Understanding the Lattice Nitrogen Stability and Deactivation Pathways of Cubic CrN Nanoparticles in Electrochemical Nitrogen Reduction Reaction

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1. Chemicals and Materials

Chromium chloride (CrCl$_3$·6H$_2$O, Ar, Shanghai Maclin Biochemical), urea (98%, Beijing Ouhe Technology), absolute ethanol (C$_2$H$_5$OH, ≥99.7%, Beijing Tong Guang Fine Chemicals), sulphuric acid (H$_2$SO$_4$, GR, XiLong Scientific), ultrapure ammonia (NH$_3$, ≥99.999%, Beijing HuaTong JingKe Gas Chemical Industry) were used as received.

2. Materials Synthesis

2.1. Synthesis of Cr-Urea Xerogel

Chromium-urea (Cr[OC(NH$_2$)$_2$]$_6$Cl$_3$) coordination compound xerogel was synthesized using a modified method from previous report[1]. 10.6580 g (0.040 mol) CrCl$_3$·6H$_2$O was dissolved in absolute ethanol to get concentrated solution. 14.4144 g (0.240 mol) urea was dissolved in 20 ml absolute ethanol to get saturated solution. The concentrated CrCl$_3$/ethanol solution was added dropwise into saturated urea/ethanol solution at 60-80 °C under constant magnetic stirring. After mixing, the mixture solution was refluxed for 1-2 h, then heated at 80 °C to evaporate all the solvents. The dried sample was grey-green xerogel of Cr-urea coordination compound. The xerogel was soluble to water but not soluble to ethanol. The bulk xerogel was grounded into fine powders and stored in vacuum dryer for further use.

2.2. Synthesis of Chromium Nitride Nanoparticles

Chromium nitride nanoparticles (CrN NPs) were synthesized by calcination of the Cr-urea xerogel powders in NH$_3$ atmosphere. Grounded Cr-urea xerogel fine powders were loaded in an alumina crucible and placed in a tube furnace, heated to 600 °C at 1°C min^{-1} and kept for 2 h under NH$_3$ flow, then naturally cooled down to room temperature. The as-prepared CrN NPs dark-grey powders were cleansed at 200 °C for 12 h in vacuum oven to remove weakly adsorbed ammonia on the surface, then stored in vacuum dryer.

2.3. Preparation of Working Electrodes

Typically, 10 mg CrN NPs catalyst and 20 μL 5% Nafion solution were added into 1980 μL absolute ethanol, and then dispersed by sonication for 2 h to form a homogeneous ink. Then 100 μL of the catalyst ink was loaded onto a carbon fiber paper (CFP) electrode with area of 1×1 cm^2 and dried with the assistance of an infrared heating lamp to achieve the mass loading of ~0.5 mg cm^{-2}. As-prepared CrN/CFP working electrodes were heated at 100 °C for 6 h in vacuum oven to remove residue solvent and possible nitrogen contaminants, then stored in vacuum dryer.

3. Materials Characterization

Powder X-ray diffraction (PXRD) patterns of all the synthesized samples were recorded by a Rigaku SmartLab X-ray diffractometer operating at 45 kV and 200 mA with Cu Kα radiation (λ=1.5406 Å). Scanning electron microscopy (SEM) and corresponding energy-dispersive spectroscopy (EDS) elemental mapping images were taken using Hitachi Regulus 8220. Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images and selected area electron diffraction (SAED) patterns were taken using FEI Tecnai F30. X-ray photoelectron spectroscopy (XPS) was measured by a Kratos Axis Ultra Imaging Photoelectron Spectrometer equipped with a monochromatic Al-Kα X-ray source (hν=1468.7 eV) and calibrated at C 1s = 284.8 eV. The C, N, H conents of samples were analyzed by a vario EL CHN elemental analyzer (Elementar Analysensysteme, Germany). Inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements were performed by Thermo IRIS INTREPID with sensitivity up to ppm level. Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed by PerkinElmer NexION 350X with sensitivity up to ppt level. UV-Vis-NIR spectra were collected by an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. Ammonia temperature-programmed desorption (NH$_3$-TPD) measurements were performed using a Quantachrome Pulsar TPR/TPD automatic chemisoption analyzer with TCD detector and He carrier gas, using 50 mg sample for each test, and the desorption ramping rate was 10 °C min^{-1}. All the water used in this work is ultra-pure (UP) deionized water (18.2 MΩ) produced by a Master-S15 Ultra Pure Water Purification System.

