Electrochemical deuterated ammonia (ND_3) production at A cm^{-2} current densities

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Experimental Procedures

Chemicals and materials

Isopropanol (C_3H_8O, ≥99 wt%), potassium nitrate (KNO_3, ≥99.0 wt%), trisodium citrate dihydrate ($C_6H_5Na_3O_7·2H_2O$, ≥99.0 wt%), phosphoric (H_3PO_4, 85 wt%), Sodium nitroferricyanide (III) dihydrate ($Na_2Fe(CN)_5(NO)·2H_2O$, ≥99.0 wt%), Sodium Hypochlorite (NaClO, Cl≥12 wt%) and hydrochloric acid (HCl, 36 wt%) were all purchased from Sinopharm Chemical Reagent Co., Ltd. Potassium hydroxide (KOH, 85 wt%), Potassium nitrite (KNO_2, ≥97 wt%) Hydrazine-d4 dideuteriochloride (ND4Cl, ≥99.9 wt%), ammonium chloride (NH_4Cl, 99.8 wt%), salicylic acid ($C_7H_6O_3$, 99.5 wt%), p−aminobenzenesulfonamide ($C_6H_8N_2O_2S$, >99.8 wt%), N−(1−naphthyl) ethylenediamine dihydrochloride ($C_{12}H_{14}N_2·2HCl$, >98 wt%), Nafion ionomer (5 wt%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Polytetrafluoroethylene preparation (PTFE, 60 wt%) was obtained from SUDASUJIAO Co., Ltd. (Dongguan, China). Nash reagent (>98 %) was purchased from Innochem Co., Ltd. (Shanghai, China). Purity nitrogen gas (99.9 %) was obtained from BEIWEN Co., Ltd (Beijing, China). All the chemicals were used without further purification.

Catalyst preparation

All the catalysts utilized in this work (*Fe-N-C* and *Co-N-C* were purchased from the XFNANO Co., Ltd. (Jiangsu, China) and Zhongke Materials Co., Ltd. (*Fe-C* and *Co-C*)). and directly used without any treatments.

Working electrode preparation

The working electrode was prepared by spray coating the catalyst ink onto a hydrophilic carbon paper,

which was purchased from the SCI Materials Hub Co., Ltd. (Anhui, China). In a typical preparation of the catalyst furnishing electrode, a catalyst ink that contained 10 mg *Fe-N-C*, 250 μL isopropanol, 750 μL deionized (DI) water and 30 μL Nafion ionomer solution (5 wt%) was mixed and sonicated for 30 min. Then, the catalyst ink was slowly sprayed coating onto a hydrophilic carbon paper with a size of 2.5 cm × 2.5 cm.

Material characterizations

X−ray diffraction (XRD) patterns were collected on a Bruker D8, and the source was a Cu-Kα radiation (λ = 1.54056 Å) at 40 kV and 40 mA. Scanning electron microscopy (SEM) images were obtained on Hitachi S-4800 operated at 2 kV. Transmission electron microscopy (TEM), High-resolution TEM (HRTEM), high-angle annular dark-field scanning TEM (HAADF-STEM) and Energy dispersive X-ray (EDX) mapping images were acquired using JEOL JEM-2100F field emission electron microscope operating at 200 kV. X−ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250Xi spectroscope using Al-Kα x-rays as the excitation source. All binding energies were calibrated with C1s spectrum with peak intensity at 284.8 eV. The XAS measurements were conducted at spring 8, Japan Synchrotron Radiation Facility (JSRF). The data were all collected in transmission−yield mode and the energy was calibrated accordingly to the absorption edge of pure Fe foil.

Electrochemical measurements of nitrate reduction reaction

The nitrate reduction reaction performance was first assessed in a flow electrolyzer using a three−electrode system. An Ag/AgCl electrode worked as the reference electrode, an Ni foam as the counter electrode, and the catalyst coated electrode as a working electrode. In a typical NO_3^-

reduction reaction (NO3RR) performance test, 1 M KOH and 0.1 M KNO_3 mixture was pumped at 55 mL min^{-1} after N_2 purging. 1 M KOH solution was used as anolyte at 55 mL min^{-1}. The further measurements were proceeded on the MEA type electrolyzer and were kept consistent conditions with the above flow electrolyzer except for the use of two−electrode system.

The electrochemical performance of the catalyst was recorded by an electrochemical workstation (CHI630E, from CH Instruments, Shanghai). Electrochemical performance was investigated in the galvanostatic mode. The duration of reaction at each applied current is usually 60 min, except for the special illustration in the other typical test. Electrochemically active surface areas (ECSAs) of the catalysts were investigated in a potential window where no Faradaic process occurred in an electrolyte of 1 M KOH at different scanning rates of 5, 10, 20, 30, 40 and 50 mV s^{-1}.

All potentials were converted to the reversible hydrogen electrode (RHE) using this equation, E (vs. RHE) = 0.21+E (vs. Ag/AgCl) +0.0591*pH. All the potentials were corrected vs. RHE and without *iR* compensation.

Electrochemical deuteration ND_3 synthesis

The electrochemical ND_3 production in this work was carried out in the MEA-type electrolyzer. The catholyte was consisted of 1.0 M KNO_3 and 0.3 M K_2SO_4 in 50 mL D_2O, and the anolyte there is the same as the catholyte except for the absence of the KNO_3.

Products detection and Faradaic efficiency calculations

The main N-containing product NH_3, NO_2^- and NO_3^-, and the electrolytic ND_3 was collected from the flow−out catholyte and quantified by UV−vis spectrophotometer (UV−2700i).

For NH_3 quantification, the NH_3 concentration was quantified by the Nessler Reagent method. Typically, the electrolytes sampled after electrolysis for 1 h were mixed with 0.2 mL of Nessler reagent for the chromogenic reaction. The absorbance of the mixed solution was measured at a wavelength of 420 nm after keeping it at room temperature for 30 min. The quantitation of NH_3 was performed by the standard curves, which was built using standard NH_4Cl solutions in 1 M KOH (Figure S15c).

For ND_3 quantification, the ND_3 concentration was also quantified by the Nessler Reagent method but all the electrolyte and diluent were utilized the D_2O to eliminate the interference of hydrogen atoms. Similarly, the standard curves which was used for the quantification of ND_3 were built using standard ND_4Cl solutions in D_2O and K_2SO_4 (Figure S15d).

For NO_2^- quantification, a mixture of 3 mL liquid electrolyte, 3 mL 1 M hydrochloric acid and 100 μL color reagent was measured after keeping in dark at room temperature for 20 min. The color reagent was prepared by dissolving 4 g p-aminobenzenesulfonamide, 10 mL phosphoric acid and 0.2 g N-(1−naphthyl) ethylenediamine dihydrochloride in DI water to 100 mL. The concentration of NO_2^- was calculated based on the absorbance at a wavelength of 540 nm and the standard curve made beforehand using standard KNO_2 solution in 1 M KOH (Figure S15b).

For NO_3^- quantification, a mixture of 3 mL liquid electrolyte with 40 μl of 1M HCl with 4.0 μl of 0.8wt% sulfamic acid solution was measured after keeping for 20min at ambient conditions. The absorption intensities at wavelengths of 220 and 275nm were then recorded by UV–vis spectrophotometry (UV−2700i). The final absorbance was calculated using the equation: $A=A_{220nm} - A_{275nm}$. The concentration–absorbance curve was calibrated using a series of standard potassium

nitrate solutions with a linear fitting prepared in advance. Nitrate product concentration was then calculated based on the tested absorbance and the standard calibration curve (Figure S15a).

The energy consumption and carbon emission analysis

In this section, we calculated the energy consumption of per mol ND_3 using the Gibbs free energy, and then the corresponding carbon emission was calculated based on the assumption that the consumed energy was powered by natural gas (NG).

We simplified the industrial production processes and ignored part of the industrial details, the results were displayed in Figure 1b and 2a. The hydrolysis of metal nitrides, such as Mg_3N_2 or Ca_3N_2, using deuterium oxide (D_2O), the direct synthesis of D_2 and N_2 from the Haber-Bosch process and the proposed electrochemical ND_3 production using renewable electricity are shown as below:

The hydrolysis of metal nitrides

The energy consumption of hydrolysis of metal nitrides (Mg_3N_2 or Ca_3N_2) consisted of the three steps: the industrial production of the active metals, the metal nitride synthesis and the metal nitride hydrolysis. The involved eqs.1-6 are shown below:

$$MgO + C = Mg + CO \quad (1)$$

$$3Mg + N_2 = Mg_3N_2 \quad (2)$$

$$Mg_3N_2 + 6D_2O = 2ND_3 + 3Mg(OD)_2 \quad (3)$$

$$6CaO + 2Al = 3Ca + 3CaO.Al_2O_3 \quad (4)$$

$$3Ca + N_2 = Ca_3N_2 \quad (5)$$

$$Ca_3N_2 + 6D_2O = 2ND_3 + 3Ca(OD)_2 \quad (6)$$

We have looked up the standard thermodynamic values, and assumed the energy efficiency is 70 % for the calcination. The theoretical energy consumption only depends on the first two stages. For the equations 1-2 and 4-5:

$$G(1) = [-137.27704 - (-568)]\ kJ/mol = 430.723\ kJ/mol$$

$$G(2) = -400.8272\ kJ/mol$$

Then for per mole of ND_3, the energy consumption of Mg_3N_2 formation is:

$$G(Mg_3N_2) = [G(1) \times 0.001 \div 0.7 \times 3 + G(2) \times (-0.001) \div 0.7] \div 2\ MJ/mol$$

$$= \mathbf{1.209}\ MJ/mol$$

$$G(4) = [-2208.7336 \times 3 + 6 \times 603.542]\ kJ/mol = -3004.9088\ kJ/mol$$

$$G(5) = -121\ kJ/mol$$

Then for per mol of ND_3, the energy consumption of Ca_3N_2 is (Determination of Standard Gibbs Energy of Formation of CaN)[1]:

$$G(Ca_3N_2) = [G(4) \times (-0.001) \div 0.7 + G(5) \times (-0.001) \div 0.7] \div 2\ MJ/mol$$

$$= \mathbf{2.233}\ MJ/mol$$

The heating value for NG is 0.857 MJ per mole of NG. Therefore, the carbon emission of per mole of NG is assumed to be 50.135 per gram of CO_2 (50.135 g_{CO2}/mol_{NG}) which calculated by the U.S. Department of Energy[2]. The carbon emissions shown as below:

For Mg_3N_2, the NG consumption is:

$$NG\ \ consumption\ \ (Mg_3N_2) = G\ \ (Mg_3N_2) \div 0.857\ \ mol_{NG} = \mathbf{1.384}\ \ mol\ \ NG$$

the carbon emission is:

$$Carbon\ \ emission\ \ (Mg_3N_2) = \ \ NG\ \ consumption\ \ (Mg_3N_2) \times 50.135\ \ g\ \ CO_2$$

$$= \mathbf{69.40}\ \ g\ \ CO_2$$

For Ca_3N_2, the NG consumption is:

$$NG\ \ consumption\ \ (Ca_3N_2) = G\ \ (Ca_3N_2) \div 0.857\ \ mol_{NG} = \mathbf{2.556}\ \ mol\ \ NG$$

the carbon emission is:

$$Carbon\ \ emission\ \ (Ca_3N_2) = \ \ NG\ \ consumption\ \ (Ca_3N_2) \times 50.135\ \ g\ \ CO_2$$

$$= \mathbf{128.14}\ \ g\ \ CO_2$$

The direct synthesis of D_2 and N_2

We reference the standard Ammonia Production Processes[3] and listed the main energy consumption processes (Figure 1b and 2a): natural gas consumption (reformer feed, fuel and others), energy to high pressure (HP) steam system (primary reformer, secondary reformer and others), steam use (steam for turbines, process steam, and others), losses (reforming, steam generation and others) and energy in ND_3 product.

The energy consumption is shown as below:

$$Energy\ \ consumption$$

$$= (5.56 + 1.69 + 0.08 + 0.53 + 0.32 + 0.47 + 0.84 + 0.35 + 0.13 + 1.18 + 0.57$$

$$+ 0.77 + 4.81)\ \ Gcal/tNH_3 = 17.3\ \ Gcal/tNH_3$$

$$= 17.3 \times 4.186 \times 17 \div 1000\ \ MJ/mol = \mathbf{1.231}\ \ MJ/mol$$

The NG consumption is:

$$NG\ \ consumption\ \ =\ \ Energy\ \ consumption \div 0.857\ \ mol_{NG} = \mathbf{1.409}\ \ mol\ \ NG$$

The carbon emission is:

$$Carbon\ \ emission\ \ =\ \ NG\ \ consumption\ \ \times 50.135\ \ g\ \ CO_2 = \mathbf{70.652}\ \ g\ \ CO_2$$

The proposed electrochemical ND_3 production

To calculate the energy consumption per mole of ND_3, we first calculated the theoretical value based on the Gibbs free energy of per mole of ND_3 from the equation 7 below:

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^- \quad (7)$$

$$G(7) = [9 \times 157.27656 + 16.48496 - 111.33624 - 6 \times 237.17]\ \ kJ/mol$$

$$= -102.38224\ \ kJ/mol$$

Next, we calculated the energy efficiency based the experimental results (Figure 3d and 6b) in our work. At a current density of 200 mA cm^{-2}, the cathodic potential is about 1.2 V and the theoretical potential of NO_3^- reductio reaction is 0.69 V, the maximum Faradic efficiency of ND_3 (FE_{ND3}) is approximately 92 %. Then the energy efficiency is calculated as below:

$$Energy\ \ Efficiency\ \ of\ \ ND_3\ \ (EE_{ND3}) = \frac{E_{theory}}{E_{cell}} \times FE_{ND3} = \frac{0.69\ \ V}{1.2\ \ V} \times 92\ \ \% = 0.53$$

The modified consumption of electricity is:

$$Energy\ \ consumption = \frac{G(7) \times (-0.001)}{EE_{ND3}} = \mathbf{0.1935}\ \ MJ/mol$$

$$Electricity\ \ consumption = Energy\ \ consumption \div 3.6\ \ KWh/mol = \mathbf{0.05376}\ \ KWh/mol$$

We consider the practical carbon emission resulted from the grid carbon emission factor as 0.3 kg

CO_2 of per KWh in this work:

$$Carbon\ \ emission = \ \ Electricity\ \ consumption \times 0.3 \times 1000\ \ g\ \ CO_2/mol$$

$$= \mathbf{16.13}\ \ g\ \ CO_2/mol$$

Technoeconomic analysis

We carried out a technoeconomic analysis (TEA) based on the modified model from the previously published work[4,5] to ascertain the economic effectiveness of the electrolytic ND_3. The result in the manuscript (Figure 7e) represented the model we used to calculate the plant-gate levelized cost (unit: US$) for the synthesis of per kilogram (kg) of ND_3. In this process, we considered the costs for the electrolyzer, catalyst, membrane, installation, balance of plant, input chemicals, electricity, ND_3 separation, as well as other operational costs. It's worth noting that the cost for the distribution is not considered due to the differences in different regions.

