Supporting Information

A Biomimetic MoFe-N-C for efficient N$_2$ electroreduction to NH$_3$

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Experimental section

Materials. Formamide (FA) was purchased from Xilong Chemical Co., Ltd. Zinc chloride ($ZnCl_2$), molybdenum pentachloride ($MoCl_5$), ferrous chloride ($FeCl_2$), and benzaldehyde ($C_9H_{11}NO$) were purchased from Aladdin Reagent Co., Ltd (Shanghai). Hydrochloric acid (HCl), potassium hydroxide (KOH), lithium sulphate (Li_2SO_4), sodium hypochlorite (NaClO), trisodium citrate dehydrate ($C_6H_5Na_3O_7$), sodium nitroprusside ($Na_2Fe(CN)_5NO\cdot2H_2O$), salicylic acid ($C_7H_6O_3$), sodium thiosulfate ($Na_2S_2O_3$), and potassium dichromate ($K_2Cr_2O_7$) were bought from Beijing Chemical Plant. Hydrazine hydrate ($N_2H_4\cdot H_2O$) was purchased from Sigma-Aldrich Chemical. Absolute ethanol was purchased from Tianjin Kemeiou Chemical Reagent Co., Ltd. Nafion DuPont was purchased from DuPont China. Conductive carbon black was purchased from Xianfeng Nano Material Technology Co., Ltd. All chemical reagents can be used without further purification. Deionized water was used for the entire experiment.

Preparation of Fe-NC, Mo-NC, and MoFe-NC. Typically, $ZnCl_2$ (0.874 g), $FeCl_2$ (0.219 g), and $MoCl_5$ (0.102 g), were dissolved in FA (80 mL) after continuously stirring for 30 min. The solution was then transferred into a 100 mL Teflon-lined autoclave. The autoclave was sealed and kept at 180 °C for 12 hours, and then cooled naturally to room temperature. A solid product was obtained via centrifugation. It was then washed alternately with deionized water and ethanol by centrifugation, then collected and dried in oven at 60 °C for 12 h. The solid product, also known as the precursor of f-MoFe-NC, was finally heated from room temperature to 950 °C in argon protection at a ramp of 5 °C min^{-1} and maintained at this temperature for 2 h. The obtained product was washed with 5% HCl and deionized water, and dried in a vacuum oven at 60 °C to obtain MoFe-NC. To investigate the effect of Fe and Mo atoms on NRR, only $FeCl_2$ (0.219 g) or $MoCl_5$ (0.102 g) was added as dopant in the above process, and the resulting samples were correspondingly named as Fe-NC or Mo-NC.

Material characterizations. The morphologies were characterized with scanning

electron microscope (SEM, Nova NanoSEM 230) images, high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2100, accelerating voltage = 20 kV) images, and energy dispersion spectra were collected from the transmission electron microscope (JEOL, JEM-2100, accelerating voltage = 20 kV). X-ray diffraction (XRD) data were obtained from a Shimadzu XRD-6000 (CuKα radiation, λ= 1.5406 Å, 40 kV) in the 2θ range of 5-80˚. Elemental analysis of Mo and Fe in the MoFe-NC sample was conducted by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 720es). Raman spectroscopy were recorded on LabRAM ARAMIS Raman spectrometer (HORIBA Jobin Yvon). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The specific surface area of samples was measured by Brumauer-Emmett-Teller (BET). The pore structure of samples were studies using BJH method at 77 K with the N_2 adsorption-desorption isotherms (Micromeritics ASAP 2460). Spectrophotometric absorbance data were measured on a UV-Vis spectrophotometer. The XAFS spectra of Mo and Fe K-edge were tested in the 1W1B station line fluorescence mode of the Institute of High Energy Physics, Chinese Academy of Sciences, and the standard metal foil standard samples were tested in the transmission mode.