4. Electrochemical Measurements

4.1. Pretreatment of Nafion Membranes

The Nafion 117 membranes were pretreated in 5 wt% H_2O_2 aqueous solution at 80°C for 1 h and soaked in deionized water for 1 h, followed by boiling in 5 wt% H_2SO_4 at 80°C for 1 h and soaked in deionized water for another 1 h.

4.2. Experimental Setup

Electrochemical NRR reactions were carried out in a standard gas-tight H-typed two-compartment electrolysis cell with temperature-controlled circulating water bath on both sides. 0.05 M H_2SO_4 aqueous solution (pH = 1) was used as electrolyte. Nafion 117 membrane was used to separate the cathodic and anodic compartments. As-pretreated Nafion membranes were soaked in electrolyte for several minutes before use. Before reaction, 15 mL of 0.05 M H_2SO_4 solution was added into the cathode and anodic compartments, respectively. A 10 mm magnetic stirrer was added in the cathodic chamber. Dry ultra-pure nitrogen gas (>99.999%) (or ultra-pure Ar, in the case of reference experiments) was firstly passed through an 100 mL adsorption bottle filled with 80 mL 0.5 M H_2SO_4 to remove any possible ammonia and soluble nitrogen contaminants, then bubbled into the catholyte by a mass flow controller (D07-9E, Beijing Sevenstar Electronics, calibrated by ultra-pure nitrogen, full scale 100 sccm). The outlet gas tube was connected with an ammonia trap filled with 20 mL of 0.05 M H_2SO_4 aqueous solution as adsorbent liquid to collect any ammonia escaped from the electrolyte. Before each test, N_2 or Ar gas was bubbled into the catholyte at a flow rate of 50 sccm and inlet pressure of 1 bar for 30 min, then remained constantly purged at low flow rate of 10 sccm during the whole electrolysis process. Magnetic sitrring was applied to the cathodic chamber constantly during testing to improve diffusion and mass transfer. PTFE tubes with diameter of 3 mm were used to connect all the equipment used. All containers and equipment used in the experiments were rinsed with 0.05 M H_2SO_4 solution and washed with excess amount of UP water before use. No ir-compensation was applied for all the electrochemical tests in this work. All the current

densities were normalized to the geometric surface area. Reaction temperatures of all the experiments were controlled at 25 °C by circulating water bath to exclude influence from enrivonmental temperature variation.

4.3. Electrochemical NRR measurements

Electrochemical NRR measurements were performed on a CHI-760E electrochemical workstation using a three-electrode configuration. Working electrode loaded with electrocatalyst and Ag/AgCl/KCl(sat.) reference electrode were placed in the cathode compartment; Pt foil counter electrode was placed in the anode compartment. All potentials were measured against the Ag/AgCl reference electrode and converted to the reversible hydrogen electrode (RHE) reference scale using the following equation:

E (vs. RHE) = E (vs. Ag/AgCl) + 0.1989 + 0.0591 × pH (Eq. S1)

Cyclic voltammetry (CV) curves were collected at a scanning speed of 50 mV/s between -0.8 V and +0.1 V at a scanning speed of 50 mV s^{-1}.

Chrnoamperometric (I-t) tests were carried out at fixed potentials under constant nitrogen stream (10 sccm) and magnetic stirring. Before each testing, the working electrodes were emersed in fresh 0.05 M H_2SO_4 solution for 30 min to remove possible adsorbed nitrogen contaminants, then washed with large amount of UP water. To maintain the original initial activity of the CrN catalyst, no additional electrochemical treatment was applied to the working electrodes before I-t tests. After reaction, catholyte, anolyte and adsorbent solution in the downstream ammonia trap bottle were collected separately for product quantification. New working electrodes and fresh electrolytes were used for each test.