Here, we demonstrated the results of NO_3RR and deuteration to ND_3 based on the performance (FE_{ND3}: 92 %, full-cell potential (V_{cell}): 2.23 V), which achieved using the *Fe-N-C* catalysts at the operation current density of 200 mA cm^{-2} in the A = 1 cm^2 MEA based electrolyzer with the catholyte consisted of concentration of 1 M KNO_3 and 0.3 M K_2SO_4 in D_2O and the anolyte: 0.3 M K_2SO_4 in D_2O, the details for the TEA calculation are listed below.

1. Electrochemical device: the cost of the electrolyzer, catalyst, and membrane.

Assuming the production capacity of the plant is 1 tonne of ND_3 per day, the total current needed is:

$$Total\ \ current\ \ needed\ \ [A]$$

$$= \frac{\frac{ND_3\ \ production\ \ [g/day]}{molecular\ \ weight\ \ \left[\frac{g}{mol}\right] \times 86400\ \ [\frac{s}{day}]} \times electrons\ \ transferred \times Faraday's\ \ constant}{FE_{ND3}}$$

$$= \frac{\frac{1 \times 10\text{^}6\ \ g/day}{20\ \ g/mol \times 86400\ \ s/day} \times 8 \times 96485\ \ C/mol}{0.92} = 485532.41\ \ A$$

The consumed power based on the V_{cell} (2.23 V) in this process as follows:

$$Power\ \ Consumed\ \ [W] = Total\ \ current\ \ needed\ \ [A]\ \ \times V_{cell}\ \ [V] = 485532.41\ \ A \times 2.23\ \ V$$

$$= 1082.74\ \ KW$$

From the DOE H2A analysis for central grid electrolysis, the electrolyzer cost for the stack component we used is \$250.25/kW with a reference current density of 175 mA cm^{-2} in a reported work[6]. Thus, the total electrolyzer cost is:

$$Total\ \ Electrolyzer\ \ Cost\ \ (\$)$$

$$= Power\ \ Consumed\ \ [KW] \times Electrolyzer\ \ Cost\ \ \left[\frac{\$}{KW}\right]$$

$$\times \frac{base\ \ current\ \ density\ \ \left[\frac{mA}{cm^{-2}}\right]}{input\ \ current\ \ density\ \ \left[\frac{mA}{cm^{-2}}\right]} = 1082.74\ \ KW \times 250.25 \frac{\$}{KW} \times \frac{175\ \ \frac{mA}{cm^{-2}}}{200\ \ \frac{mA}{cm^{-2}}}$$

$$= \$237085.63$$

As the total electrolyzer cost above is the one-time cost for the electrolyzer, we need to convert it to a cost for generating one tonne of ND_3. We assume the lifetime of the electrolyzer is 20 years with no salvage value at the end of the plant's lifetime and a plant capacity factor of 0.9 which means the plant produces ND_3 328.5 days per year. The electrolyzer cost per tonne of ND_3 is:

$$Electrolyzer\ \ cost\ \ [\frac{\$}{ND_3\ \ production}] = \frac{CRF_{electrolyzer} \times Total\ \ Electrolyzer\ \ Cost\ \ [\$]}{Capacity\ \ factor \times 365\ \ \frac{day}{year} \times production\ \ [\frac{tonne\ \ ND_3}{day}]}$$

Herein, the capital recovery factor (CRF) is based on a discount rate (we use 7% for all the CRF calculations) and the material lifetime.

$$CRF_{electrolyzer} = \frac{i(1+i)^{lifetime}}{(1+i)^{lifetime}-1}$$

$$Electrolyzer\ \ cost\ \left[\frac{\$}{ND_3\ \ production}\right] = \frac{\frac{0.07(1.07)^{20}}{(1.07)^{20}-1} \times \$237085.63}{0.9 \times 365\,\frac{day}{year} \times 1\ \ tonne\frac{ND_3}{day}} = \mathbf{68.13}\ \ \$/tonne\ \ ND_3$$

For the catalyst and membrane cost, we assume that their total one-time cost is 5% of the electrolyzer cost with a lifetime of 5 years. We can then reduce to a cost per tonne of n-propanol using the same method as above:

$$Catalyst\ \ and\ \ membrane\ \ cost\ \left[\frac{\$}{tonne\ \ ND_3}\right]$$

$$= \frac{CRF_{catalyst\ \ and\ \ membrane} \times Total\ \ Electrolyzer\ \ Cost\ \ [\$] \times 5\%}{Capacity\ \ factor \times 365\ \ \frac{day}{year} \times production\ \ \left[\frac{tonne\ \ ND_3}{day}\right]}$$

$$= \frac{\frac{0.07(1.07)^5}{(1.07)^5-1} \times \$237085.63 \times 0.05}{0.9 \times 365\,\frac{day}{year} \times 1\ \ \frac{tonne\ \ ND_3}{day}} = \mathbf{8.80}\ \ \frac{\$}{tonne\ \ ND_3}$$

2. Electricity cost

By assuming the electricity price is 3 c/kWh (according to the price of electricity in Beijing, 2023), the electricity cost per tonne of ND_3 is:

$$Electricity\ \ cost\ \left[\frac{\$}{tonne\ \ ND_3}\right] = \frac{Power\ \ Consumed\ \ [KW] \times 24\ \ hours \times electricity\ \ price\ \ \left[\frac{\$}{KWh}\right]}{n\ \ \left[\frac{tonne\ \ ND_3}{day}\right]}$$

$$= \frac{1082.74\ \ KW \times 24\ \ hours \times 0.03\ \ \frac{\$}{KWh}}{1\ \ \frac{tonne\ \ ND_3}{day}} = 779.57\ \ \frac{\$}{tonne\ \ ND_3}$$

3. Gas separation cost

We employed the ammonia recovery with the Sweeping Gas Membrane Distillation (SGMD) model[7] to evaluate the ND_3 separation cost in this process. The gases in the cathode output at 200 mA cm^{-2}, the FE_{ND3} is 92 %. With 1 tonne of ND_3 produced per day via electrocatalysis NO_3^- reduction and deuteration to ND_3, we used the "air stripper" for reference and the energy intensity is 0.5 kWh/kg N, thus, the calculation cost of per tonne ND_3 separation cost as below:

$$ND_3\ \ Sparation\ \ Cost\ \left[\frac{\$}{tonne\ \ ND_3}\right]$$

$$= \frac{n\ \left[\frac{tonne\ \ ND_3}{day}\right] \times \frac{M_N\ \left[\frac{g}{mol}\right]}{M_{ND_3}\ \left[\frac{g}{mol}\right]} \times Cost\ \ of\ \ separation\ \left[\frac{KWh}{kg_N}\right] \times electricity\ \ price\ \left[\frac{\$}{KWh}\right]}{n\ \left[\frac{tonne\ \ ND_3}{day}\right]}$$

$$= \frac{1 \times 1000\ \ \frac{kg}{day} \times \frac{14}{20} \times 0.03\ \ \frac{\$}{KWh} \times 0.5\ \ \frac{KWh}{kg_N}}{1\ \ \frac{tonne\ \ ND_3}{day}} = \mathbf{10.5}\ \ \frac{\$}{tonne\ \ ND_3}$$

4. The total capital costs

By summing the above cost for the electrolyzer, catalyst, and sweeping gas membrane distillation cost, we can get the total capital costs of $87.43 per tonne of ND_3.

5. Installation cost

Based on the total capital costs, we assume a Lang factor of 1 for the calculation of equipment installation cost. The installation cost per tonne of ND_3 is as below:

$$Installation\ \ cost\ \left[\frac{\$}{tonne\ \ ND_3}\right] = Lang\ \ Factor \times Total\ \ capital\ \ costs = \mathbf{87.43}\ \ \frac{\$}{tonne\ \ ND_3}$$

6. Balance of plant (BoP)

We assume the balance of plant is 50% of the total capital costs. The balance of plant per tonne of ND_3 and the corresponding quantity of ND_3 is as below:

$$BoP\ \left[\frac{\$}{tonne\ \ ND_3}\right] = BoP\ \ Factor \times Total\ \ capital\ \ costs = 50\ \ \% \times 87.43\ \ \frac{\$}{tonne\ \ ND_3}$$
$$= \mathbf{43.71}\ \ \frac{\$}{tonne\ \ ND_3}$$

7. Input chemicals cost

For the input chemicals cost, we account for the cost from the consumed D_2O, KNO_3, and K_2SO_4.

The price of D_2O is estimated as \$1.43 per milliliter (ml) (or \$1508571.43 per tonne) based on the 2023 average D_2O price (CNY 1000 per 100 ml) in China. Thus, the cost of D_2O consumed in anode for oxygen evolution reaction in anode per day can be calculated according to the process below:

$$Cost\ \ of\ \ consumed\ \ D_2O$$
$$= \frac{Total\ \ current\ \ needed\ \ [A] \times 86400\ \ \frac{s}{day} \times molecular\ \ weight_{D_2O}\ \ [\frac{kg}{mol}]}{electrons\ \ transferred\ \ per\ \ D_2O\ \ molecular \times Faraday'\ \ Constant \times 1000}$$
$$\times 1508571.43\ \ \frac{\$}{tonne\ \ D_2O}$$
$$= \frac{485532.41\ \ A \times 86400\ \ \frac{s}{day} \times 0.02\ \ \frac{kg}{mol}}{2 \times 96485\ \ \frac{C}{mol} \times 1000} \times 1508571.43\ \ \frac{\$}{tonne\ \ D_2O} = \$5881799.36$$

Therefore, the cost of consumed D_2O in anode per tonne of ND_3 is as below:

$$Cost\ \ of\ \ consumed\ \ D_2O\ \ \left[\frac{\$}{tonne\ \ ND_3}\right] = \frac{\$5881799.36}{1\ \ tonne\ \ ND_3} = \mathbf{5881799.36}\ \ \frac{\$}{tonne\ \ ND_3}$$

Based on the market research and according to the conversion of exchange rate, we assume a price of \$0.77143 per kilogram (kg) (approximately CNY 5400 per tonne KNO_3 in China). Thus, the cost of KNO_3 consumed in cathode for nitrite reduction reaction in cathode per day can be calculated according to the process below:

$$Cost\ \ of\ \ consumed\ \ KNO_3$$

$$= \frac{Total\ \ current\ \ needed\ \ [A] \times 86400\ \ \frac{s}{day} \times molecular\ \ weight_{KNO_3}\ \ [\frac{kg}{mol}]}{electrons\ \ transferred\ \ per\ \ KNO_3\ \ molecular \times Faraday'\ \ Constant \times 1000}$$

$$\times 771.43\ \ \frac{\$}{tonne\ \ KNO_3}$$

$$= \frac{485532.41\ \ A \times 86400\ \ \frac{s}{day} \times 0.1011\ \ \frac{kg}{mol}}{8 \times 96485\ \ \frac{C}{mol} \times 1000} \times 771.43\ \ \frac{\$}{tonne\ \ KNO_3} = \$4238.67$$

Therefore, the cost of consumed KNO_3 in cathode per tonne of ND_3 is as below:

$$Cost\ \ of\ \ consumed\ \ KNO_3\ \ \left[\frac{\$}{tonne\ \ ND_3}\right] = \frac{\$4238.67}{1\ \ tonne\ \ ND_3} = \mathbf{4238.67}\ \ \frac{\$}{tonne\ \ ND_3}$$

The electrolyte is 0.3 M K_2SO_4 in D_2O solution. We estimated a fixed volume ratio of 100 L electrolyte per m^2 of electrolyzer based on our lab-scale experiments. The total volume of electrolyte needed is:

$$Volume\ \ of\ \ electrolyte\ \ [L] = \frac{Total\ \ current\ \ needed\ \ [mA]}{current\ \ density\ \ \left[\frac{mA}{cm^2}\right] \times (\frac{100\ \ cm}{1\ \ m})^2} \times 100\ \ \frac{L}{m^2}$$

$$= \frac{485532410\ \ mA}{200\ \ \frac{mA}{cm^2} \times (\frac{100\ \ cm}{1\ \ m})^2} \times 100\ \ \frac{L}{m^2} = 24276.62\ \ L$$