Electrochemical measurements. The NRR activity was measured at room temperature using an electrochemical station (CHI 760E) with a two electrolytic cell, which was separated by a Nafion 211 membrane. All tests were conducted by the three-electrode system containing 0.1 M Li_2SO_4 electrolyte, Pt foil was used as a counter, and saturated Ag/AgCl were acted as the reference electrode., and samples was dropped on carbon paper as a working electrode. The samples were prepared by mixing 5.0 mg of catalyst powder, 950 μL ethanol, and 50 μL 5% Nafion solution under ultrasonic condition for 1 h. Then, 100 μL of ink was carried onto carbon paper with an area of 1×1 cm^2, and followed by drying at 25 °C to obtain a working electrode. The purity of the N_2 and Ar used in the experiments was 99.999%. The potentials in all tests were calibrated using the following equation: E (V vs. RHE) = E (V vs. Ag/AgCl) + 0.197 V + 0.059 V * pH.

In NRR chronoamperometry experiments, 60 mL of electrolyte solution was first saturated with N_2 for at least 30 min and then tested in a N_2-saturated 0.1 M Li_2SO_4 electrolyte while the throughout test was stirred at 500 rpm. The NRR catalytic activity was assessed by cyclic voltammetry (CV) with a scan rate of 50 mV s^{-1}, and linear scanning voltammetry (LSV) curves at the scan rate of 5 mV s^{-1}. Subsequently, a constant potential test was carried out in a N_2 saturated solution of 0.1 M Li_2SO_4 solution for 1 h. Corresponding tests were also carried out in an Ar-saturated 0.1 M Li_2SO_4 solution as a control experiment.

Determination of NH_3. The NH_3 produced was captured as NH_4^+ ions in aqueous solution and measured spectrophotometrically using the indophenol blue method. For measurements performed in 0.1 M Li_2SO_4 electrolyte, calibration curves were prepared as follows. A series of standard solutions of NH_4^+ at different concentrations in 0.1 M Li_2SO_4 were prepared and mixed with 2.0 mL of 1.0 M NaOH solution containing $C_7H_6O_3$ and 5 wt% $C_6H_5Na_3O_7 \cdot 2H_2O$, 1.0 mL of 0.05 M NaClO and finally 0.2 mL of catalyst solution (1 wt% $Na_2[Fe(NO)(CN)_5] \cdot 2H_2O$) was mixed. After incubation for 2 h at room temperature, the absorption at 655 nm was measured by UV-Vis spectrophotometry to provide a standard curve for the determination of NH_3 (**Figure S7**), which showed a good linear relationship between NH_4^+ concentration and absorbance. 2.0 mL of electrolyte after NRR process was dispersed into the above chromogen (2.0 mL of mixture solution consisting of 0.1 M NaOH, $C_7H_6O_3$, and 5 wt% $C_6H_5Na_3O_7 \cdot 2H_2O$, followed by addition of 1 mL of 0.05 M NaClO and 0.2 mL of 1 wt.% $Na_2[Fe(NO)(CN)_5] \cdot 2H_2O$). Then, UV-Vis absorption spectrum was collected after keeping 2 h at room temperature. The UV-vis absorption spectrum was measured at a wavelength of 500-800 nm. The standard curve method was used to estimate the NH_4^+ concentration in the solution.

Determination of N_2H_4. The method of Watt and Chrisp was used to detect the content of N_2H_4. The color developer is a mixture with 5.99 g of p-$C_9H_{11}NO$, 30 mL of concentrated HCl, and 300 mL of C_2H_5OH. 5.0 mL of the reacted electrolyte was taken

and mixed with 5.0 mL of the above display agent. Subsequently, absorbance measurements were taken after 20 minutes at a wavelength of 455 nm. The calibration curve obtained was employed to calculate the concentration of N_2H_4.