Electrochemical accelerated aging (EAA) was performed for electrodes to study the long-term stability. Electrodes were cycled by CV from +0.1 V to target potential at a scan rate of 100 mV s^{-1} for 50 cycles under 50 sccm Ar flow, followed by washing with excess amount of UP water. The EAA-treated electrodes were then tested under

N$_2$ or Ar for two consecutive 1 h-electrolysis with replenished electrolytes.

Cycling tests were performed using the same electrodes. Electrolytes and adsorbents were collected and refreshed each hour to quantify the ammonia produced. Catholytes after the first 1 h-electrolysis were collected for ICP-MS tests.

5. NRR Performance Evaluation

5.1. Quanfitication of Ammonia

Concentration of the ammonia produced was tested by spectrophotometric indophenol blue method. Typically, 2.000 mL of the testing solution (electrolyte or adsorbent) was mixed with 2.000 mL of 0.5 M NaOH aqueous solution containing 5 wt% salicylic acid and 5 wt% sodium citrate, followed by 1.000 mL of 0.05 M NaClO/2.0 M NaOH aqueous solution and 200 μL of 1 wt% $C_5FeN_6Na_2O$ (sodium nitroferricyanide) aqueous solution, and left standing under room temperature for 2 h. The UV-Vis absorbance was then measured by an Agilent Cary5000 UV-Vis-NIR spectrophotometer using deionzed water as reference. Concentration of ammonia was determined by the absorption peak of indophenol blue around the wavelength of 655 nm. The concentration-absorption standard curves were calibrated using cooresponding standard ammonia solutions **every time before testing products**. Standard ammonia solutions of different concentrations were prepared by dilution of standard ammonia solution (GBW(E)083341-2, TMRM®, 1000 ppm NH+ 4 in H$_2$O) by 0.05 M H$_2$SO$_4$ solution. Fig S shows the standard curve of ammonia in 0.05M H$_2$SO$_4$ solution.

5.2. Quantification of Hydrazine

Concentration of hydrazine in the electrolyte was determined by a spectrophotometric method reported by Watt and Chrisp[2]. A mixture of para-(dimethylamino) benzaldehyde (3.99 g), HCl (concentrated, 20 mL) and ethanol (200 mL) was used as a color reagent. For testing, 2 mL of reacted electrolyte was mixed with 2 mL of color reagent and stirred for 10 min, then tested for absorption at a wavelength of 463 nm. Standard solutions of different concentrations were prepared by

dilution of standard hydrazine solution (GNM-SN2H4-003-2013, GBTC®, 1000 ppm N_2H_4 in 1.0 mol L^{-1} HCl) by 0.05 M H_2SO_4 solution. Fig S11 shows a typical standard curve of hydrazine at 463 nm. Since no hydrazine was detected in the electrolytes, adsorbents were not tested.

5.3. Calculation of Faraday efficiency and ammonia formation rate

Faraday efficiency is calculated using the following equation:

$$FE = 3 \times n(NH_4^+) \times F / Q \text{ (Eq. S2)}$$

Where $n(NH_4^+)$ is the total measured amount of ammonia (mol), F is the Faraday Constant, Q is the total charge consumed (C), 3 is the electron transfer number per ammonia molecule.

$$n(NH_4^+) = (V_c \times c(NH_4^+)_c + V_a \times c(NH_4^+)_a + V_{ads} \times c(NH_4^+)_{ads}) / 1000 \text{ (Eq. S3)}$$

$c(NH_4^+)_c$ is the concentration of ammonia in catholyte (mol L^{-1}), $c(NH_4^+)_a$ is the concentration of ammonia in anolyte (mol L^{-1}), $c(NH_4^+)_{ads}$ is the concentration of ammonia in adsorbent (mol L^{-1}). V_c is the volume of catholyte (15.0 mL), V_a is the volume of anolyte (15.0 mL), and V_{ads} is the volume of adsorbent (20.0 mL)

