO₄ electrolyte with a scan rate of 5.0 mV s⁻¹.

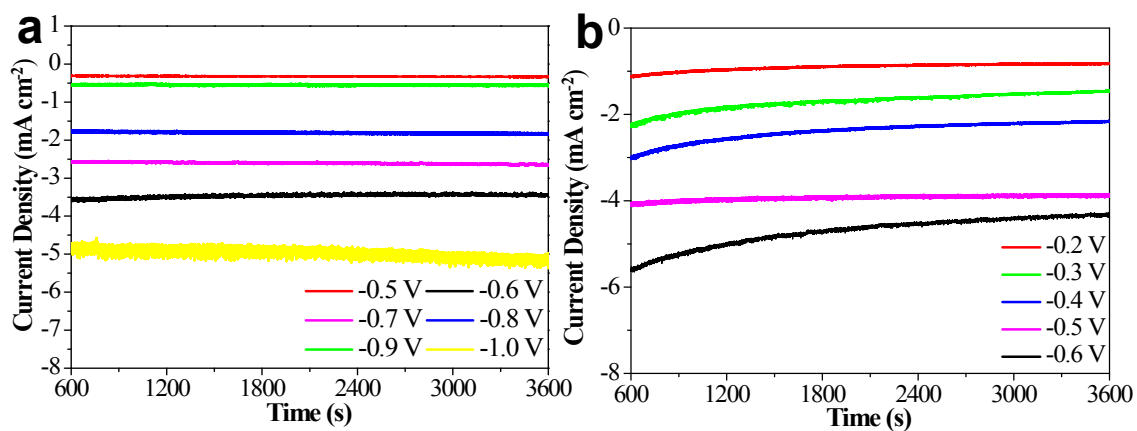


Fig. S8 Time-dependent current density curves of (a) pristine CC and (b) CC-450 for the NRR at different potentials in 0.1 M Na₂SO₄+0.02 M H₂SO₄ electrolyte.

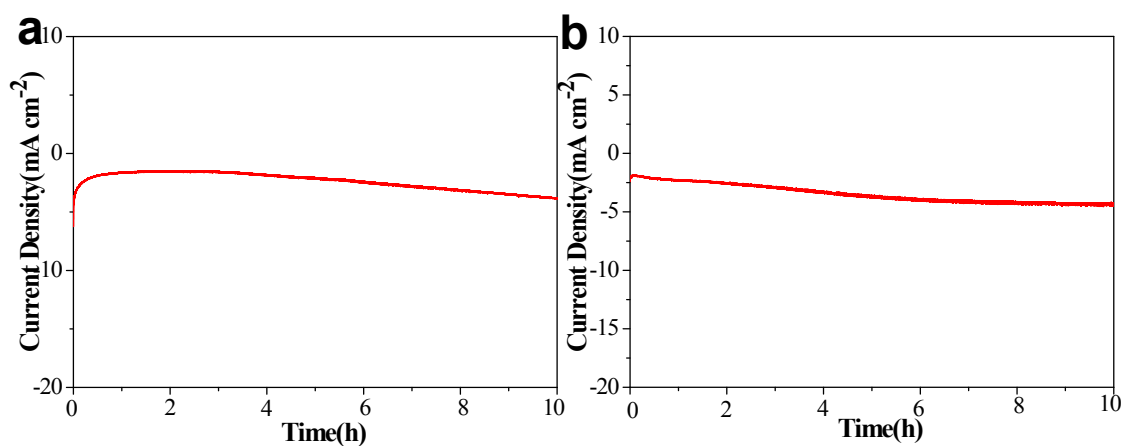


Fig. S9 The current density-time curves of the CC-450 at -0.3 V (vs. RHE) in N_2 -saturated 0.1 M Na_2SO_4 +0.02 M H_2SO_4 electrolyte for two times 10 h of NRR measurements. (a) First durability test; (b) Second durability test.