Based on the market research and according to the conversion of exchange rate, we assume a price of \$0.45714 per kilogram (kg) (approximately CNY 3200 per tonne K_2SO_4). Next, we can get the total cost of electrolyte including the cost of K_2SO_4. The calculation of the cost as shown below:

$$Cost\ of\ electrolyte\ [\$]$$

$$= Volume\ of\ electrolyte\ [L] \times molecular\ weight_{K_2SO_4}\ \left[\frac{kg}{mol}\right] \times 0.3\ \frac{mol}{L}$$

$$\times price\ of\ K_2SO_4\ \left[\frac{\$}{kg}\right] + Volume\ of\ electrolyte\ [L] \times D_2O\ price\ \left[\frac{\$}{kg}\right]$$

$$= 24276.62\ L \times 0.17426\ \frac{kg}{mol} \times 0.3\ \frac{mol}{L} \times 0.45714\ \frac{\$}{kg} + 24276.62\ L \times 1.056\ \frac{kg}{L}$$

$$\times 1508.571\ \frac{\$}{kg} = \$38674473.95$$

By assuming an electrolyte lifetime of one year, we calculate a new CRF:

$$CRF_{electrolyte} = \frac{0.07(1.07)^1}{1.07^1 - 1}$$

For producing 1 tonne of ND_3, the cost of electrolyte is calculated as below:

$$Cost\ of\ electrolyte\ \left[\frac{\$}{tonne\ ND_3}\right] = \frac{CRF_{electrolyte} \times Cost\ of\ electrolyte\ [\$]}{Capacity\ factor \times 365\ \frac{day}{year} \times production\ \left[\frac{tonne\ ND_3}{day}\right]}$$

$$= \frac{1.07 \times \$38674473.95}{0.9 \times 365\ \frac{day}{year} \times 1\ \frac{tonne\ ND_3}{day}} = \mathbf{125971.6503}\ \frac{\$}{tonne\ ND_3}$$

We can get the input chemicals cost per tonne of ND_3 according to the calculation below:

$$Input\ chemical\ cost\ \left[\frac{\$}{tonne\ ND_3}\right]$$

$$= Cost\ of\ consumed\ D_2O\ \left[\frac{\$}{tonne\ ND_3}\right] + Cost\ of\ consumed\ KNO_3\ \left[\frac{\$}{tonne\ ND_3}\right]$$

$$+ Cost\ of\ electrolyte\ \left[\frac{\$}{tonne\ ND_3}\right]$$

$$= \mathbf{5881799.36}\ \frac{\$}{tonne\ ND_3} + \mathbf{4238.67}\ \frac{\$}{tonne\ ND_3} + \mathbf{125971.6503}\ \frac{\$}{tonne\ ND_3}$$

$$= \mathbf{6012009.68}\ \frac{\$}{tonne\ ND_3}$$

8. Other operational costs

We also take the other operational costs (such as labor and maintenance) into account and assume this cost to be 10% of the electricity cost per tonne of ND_3, then the cost of other operation is calculated as below:

$$Other\ \ operational\ \ cost\ \ \left[\frac{\$}{tonne\ \ ND_3}\right] = Electricity\ \ cost\ \ \left[\frac{\$}{tonne\ \ ND_3}\right] \times 0.1$$
$$= \mathbf{779.57}\ \ \frac{\$}{tonne\ \ ND_3} \times 0.1 = \mathbf{77.957}\ \ \frac{\$}{tonne\ \ ND_3}$$

9. The plant-gate levelized cost

We sum the above cost of producing 1 tonne of ND_3 to display the plant-gate levelized cost as below:

$$Plant-gate\ \ levelized\ \ cost\ \ \left[\frac{\$}{tonne\ \ ND_3}\right]$$
$$= (68.13 + 8.80 + 779.57 + 10.5 + 87.43 + 43.71 + 6012009.68 + 77.957)\ \ \frac{\$}{tonne\ \ ND_3}$$
$$= \mathbf{6013085.78}\ \ \frac{\$}{tonne\ \ ND_3}$$

The plant-gate levelized cost of per kilogram (kg) ND_3 in our electrocatalytic deuteration ND_3 synthesis is about **$6013**.

10. Potential profit

We have looked up the retail price of ND_3 in the Sigma-Aldrich, China, and is $778.28 per 25 L, and thus we assume the wholesale price of ND_3 is about $600 per 25 L. In this situation, we can obtain the reference price of per kg of ND_3 is:

$$Reference\ \ price\ \ of\ \ ND_3\ \ \left[\frac{\$}{kg\ \ ND_3}\right] = \frac{\$600}{\frac{V}{V_m}\ \ [mol] \times M_{ND_3}\ \ \left[\frac{kg}{kmol}\right]} = \frac{\$600}{\frac{25}{22.4} \times 0.001\ \ kmol \times 20\ \ \frac{kg}{kmol}}$$
$$= \mathbf{26880}\ \ \frac{\$}{kg\ \ ND_3}$$

Supplementary figures

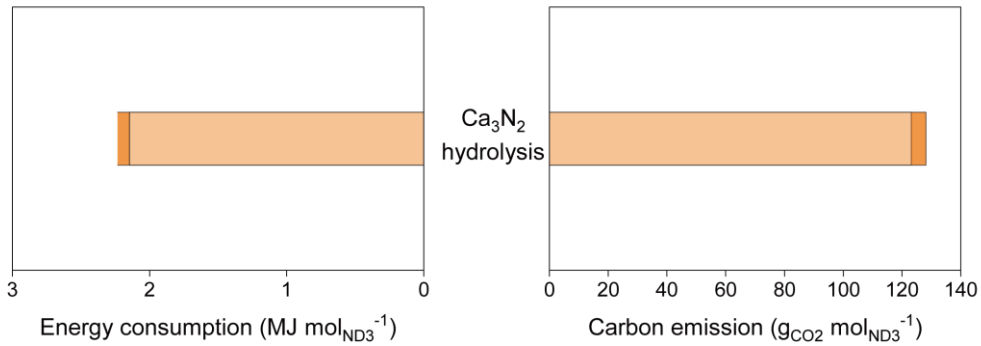

Figure S1. Assessment of energy consumption and carbon emissions associated with ND_3 production from the Ca_3N_2 hydrolyzation.

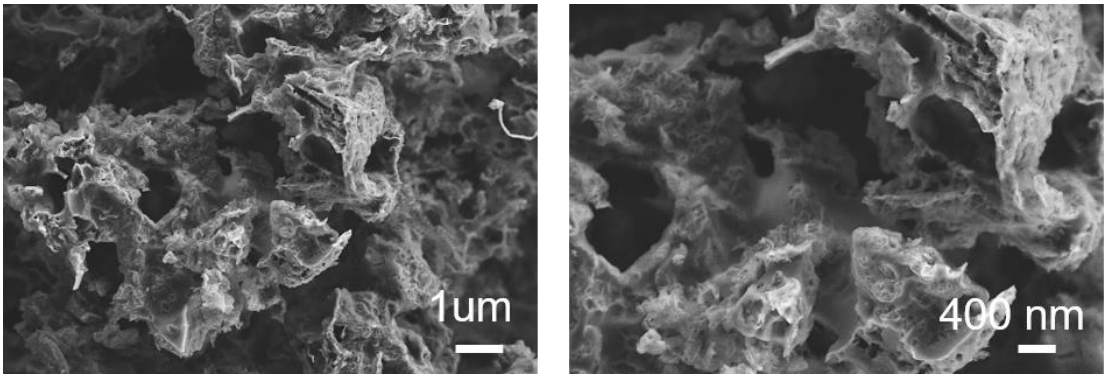

Figure S2. SEM images of the tested *Fe-N-C* catalyst.

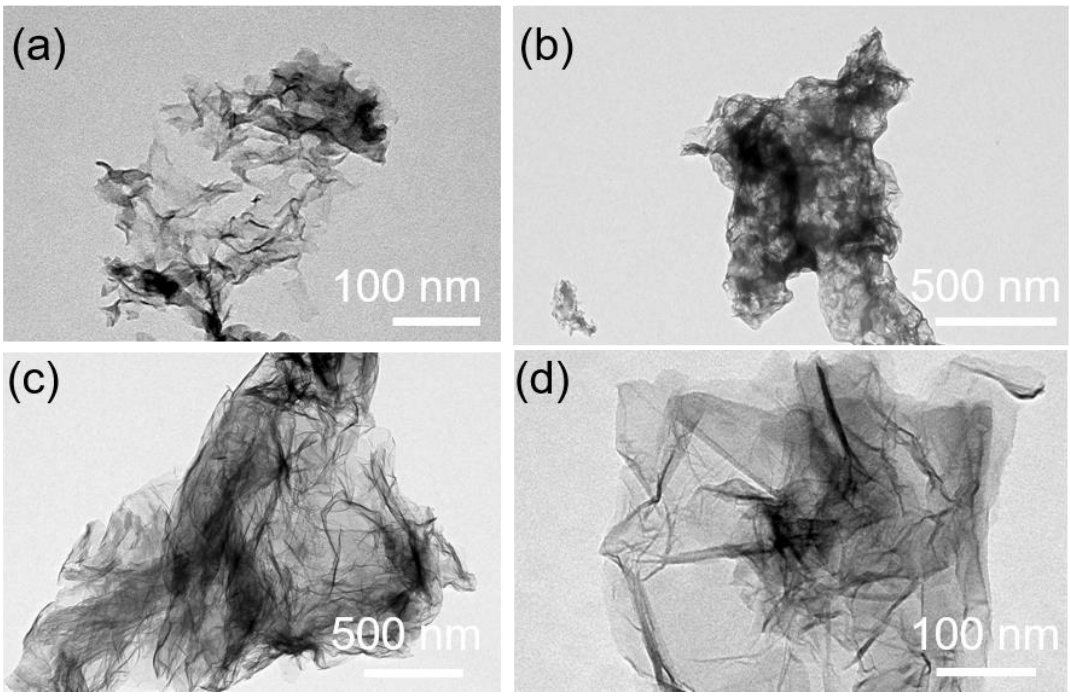

Figure S3. TEM images of the tested catalyst. (a) *Fe-N-C*. (b) *Co-N-C*. (c) *Fe-C* and (d) *Co-C*.

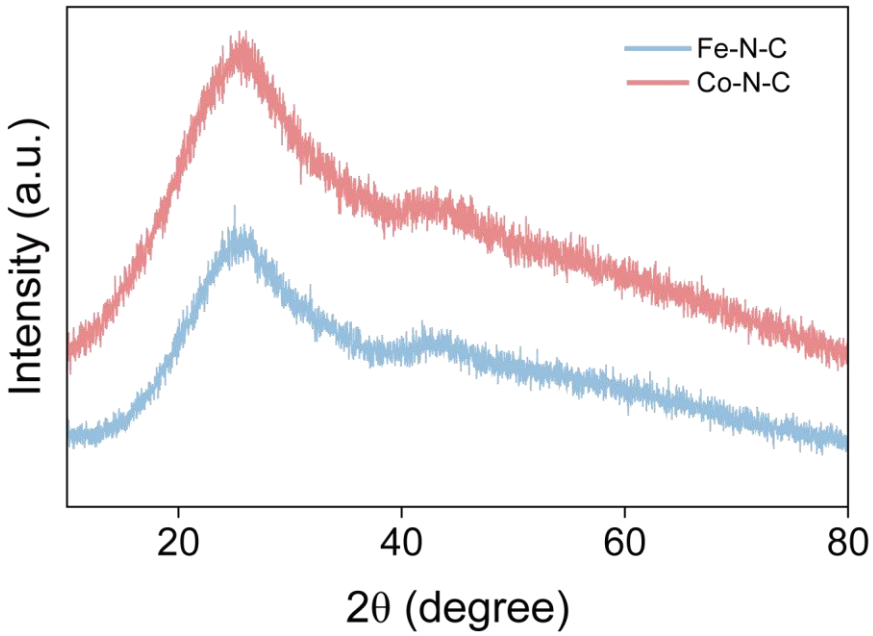

Figure S4. XRD patterns of the tested *Fe-N-C* and the compared *Co-N-C* catalysts.

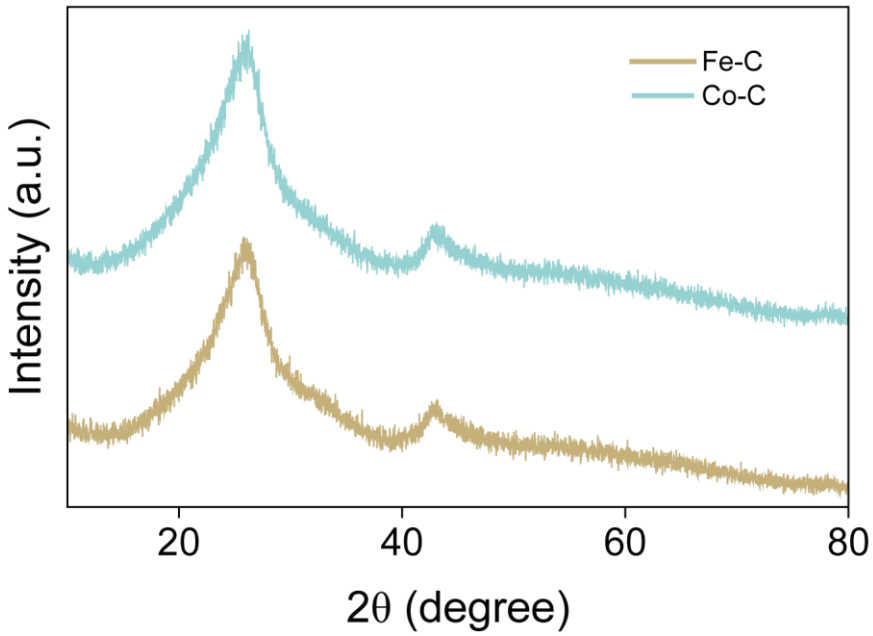

Figure S5. XRD patterns of the tested *Fe-C* and the compared *Co-C* catalysts.