Ammonia production rate is calculated using the following equation:

$$r(NH_3) = 17.043 \times n(NH_4^+) / (t \times m) \text{ (Eq. S4)}$$

17.034 is the molecular weight of ammonia, $r(NH_3)$ is the average ammonia production rate ($\mu g \ h^{-1} \ m^{-1}$ cat), t is the reaction time (h), m is catalyst weight (mg). The present ammonia production rates are normalized to the weight of catalyst for easier comparison, considering that the areal mass loading of catalysts in literature reports are not consistant.
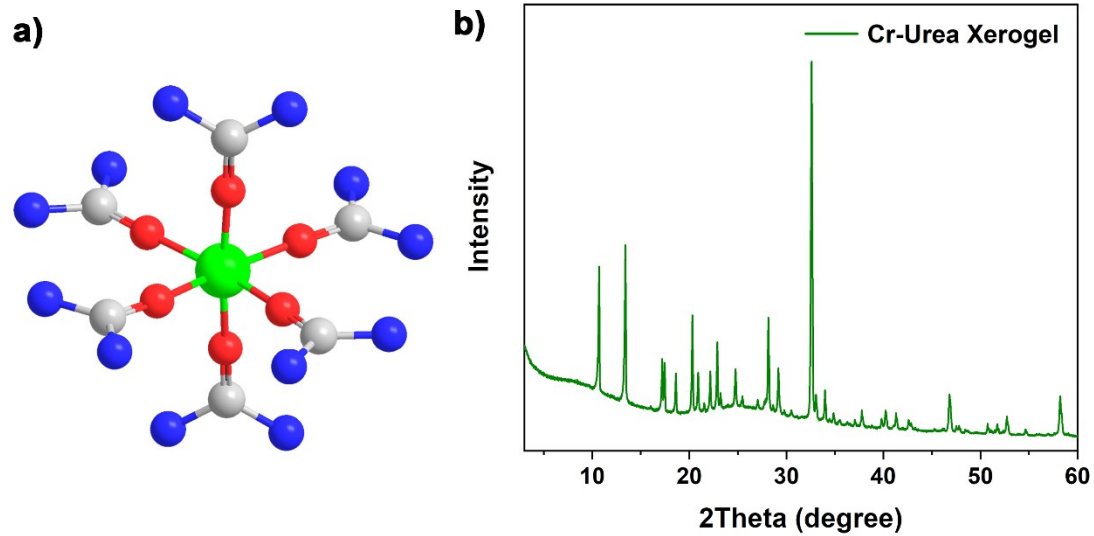
Figure S1. a) Illustration of the $Cr[OC(NH_2)_2]3+$ 6 octahedral coordination ion in the Cr-urea xerogel; b) PXRD pattern of Cr-urea xerogel
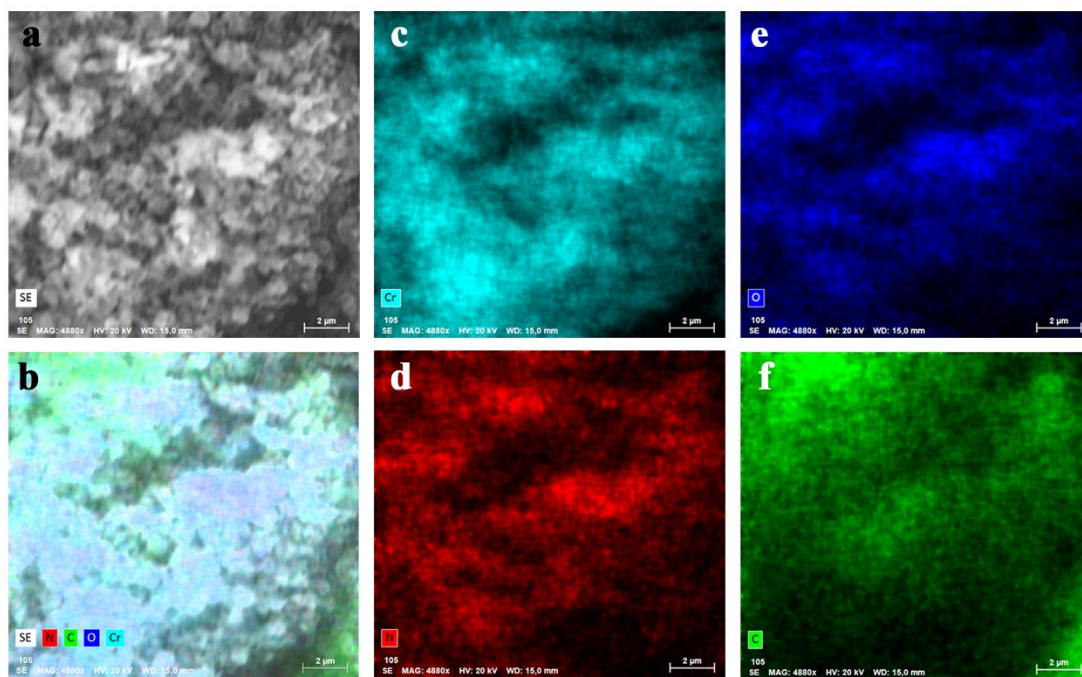
Figure S2. a) SEM image of CrN NPs, and corresponding EDS mapping: b) overlapped, c) Cr, d) N, e) O, f) C.