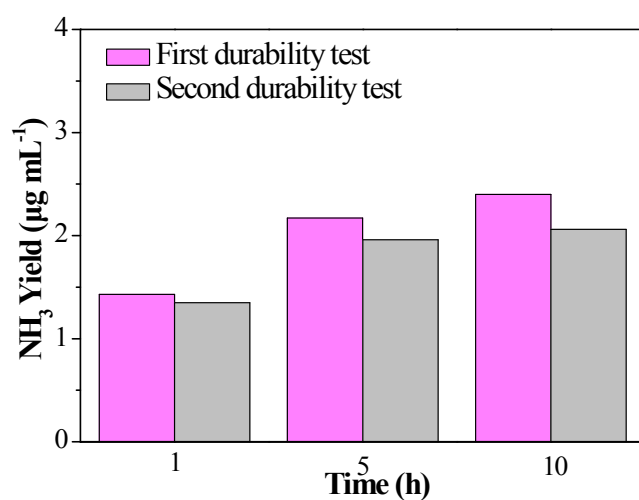


Fig. S10 The NH_3 yield obtained at -0.3 V (vs. RHE) in N_2 -saturated 0.1 M Na_2SO_4 +0.02 M H_2SO_4 electrolyte for two times 10 h of NRR measurements.

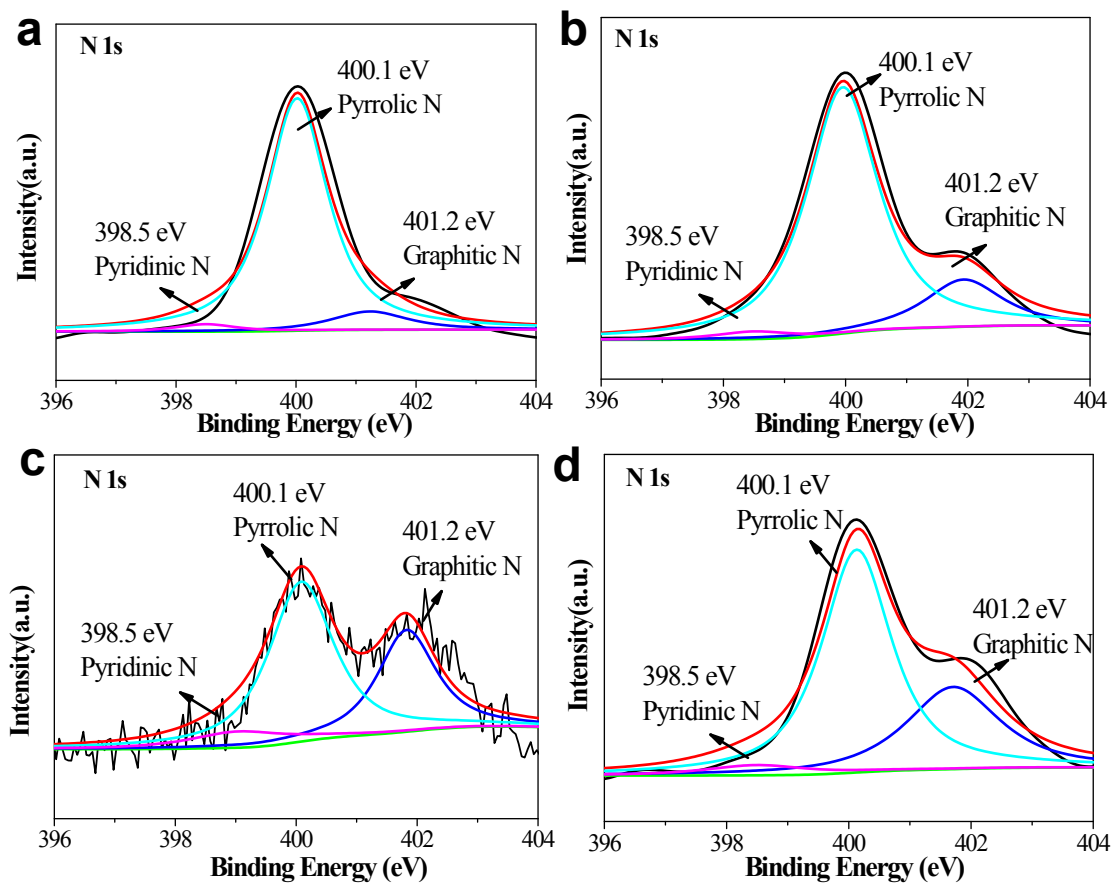


Fig. S11 The high-resolution N 1s XPS spectra of (a) pristine CC; (b) CC-250; (c) CC-350; (d) CC-450 samples after the NRR for 10 h of reaction.