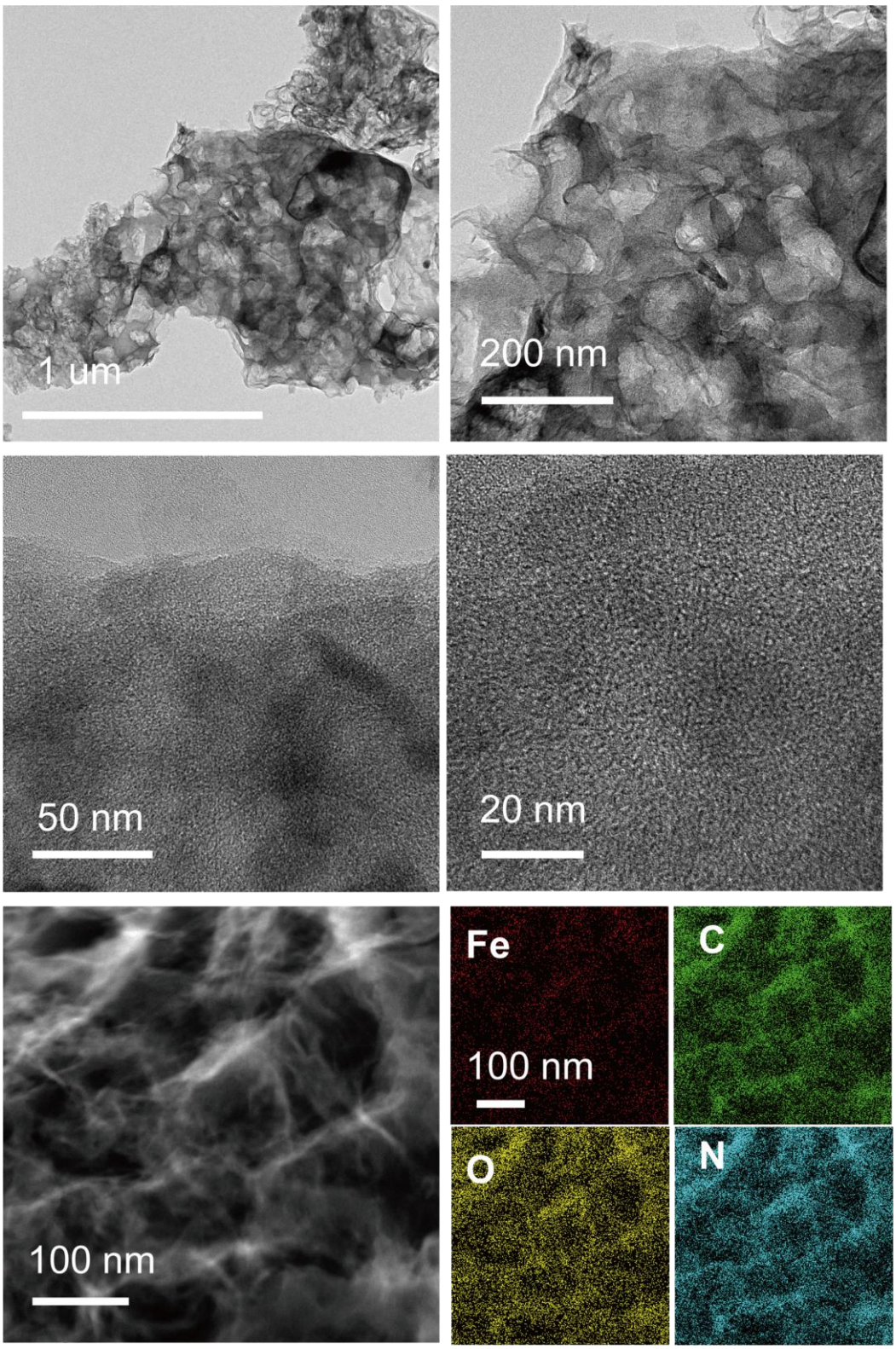

Figure S6. HRTEM images with different magnification factor and the typical EDS mapping pictures of the tested catalyst: *Fe-N-C*.

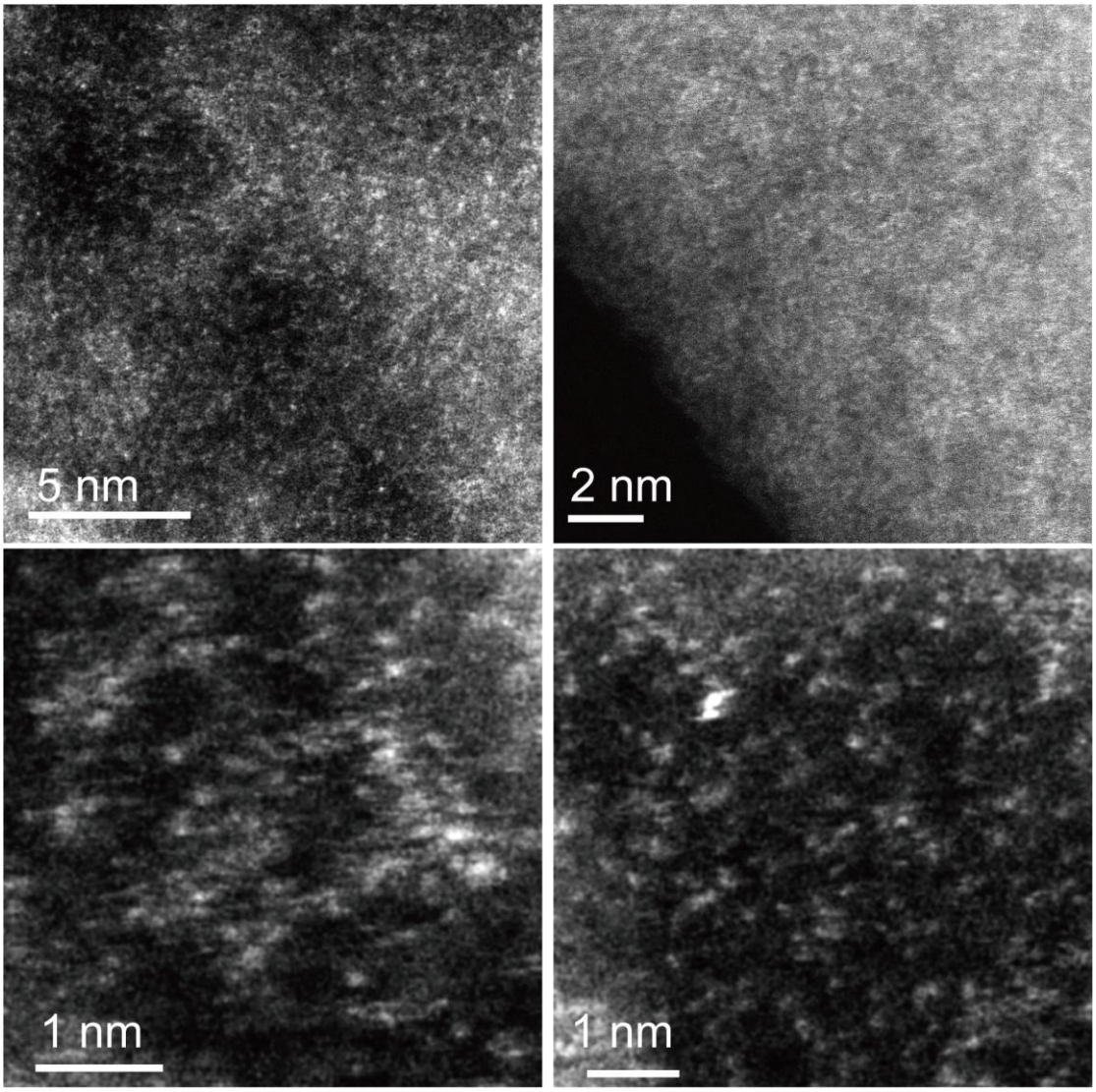

Figure S7. AC-HADDF-STEM images with different areas of the *Fe-N-C*.

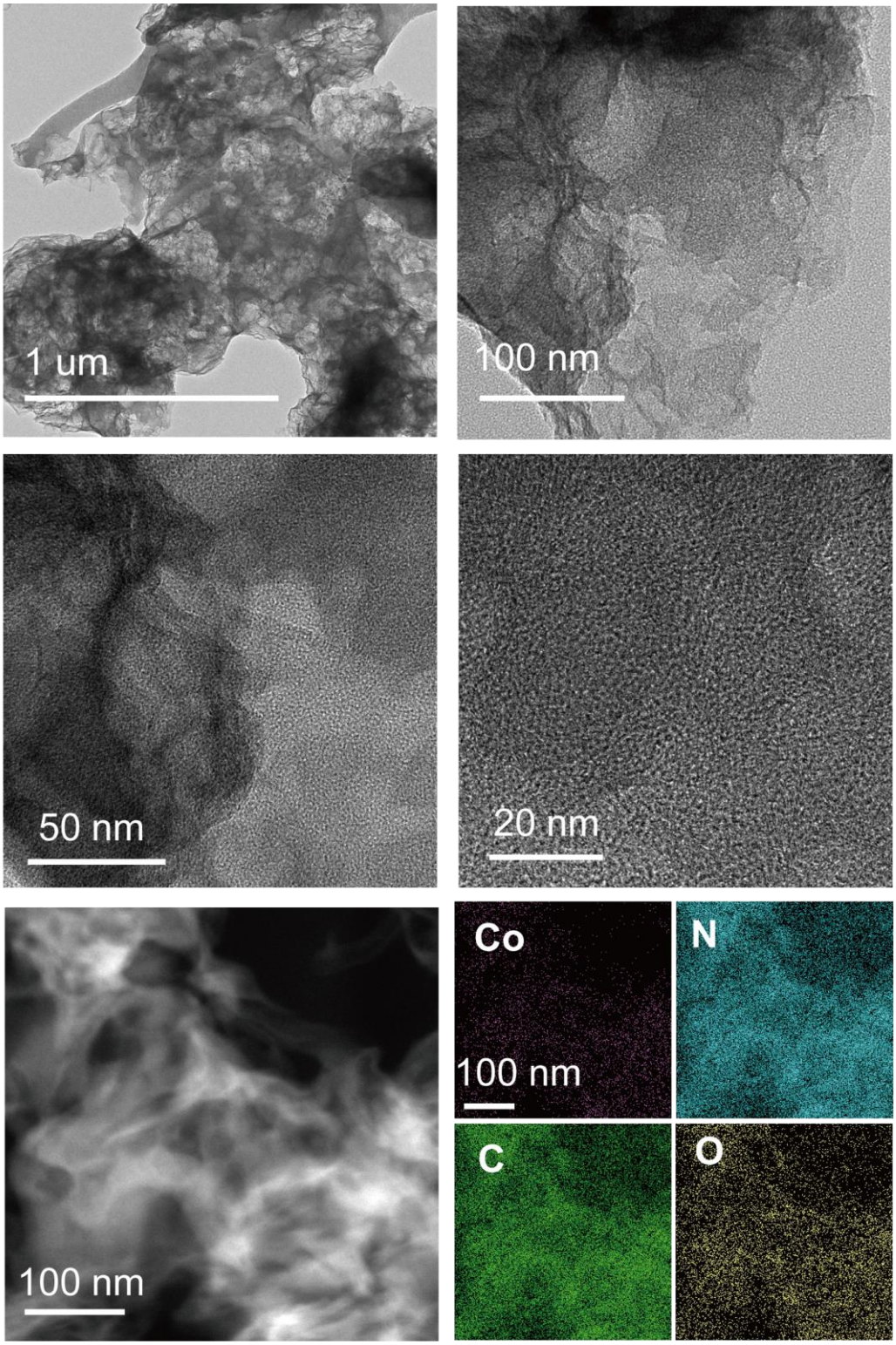

Figure S8. HRTEM images with different magnification factor and the typical EDS mapping pictures of the tested catalyst: *Co-N-C*.

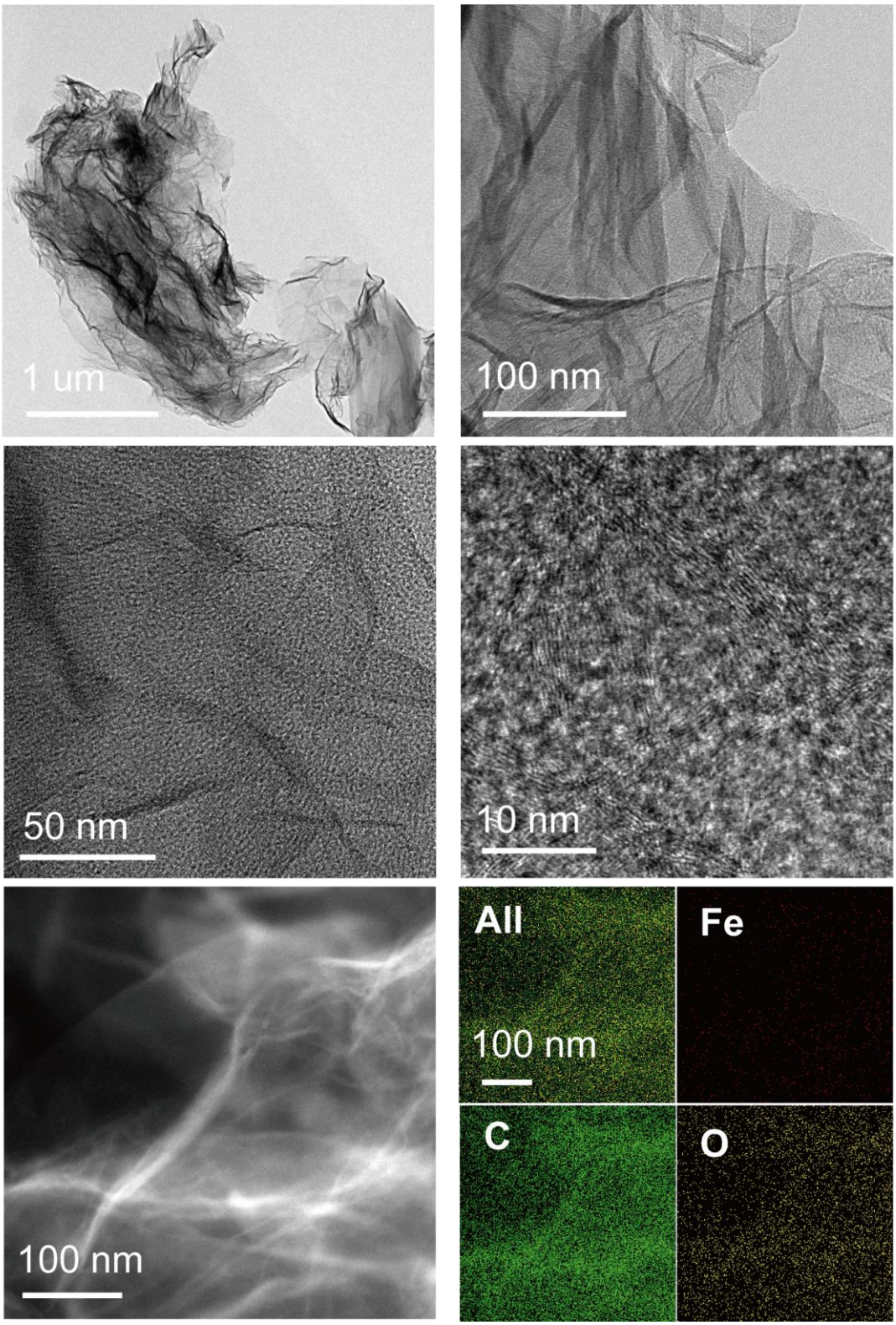

Figure S9. HRTEM images with different magnification factor and the typical EDS mapping pictures of the tested catalyst: *Fe-C*.