Calculations of NH_3 production rate and Faradaic efficiency. The NH_3 yield was calculated by following equation:

$$NH_3\ yield = \frac{c \times V}{t \times m_{cat.}} \tag{1}$$

The faradaic efficiency (FE) could be calculated as follows:

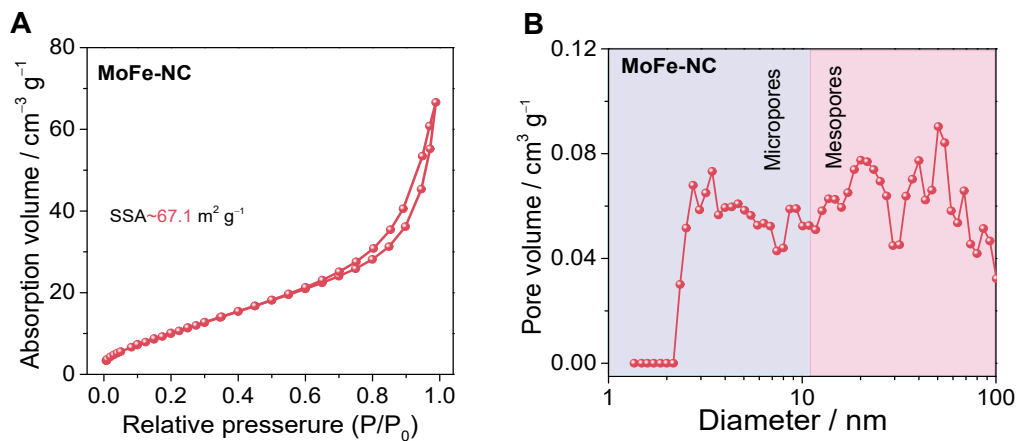$$FE = \frac{3F \times c \times V}{17 \times Q} \times 100\% \tag{2}$$