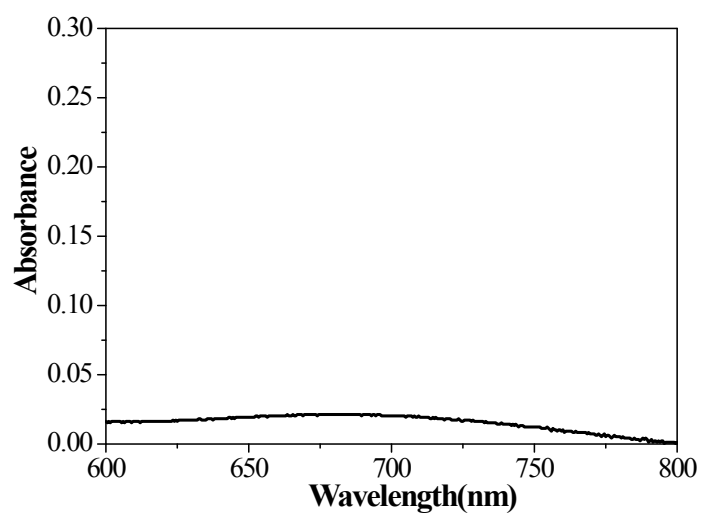


Fig. S12 UV-Vis spectra of N_2 -saturated 0.1 M Na_2SO_4 +0.02 M H_2SO_4 electrolyte (blank electrolyte) for a placement time of 2 h.

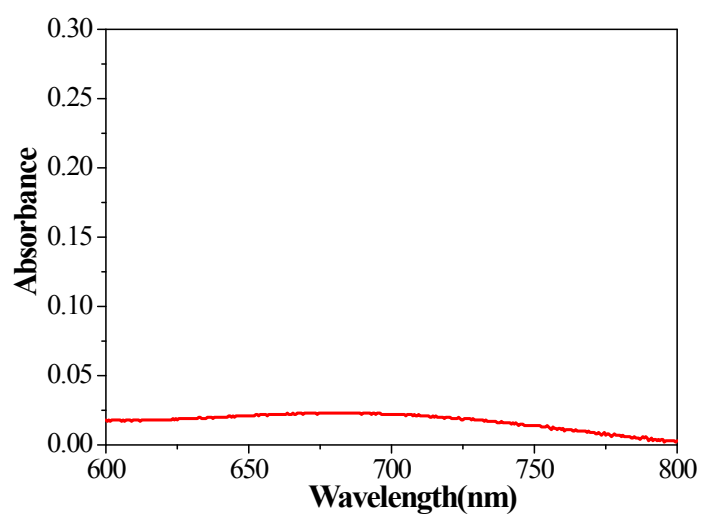


Fig. S13 UV-Vis spectra of N_2 -saturated 0.1 M Na_2SO_4 +0.02 M H_2SO_4 electrolyte under the open-circuit condition using the CC-450 for a placement time of 2 h.