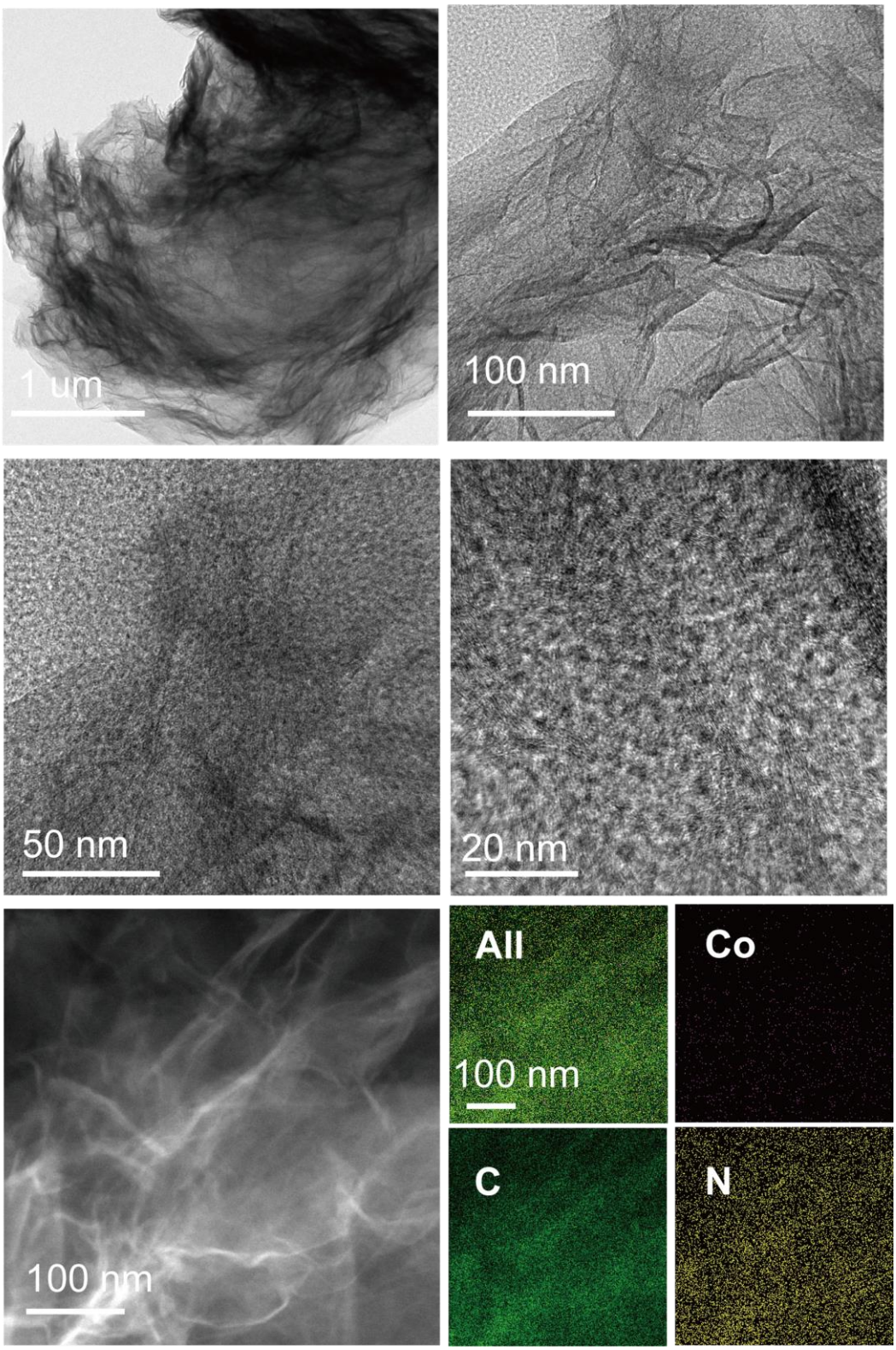

Figure S10. HRTEM images with different magnification factor and the typical EDS mapping pictures of the tested catalyst: *Co-C*.

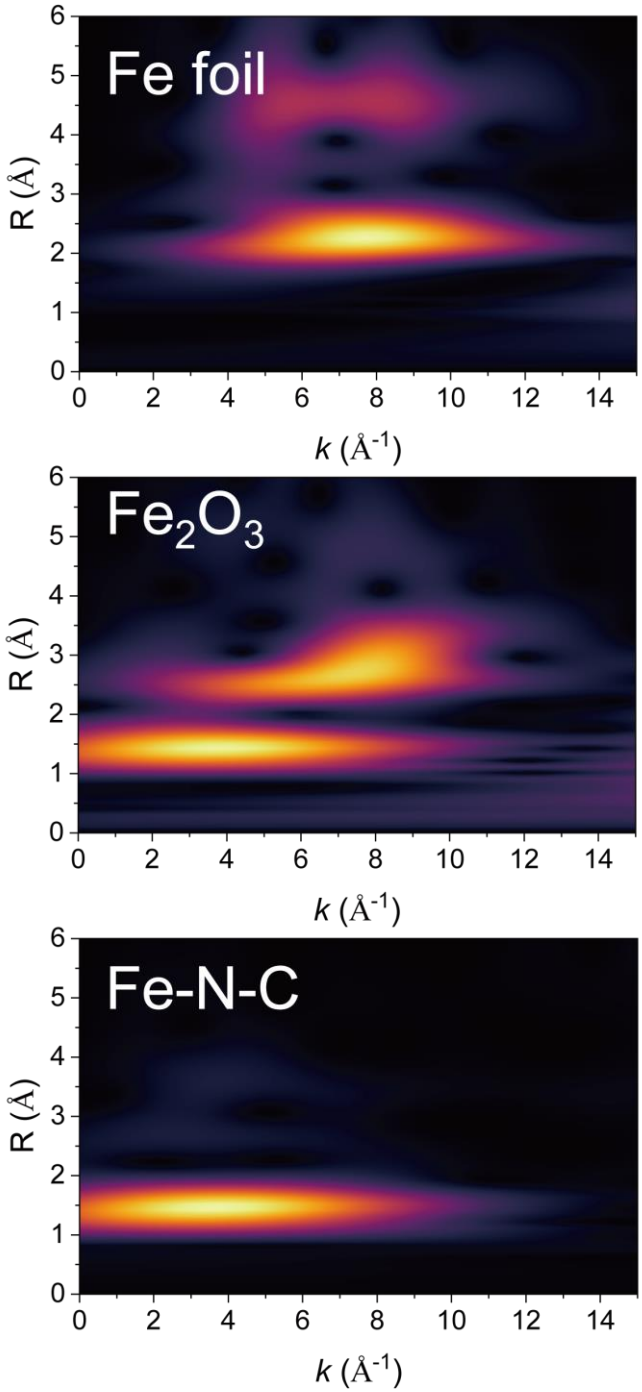

Figure S11. The Wavelet transform of the Fe K-edge. Fitting results of the EXAFS spectra of *Fe-N-C* at k-space. This result conformably demonstrated the atomically dispersed Fe in the structure.

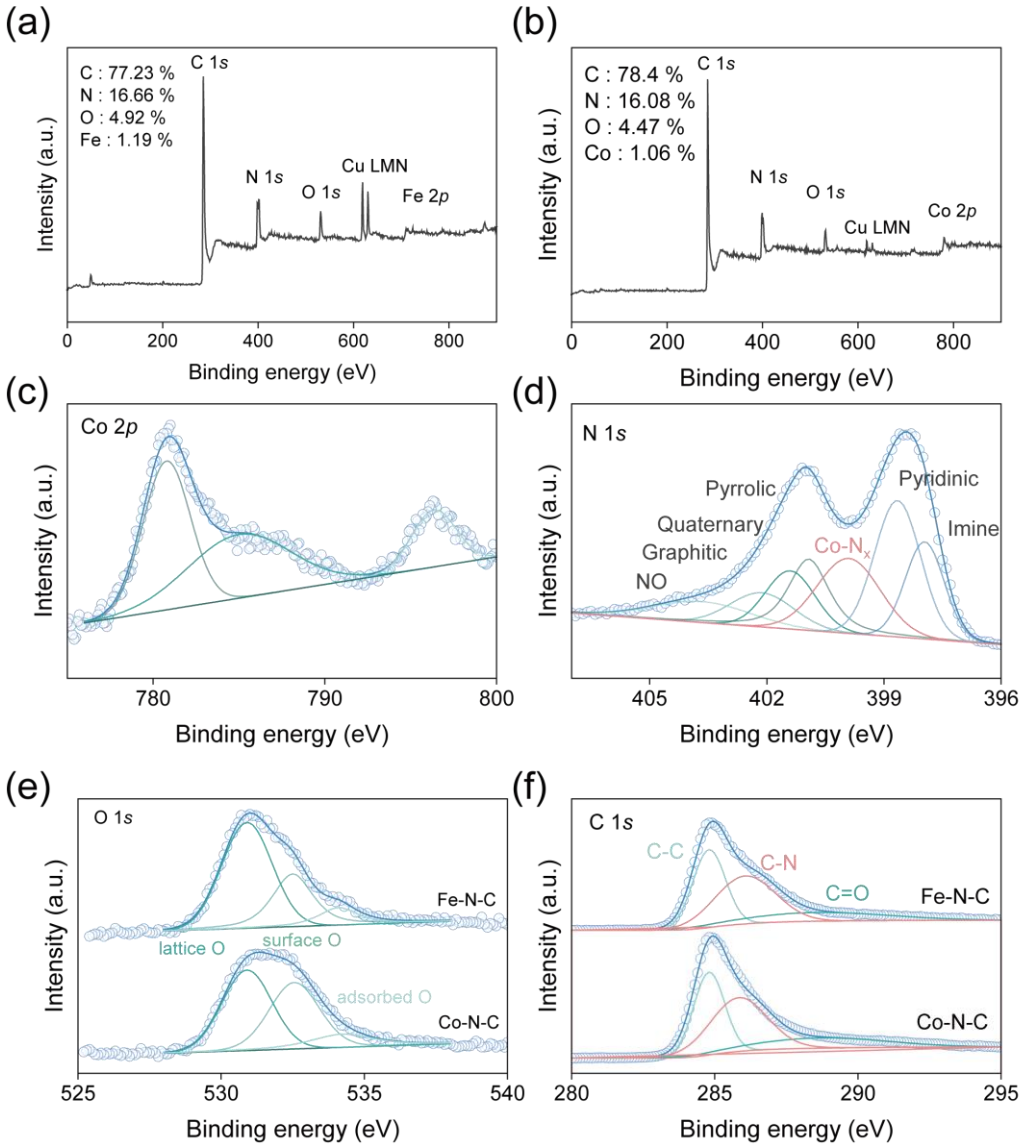

Figure S12. XPS survey spectra of (a) *Fe-N-C* and (b) *Co-N-C*. The insets data has demonstrated the approximate content of the elements. (c) Co 2p XPS spectra for the *Co-N-C*. (d) N 1s XPS spectra for the *Co-N-C*, confirming the presence of Co-N_x moieties. (e) and (f) are the O 1s and C 1s XPS spectra of the comparative catalyst *Fe/Co-N-C*. In particular, the C–N peaks in f indicate nitrogen doping on graphitic carbon.