Table S1. Elemental composition of CrN NPs catalyst

Sample	Cr content (wt%)[a]	N content (wt%)[b]	C content (wt%)[b]	H content (wt%)[b]
CrN NPs	75.9	19.08	1.49	0.36

a: from ICP-OES

b: from CHN elemental analysis

Table S2. Elemental composition comparison between surface and bulk phase of CrN

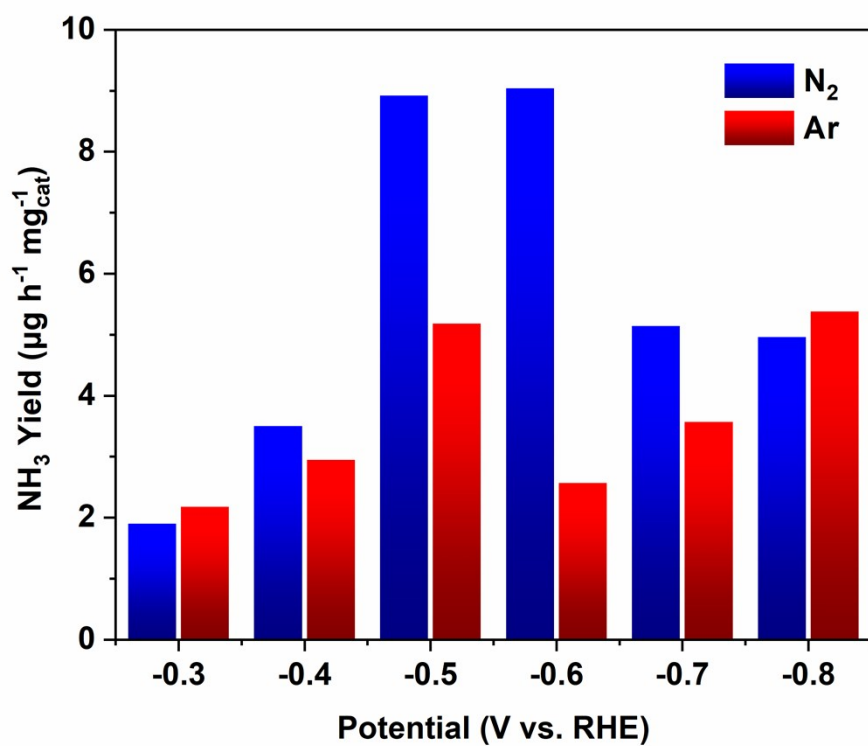|	Cr content (at%)	N content (at%)	C content (at%)	O content (at%)
Surface[a]	33.26	35.09	9.56	20.6
Bulk	41.69[b]	38.90[c]	3.54[c]	5.66[d]