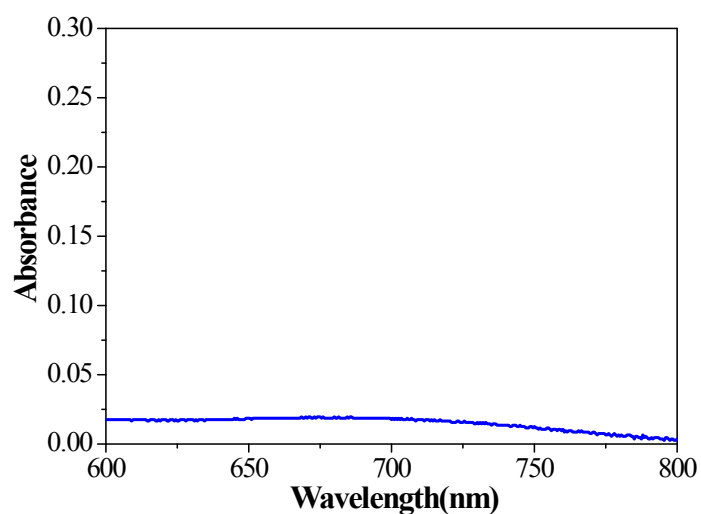


Fig. S14 UV-Vis spectra of Ar-saturated 0.1 M Na₂SO₄+0.02 M H₂SO₄ electrolyte at -0.3 V (vs. RHE) using the CC-450 for a reaction time of 2 h.

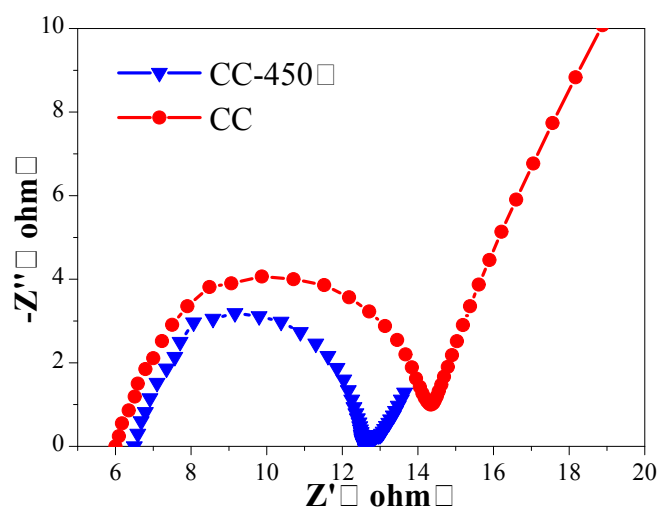


Fig. S15 The electrochemical impedance spectroscopy (EIS) analysis of pristine CC and CC-450 at -0.3 V (vs. RHE) in N₂-saturated 0.1 M Na₂SO₄+0.02 M H₂SO₄ electrolyte.

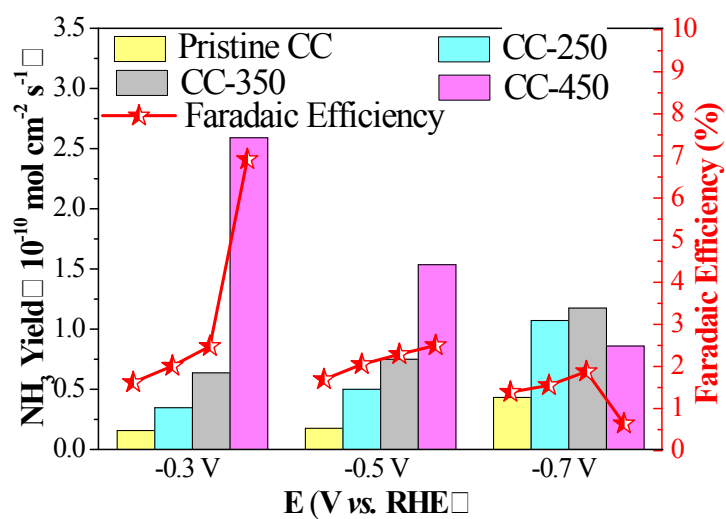


Fig. S16 The NH_3 yield and Faradaic efficiency of pristine CC, CC-250, CC-350 and CC-450 at -0.3, -0.5 and 0.7 V (vs. RHE) in N_2 -saturated 0.1 M Na_2SO_4 +0.02 M H_2SO_4 electrolyte for 1 h of reaction.