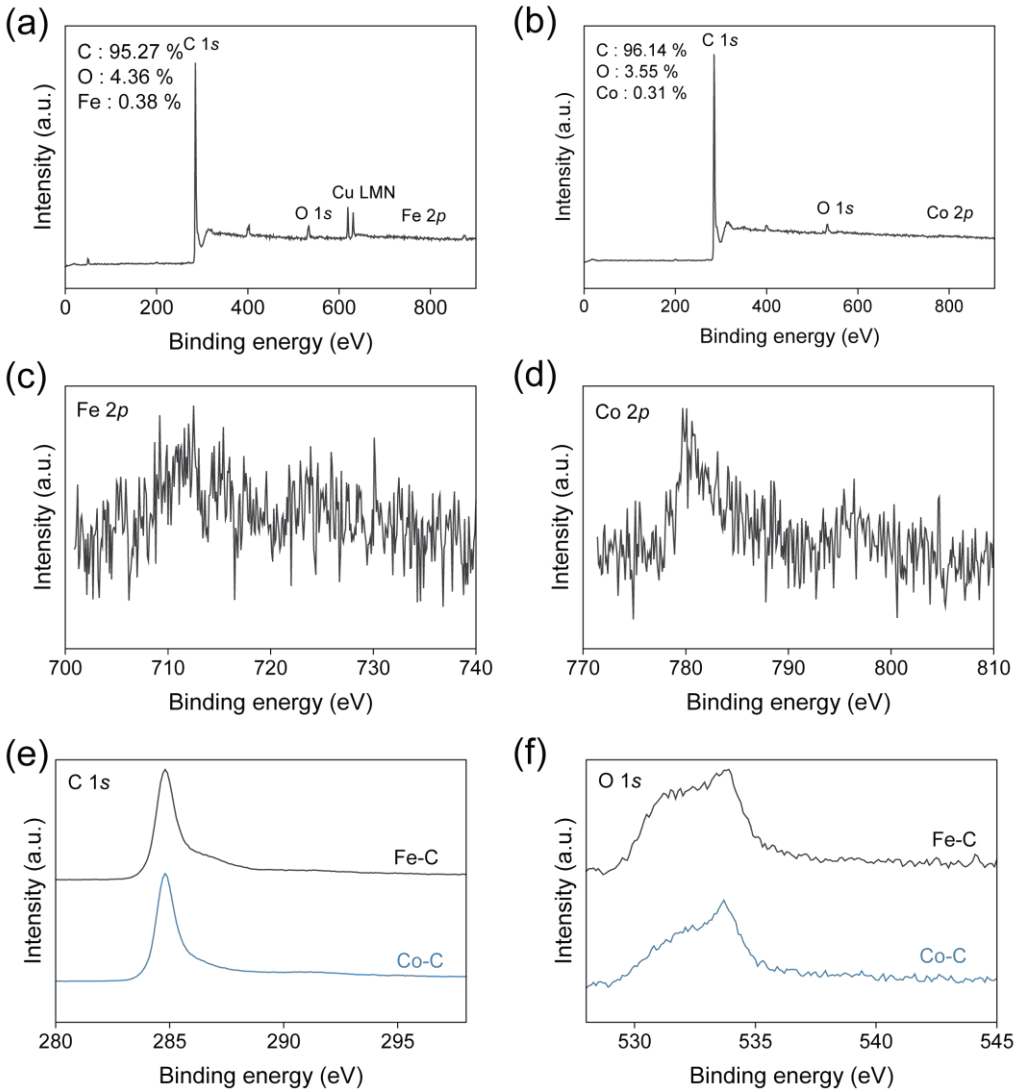

Figure S13. XPS survey spectra of (a) *Fe-C* and (b) *Co-C*. The insets data has demonstrated the approximate content of the elements. (c) and (d) display the Fe 2p and Co 2p XPS spectra of the *Fe-C* and *Co-C*. (e) and (f) are the C 1s and O 1s XPS spectra of the comparative catalysts *Fe-C* and *Co-C*.

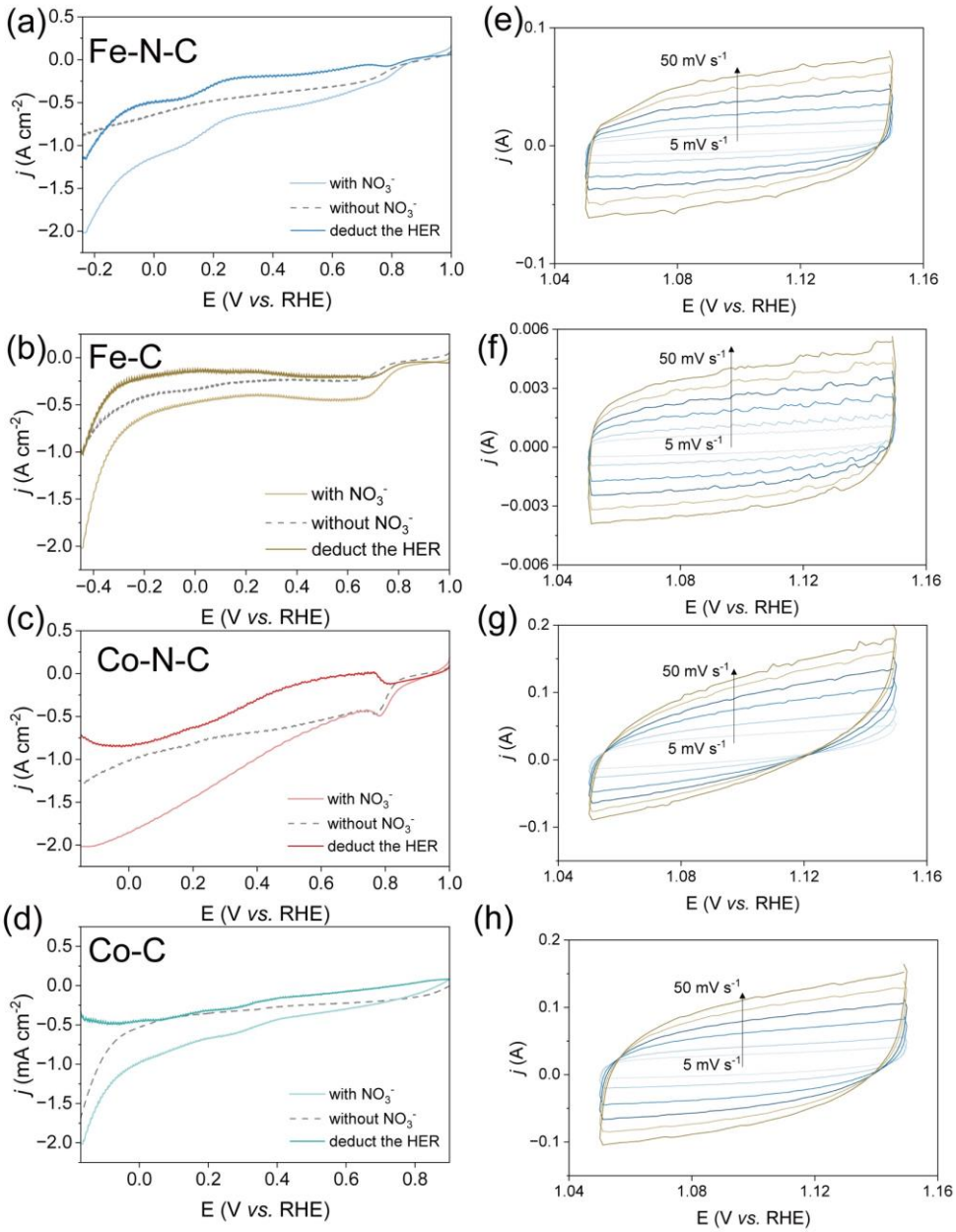

Figure S14. Basic electrochemical test. LSV curves of (a) *Fe-N-C*, (b) *Fe-C*, (c) *Co-N-C* and (d) *Co-C*. Cyclic voltammograms (CV) scan rate-current relationship and the corresponding Electrochemical active surface area (ECSA) analysis of (e) *Fe-N-C*, (f). *Fe-C*, (g) *Co-N-C* and (h) *Co-C*. All the tests are performed with 0.1 M KNO_3 in 1 M KOH aqueous solution.

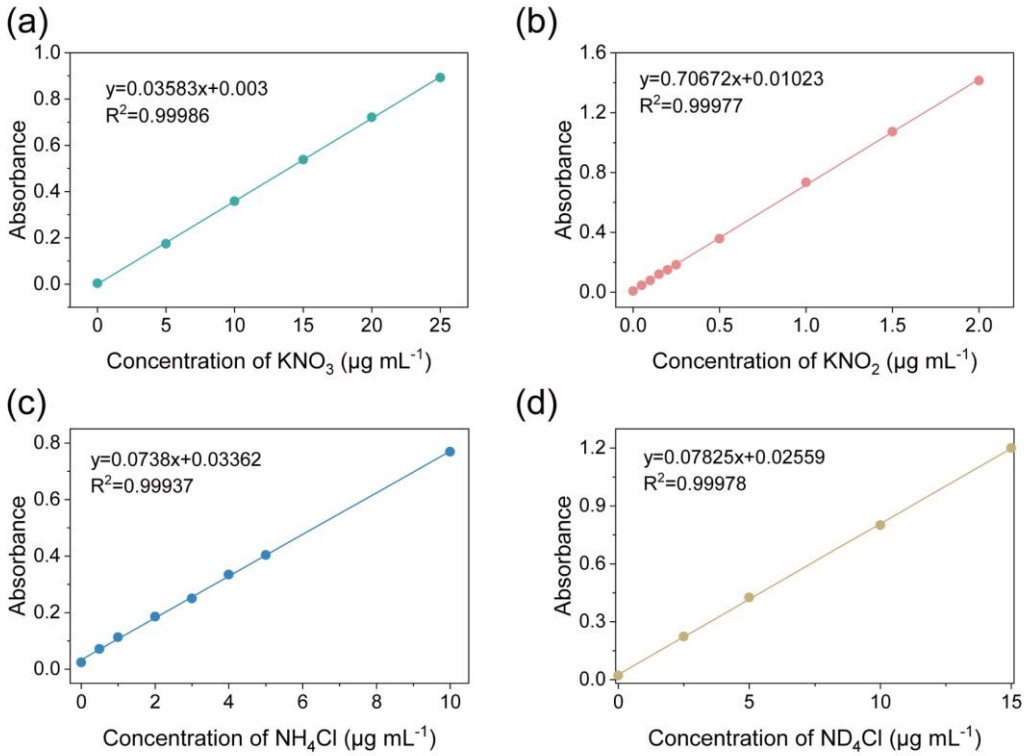

Figure S15. The linear standard curve resulted from the concentration-absorbance UV-vis calibration. The linear standard curve for the calculation of NO_3^- (a) and NO_2^- (b) with different concentration of KNO_3 and KNO_2 solutions as standards using different chromogenic reaction method reported before[8]. The linear standard curve for the calculation of NH_3 (c) and ND_3 (d) production with different concentration of NH_4Cl and ND_4Cl solutions as standards using Nessler Reagent method.

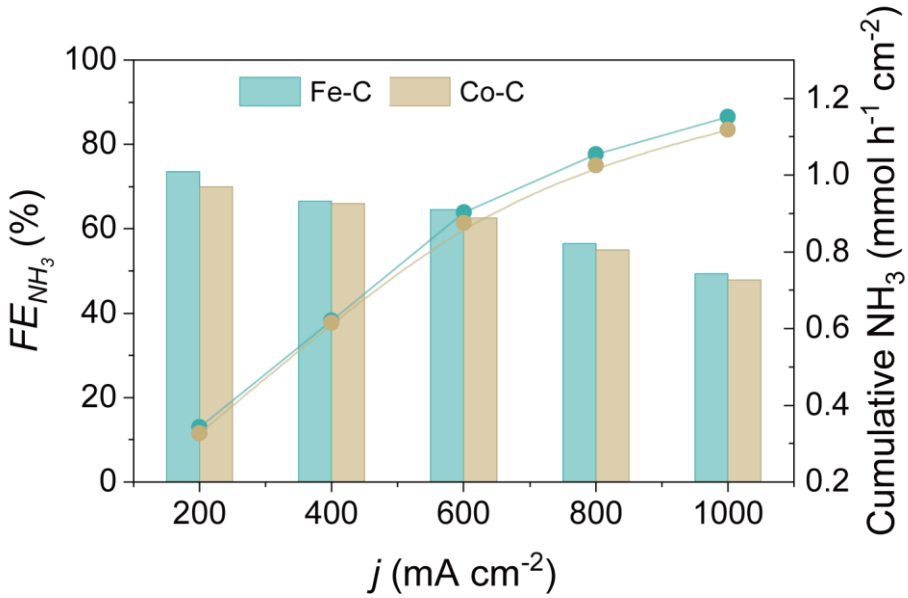

Figure S16. The Faradaic efficiencies of FE_{NH3} and NH_3 production over *Fe-C* and *Co-C* at 200-1000 mA cm^{-2} with 0.1 M KNO_3 and 1 M KOH in 50 mL H_2O.

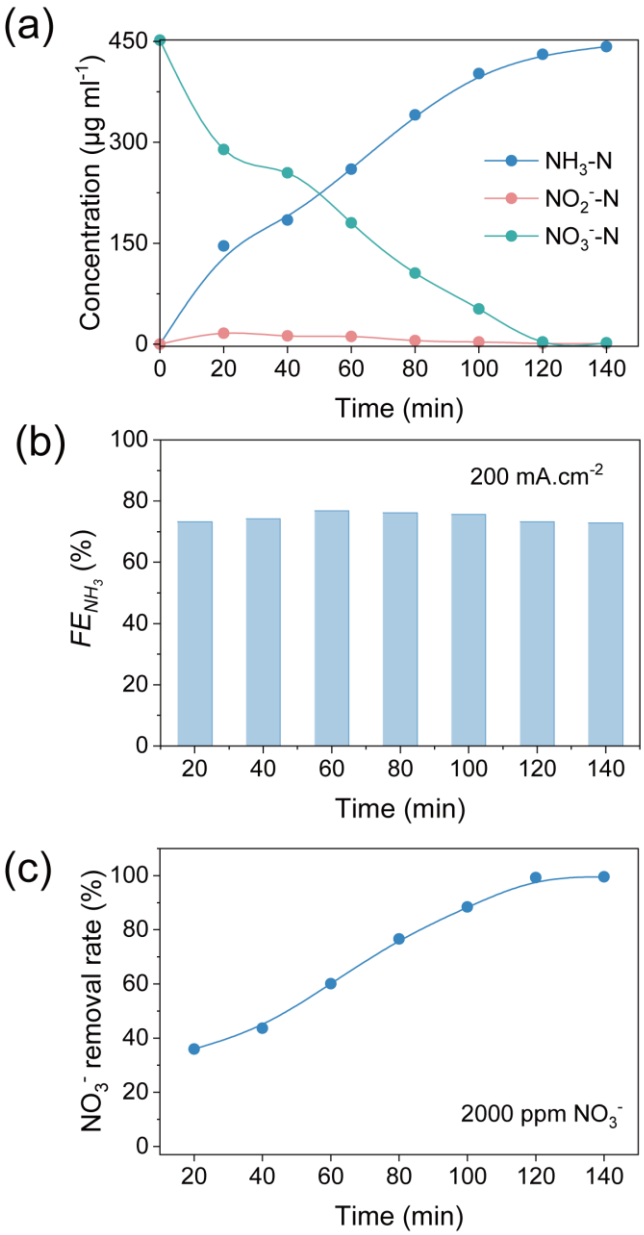

Figure S17. (a) Complete nitrate removal using *Fe-N-C* with an initial 1 M KOH with 2,000 ppm NO_3^- (equals 451.6 μg ml^{-1} NO_3^- -N) electrolyte at 200 mA cm^{-2}. b. The FE_{NH3} over the Fe-N-C at 200 mA cm^{-2} during 0-140 min. c. The rate of the NO_3^- concentration change during 0-140 min. After 2 h of electrolysis, the removal rate of NO_3^- reached 99.2%.