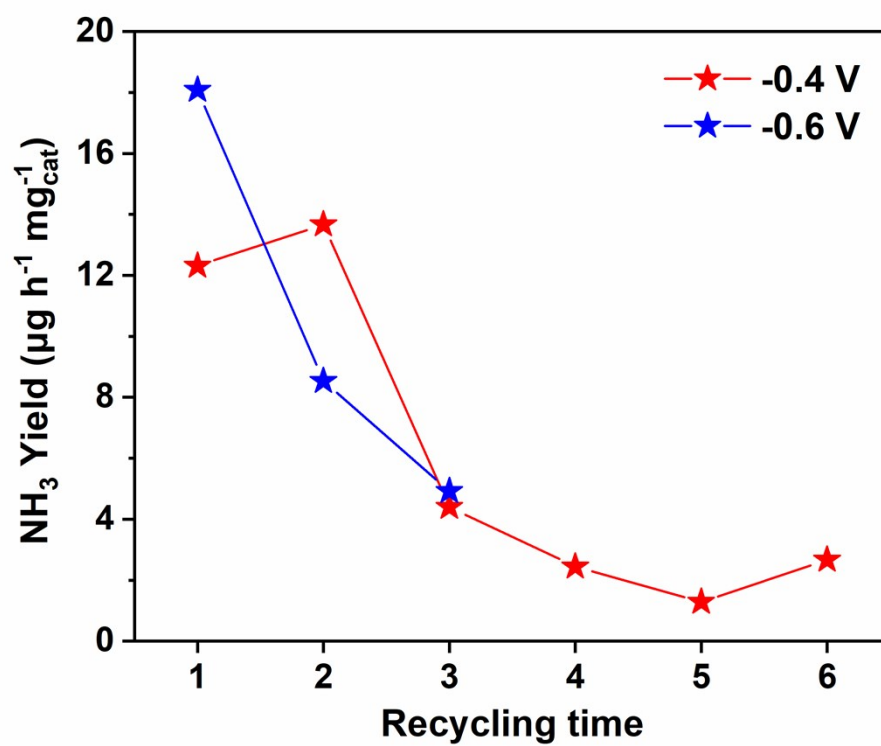a: from XPS survey spectra

b: from ICP-OES

c: from CHN elemental analysis

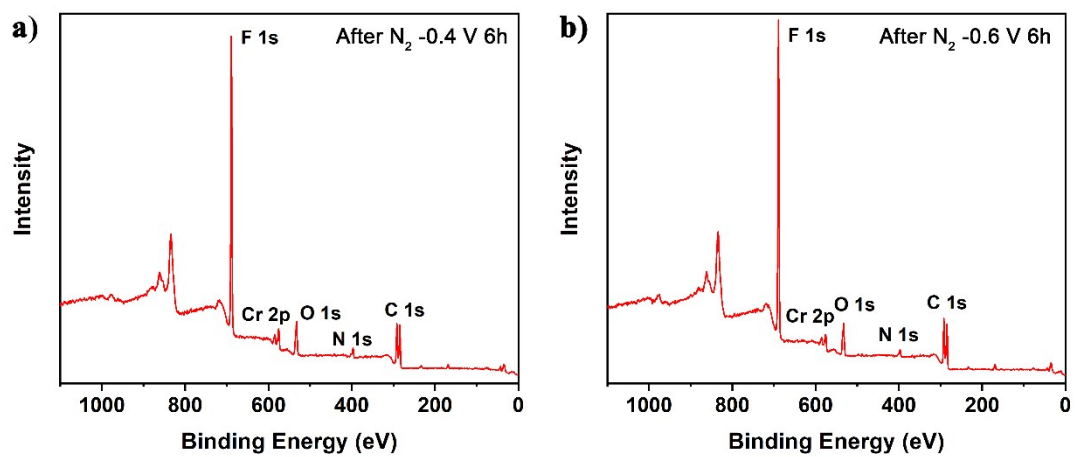d: 100% subtracting contents from other elements (Cr, C, N, H)
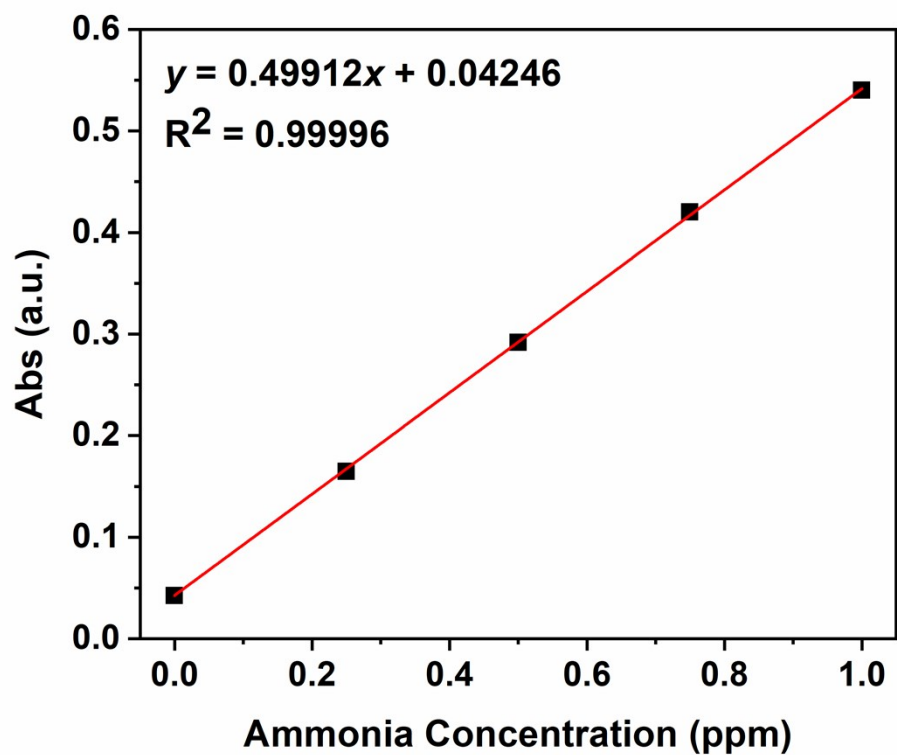
Figure S3. A typical calibration curve of NH_3 standard solutions in 0.05 M H_2SO_4 adsorbent.