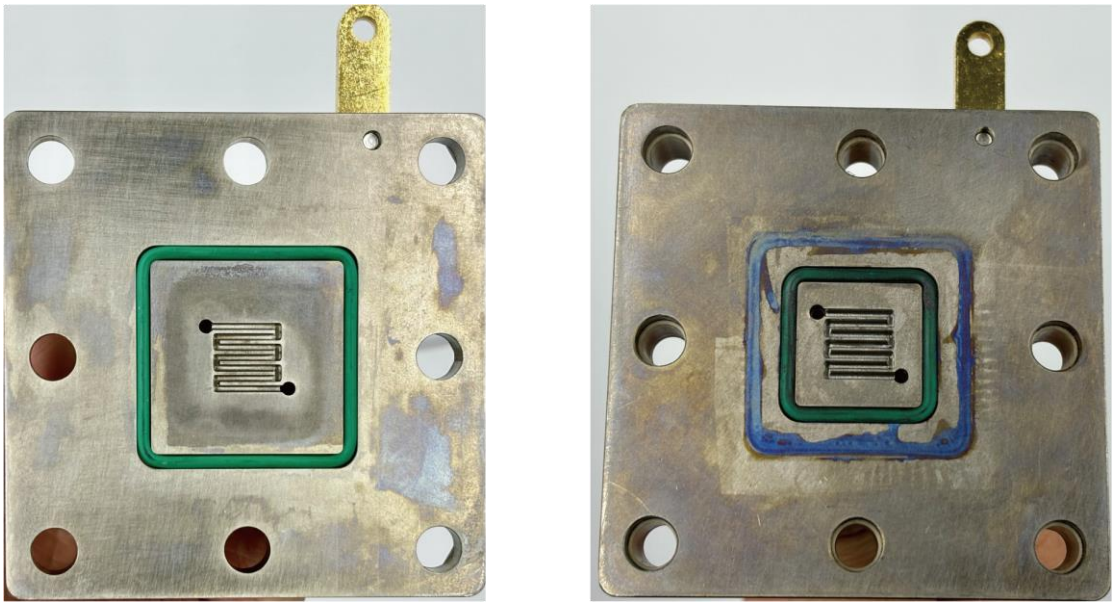

Figure S18. The physical photograph of the disassembled cathode and anode compartments, respectively from the left to right.

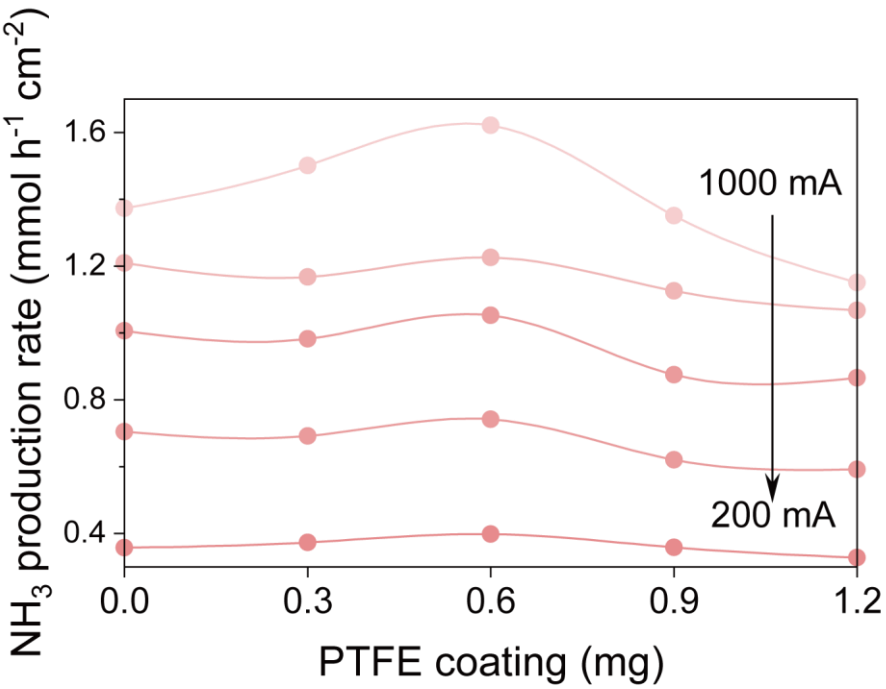

Figure S19. The variation of NH_3 yield rate of *Fe-N-C* with the different PTFE loading (mg).

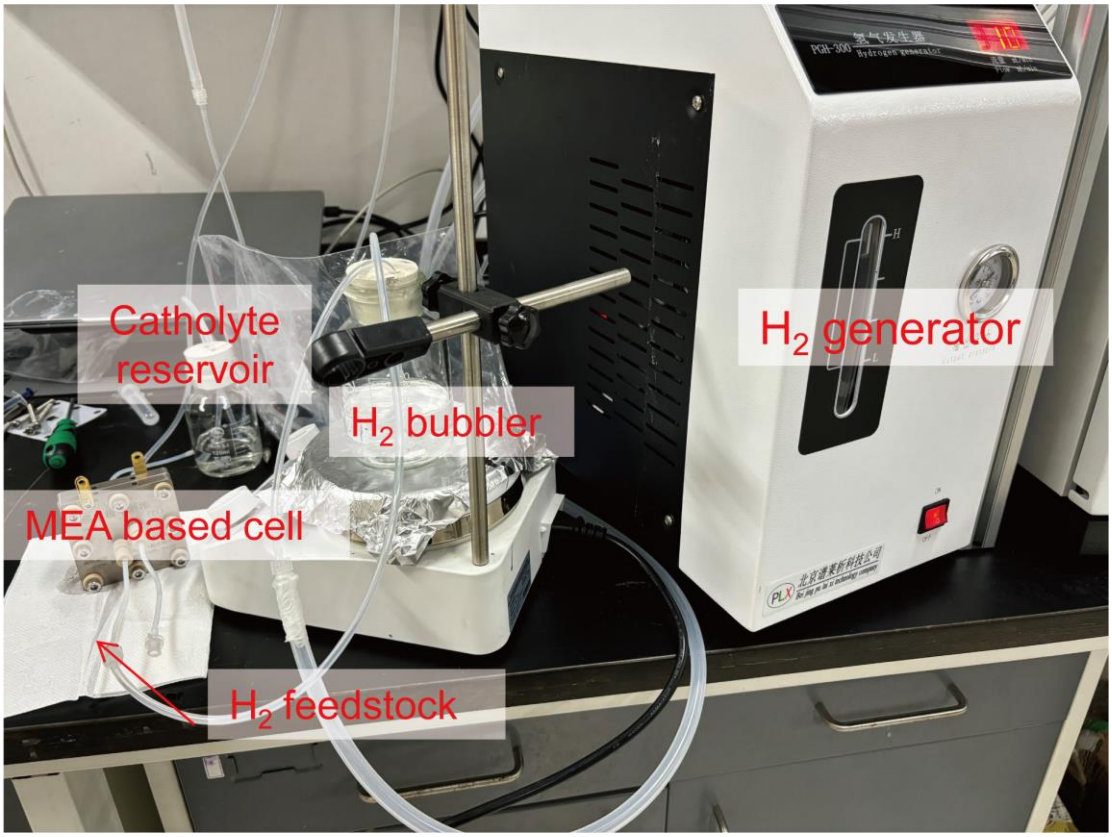

Figure S20. Photo of the experimental setup for experiments via replacing the anodic OER with the HOR for decreasing the overall voltage.

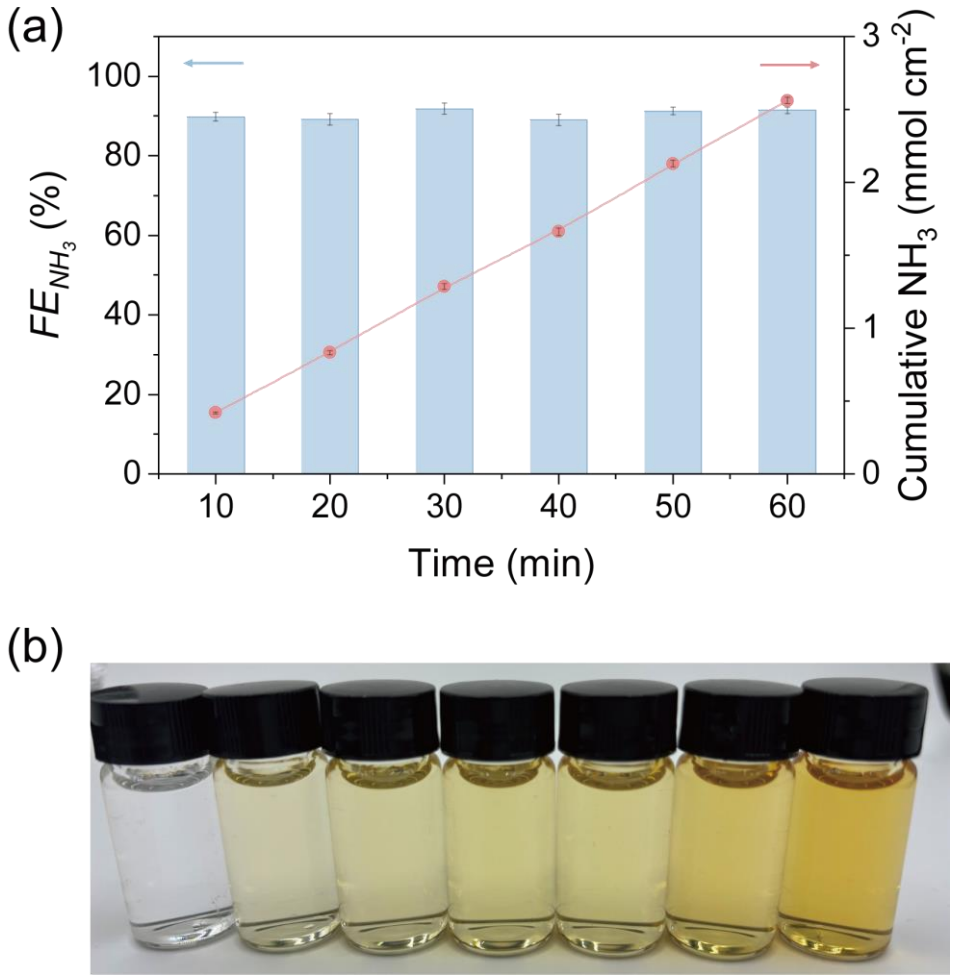

Figure S21. (a) The FE_{NH3} and NH_3 yield over the primary *Fe-N-C* at 600 mA cm^{-2} during 0-60 min with 1 M KNO_3 and 1 M KOH in 50 mL H_2O during 0-60 min, in which the electrolyte obtained was diluted by a factor of 400. (b) The physical photograph is the NH_3 product with the chromogenic reaction using Nessler Reagent.

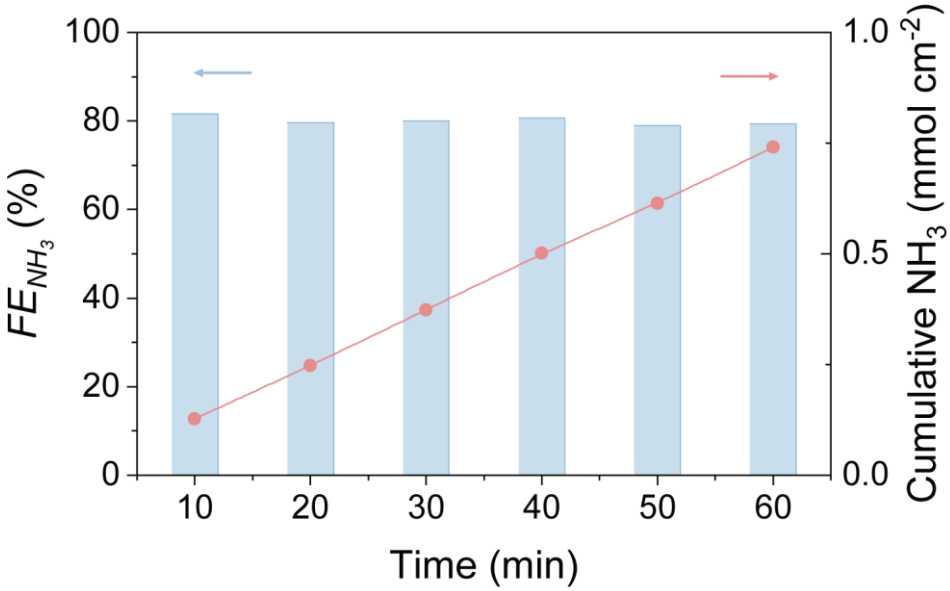

Figure S22. The FE_{NH3} and NH_3 yield over the primary *Fe-N-C* at 200 mA cm^{-2} during 0-60 min in the 0.5 M K_2SO_4 electrolyte.