Figure S4. NH$_3$ yield rate of CrN NPs catalyst at different potentials for the initial 1 h tests in N$_2$/Ar atmosphere.

Figure S5. NH_3 yield rate of CrN NPs catalyst during cycling tests.

Figure S6. XPS survey spectra of CrN/CFP electrodes after 6 h NRR electrolysis.

Table S3. Surface Cr, N contents and N/Cr ratio before and after 6 h electrolysis[a]

Sample	Cr Content (at%)	N Content (at%)	N/Cr Ratio
CrN NPs[b]	33.26	19.08	0.57
CrN/CFP after -0.4 V 6 h electrolysis[c]	0.82	3.57	4.35
CrN/CFP after -0.6 V 6 h electrolysis[c]	0.73	2.44	3.34
CrN/CFP after NH+ 4 dipping 2 h[d]	0.98	1.53	1.56

a: from XPS quantification

b: as-prepared CrN nanoparticles catalyst

c: CrN catalyst loaded onto CFP electrodes after 6 h NRR electrolysis

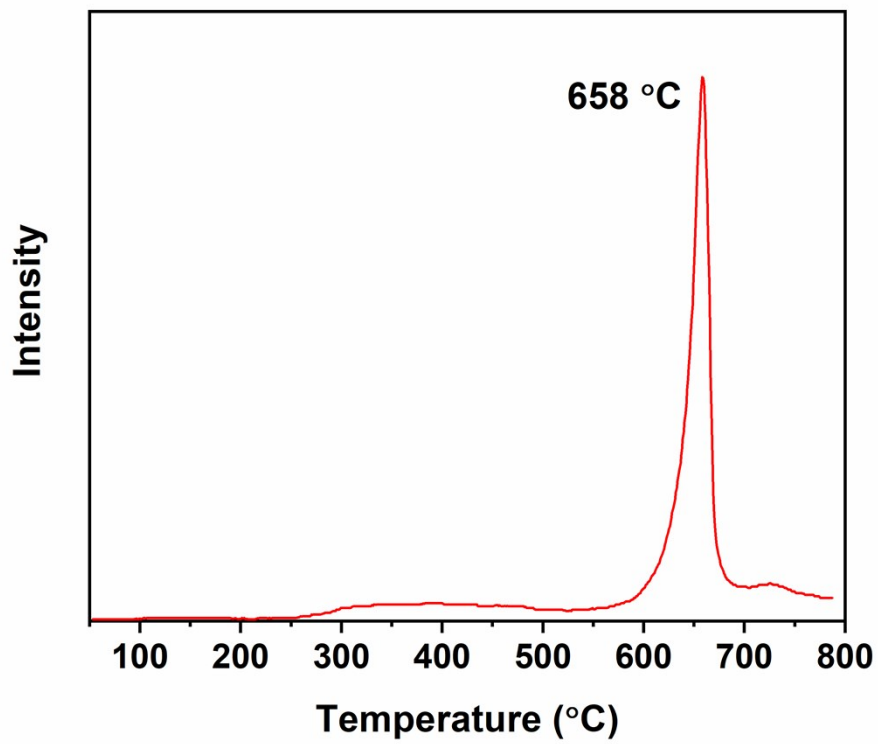d: CrN/CFP electrodes after dipping into 0.1 M NH+ 4/0.05 M H_2SO_4 solution for 2h

**Table S4**. High-resolution Cr 2p$_{3/2}$ XPS results for CrN NPs

Sample	Peak Position (eV)	Ratio (%)	Peak Position (eV)	Ratio (%)	Peak Position (eV)	Ratio (%)
CrN NPs	574.531	9.47	575.472	47.64	576.464	47.64
CrN/CFP after -0.4 V 6 h electrolysis	574.744	9.78	575.684	41.97	576.695	48.25
CrN/CFP after -0.6 V 6 h electrolysis	574.804	8.66	575.786	49.33	576.96	42.01

Table S5. High-resolution N 1s XPS results for CrN NPs

Sample	Peak Position (eV)	Ratio (%)	Peak Position (eV)	Ratio (%)	Peak Position (eV)	Ratio (%)
CrN NPs	396.637	48.93	397.815	25.72	399.685	9.76
CrN/CFP after -0.4 V 6 h electrolysis	396.97	60.18	398.16	3.38	400.27	36.44
CrN/CFP after -0.6 V 6 h electrolysis	396.966	47.32	397.31	16.96	400.841	35.71

Figure S7. NH$_3$-TPD curve for CrN NPs
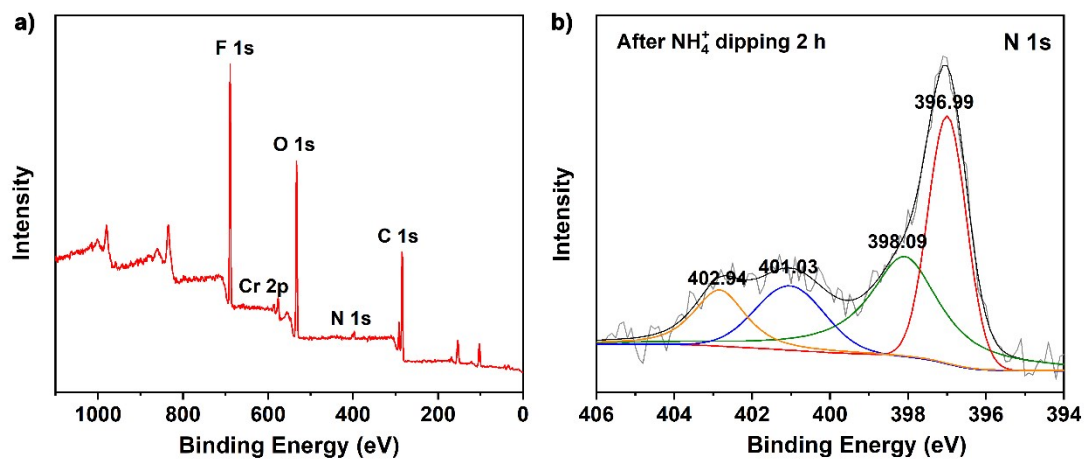
Figure S8. XPS results of CrN/CFP electrodes after dipping into 0.1 M NH+ 4/0.05 M H$_2$SO$_4$ solution for 2 h, a) survey spectra, b) N 1s.

The peaks at 401.03 and 402.94 eV correspond to adsorbed ammonia molecules and ammonium cations. The bias of peaks compared with that after electrolysis indicates the difference of nitrogen states at CrN surface, where the electrochemically generated poisoning species might not be the completely protonated NH$_3$ or NH+ 4 groups, but instead partially protonated surface nitrogen sites, which could not be desorbed.

References

[1]   Y. Qiu, L. Gao, *Mater. Res. Bull.* **2003**, *38*, 1551-1557.

[2]   G. W. Watt, J. D. Chrisp, *Anal. Chem.* **1952**, *24*, 2006-2008.