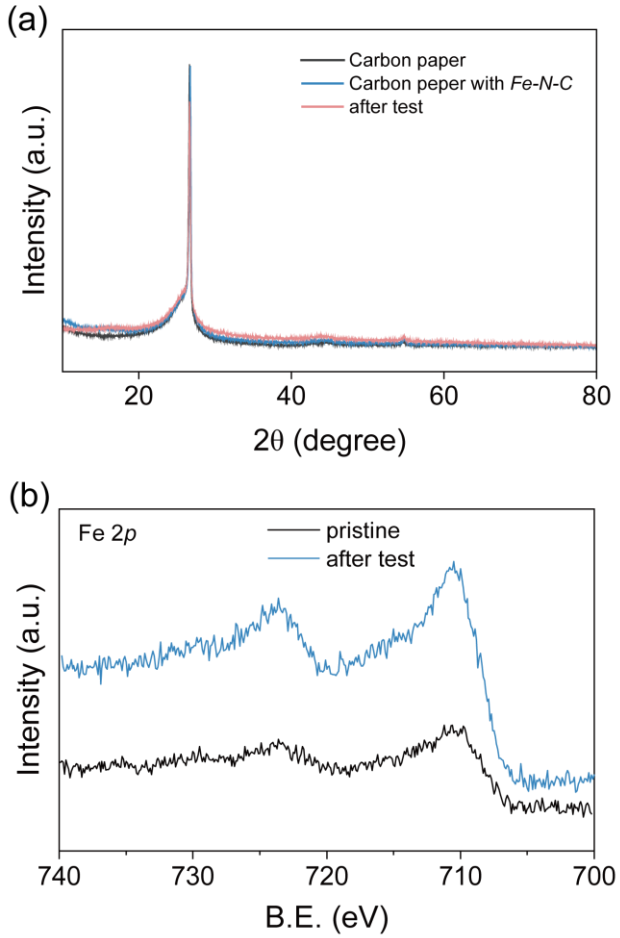

Figure S23. Comparison of the (a) XRD pattern and (b) XPS spectrum of the *Fe-N-C* before and after the long-term stability test.

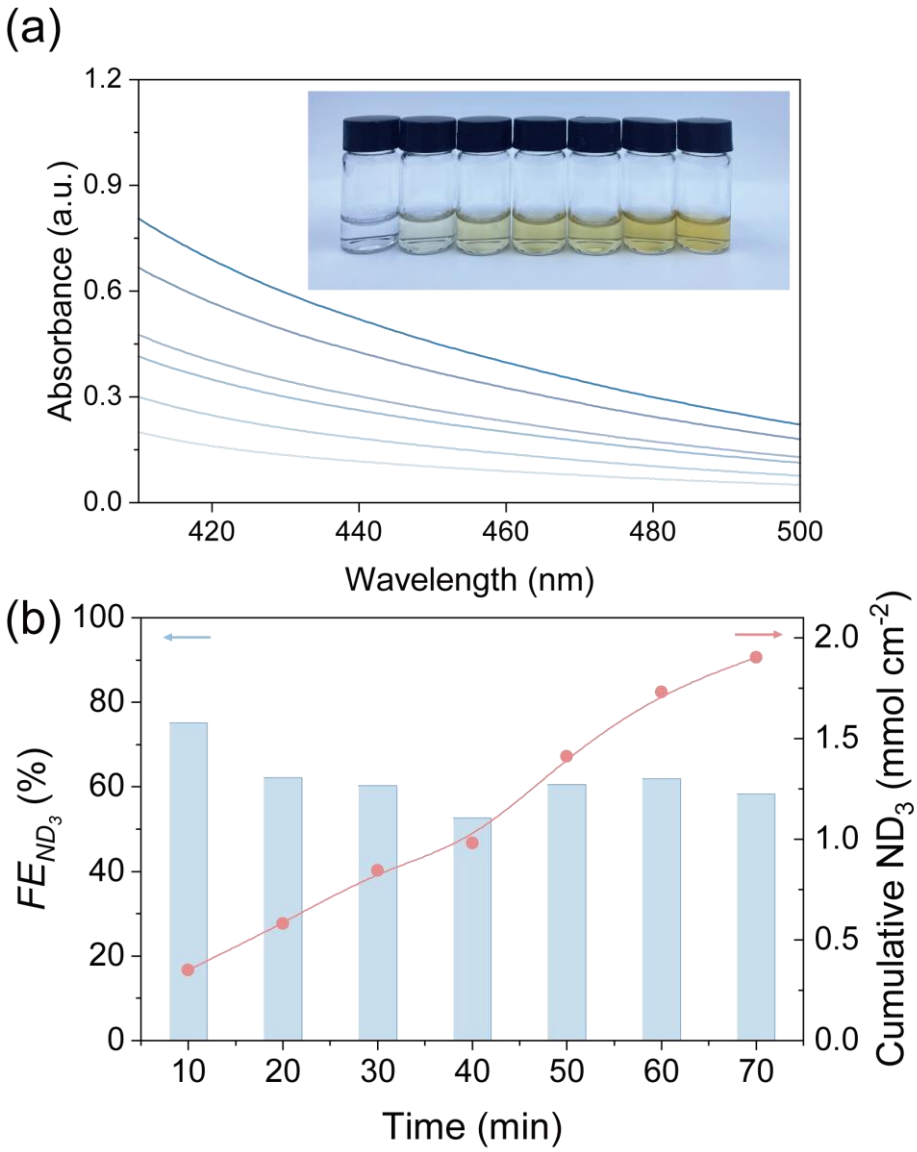

Figure S24. (a) The concentration–absorbance UV–vis resulted curves of ND_3 product via using Nessler Reagent method. Inset physical photograph is the ND_3 product with the chromogenic reaction using Nessler Reagent at 600 mA cm^{-2} with 1 M KNO_3 and 0.3 M K_2SO_4 in 50 mL D_2O during 0-60 min, in which the electrolyte obtained was diluted by a factor of 300. (b) The FE_{ND3} and ND_3 yield over the primary Fe-N-C at 600 mA cm^{-2} during 0-70 min.

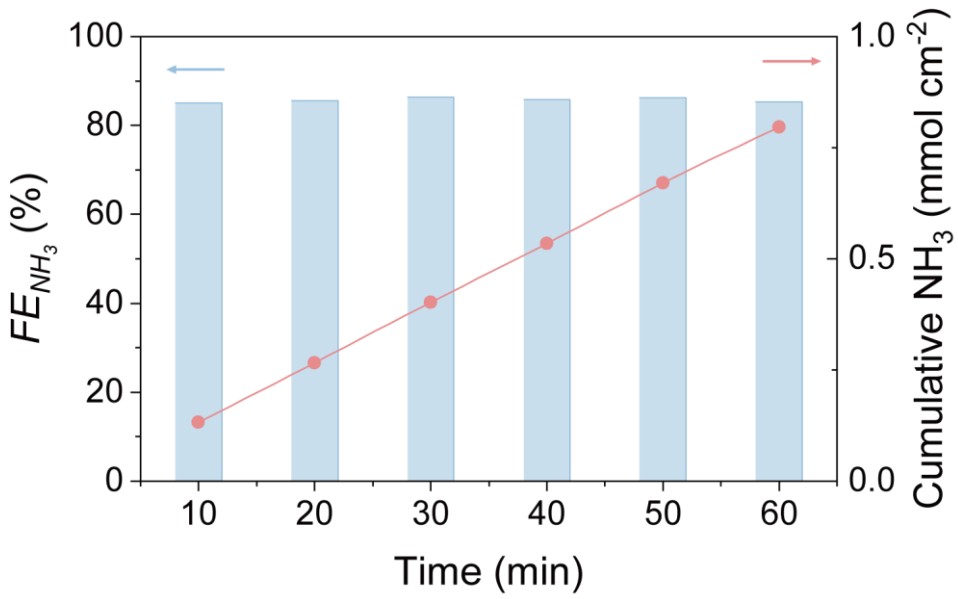

Figure S25. The FE_{NH3} and NH_3 yield over the primary *Fe-N-C* at 200 mA cm^{-2} during 0-60 min in the 0.3 M K_2SO_4 electrolyte.

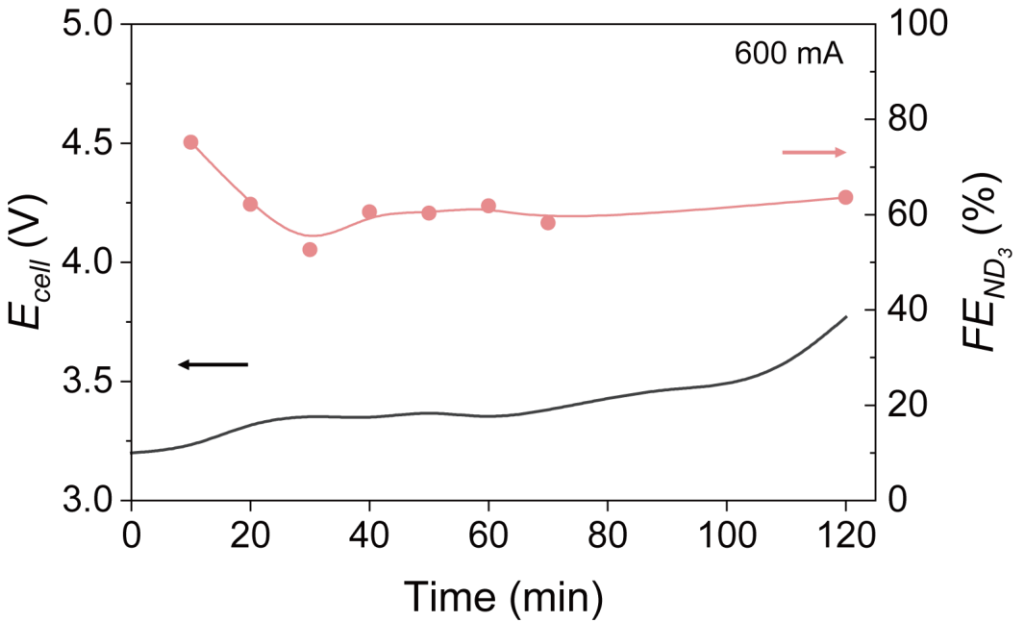

Figure S26. (a) The durability test of electrocatalysis deuteration ND_3 synthesis with *Fe-N-C* at 600 mA cm^{-2} and this test was absence of refresh the catholyte.

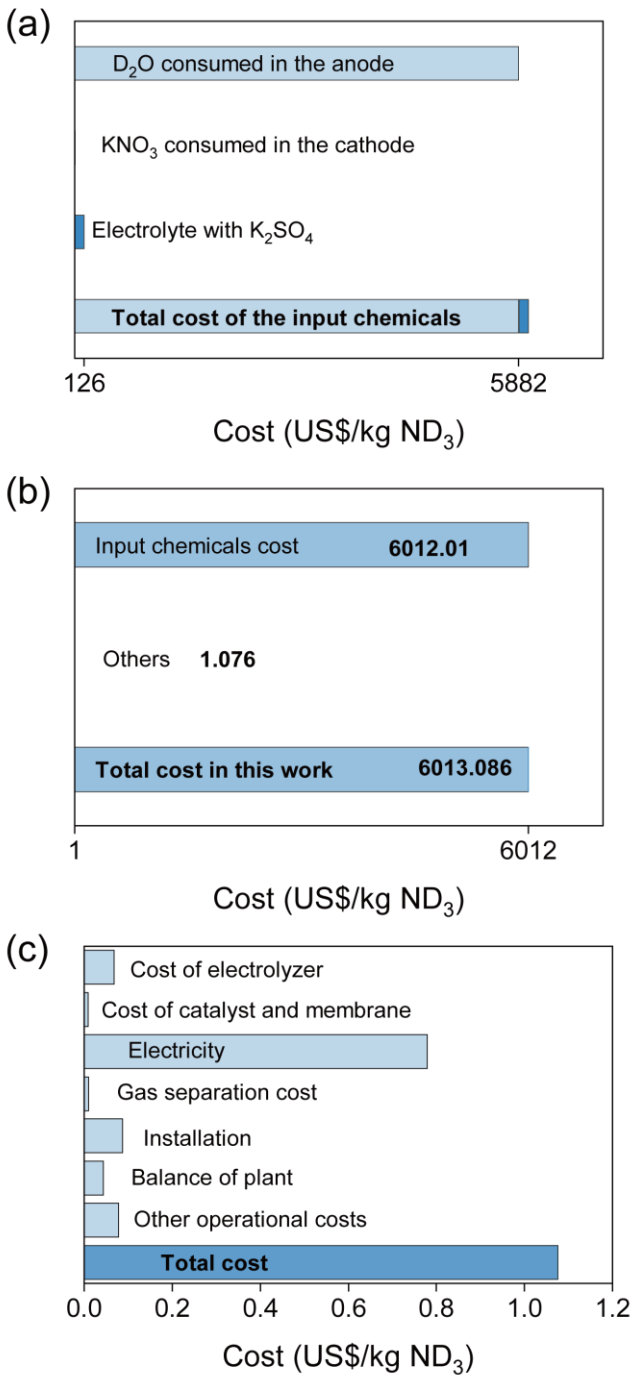

Figure S27. The TEA findings from the Figure 7: Breakdown of the plant-gate levelized cost per kg of ND_3 of the (a) total cost of the input chemicals, (b) input chemicals and others, (c) the total cost without the input chemicals.

Supplementary Table

Table S1. Structural parameters of *Fe-N-C* extracted from the EXAFS fitting.

Sample	Scattering pair	CN	R(Å)	$\sigma^2(10^{-3}Å^2)$	ΔE_0(eV)
DFT	Fe-N	4	1.91	-	-
Fe-N-C	Fe-N	4.8	1.98	8.84	5.3

CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); ΔE_0 is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model).

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