where c is the measured NH_4^+ concentration, t is the NRR time, V is the total volume electrolyte (mL), $m_{cat.}$is the is the catalyst quality. F is the Faraday constant (96485.3 C mol^{-1}), Q is the total quantity of applied electricity.
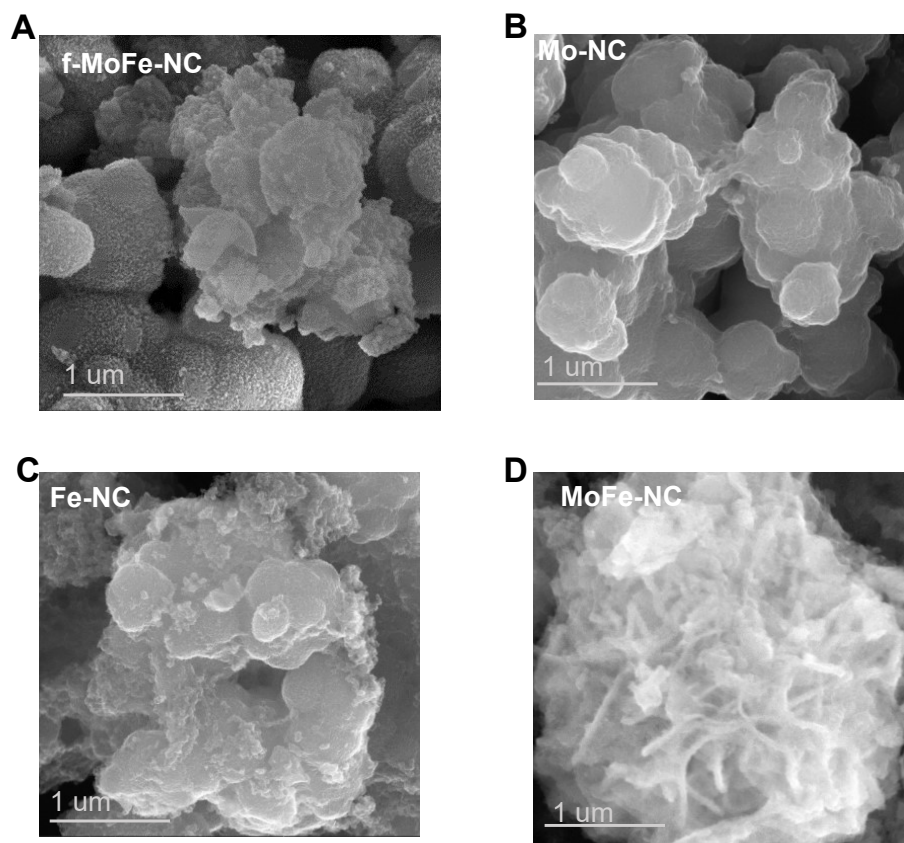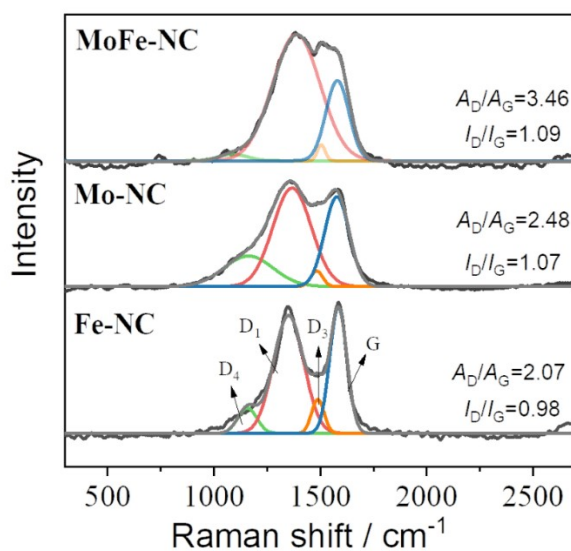
Figure S1. (A) SEM image of f-MoFe-NC, (B) SEM image of Mo-NC, (C) SEM image of Fe-NC, and (D) SEM image of MoFe-NC.
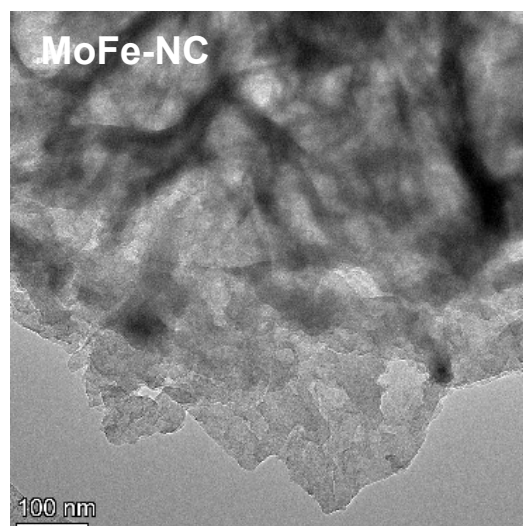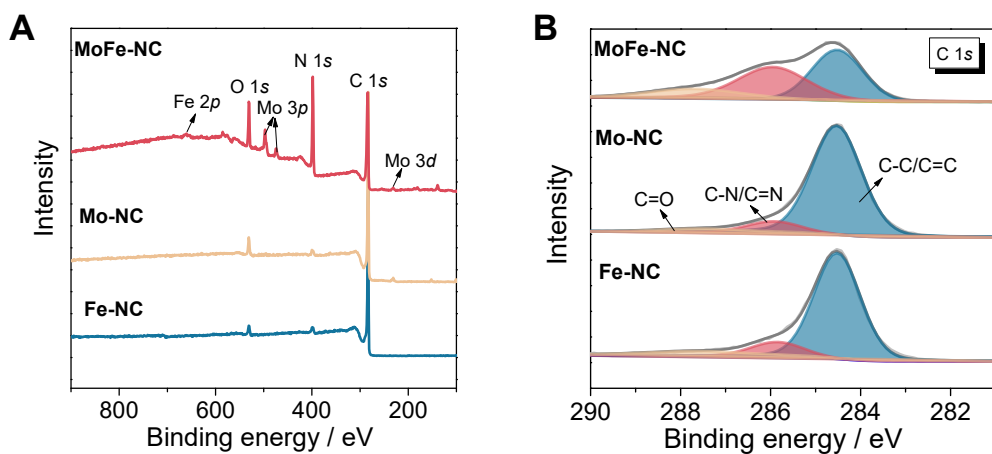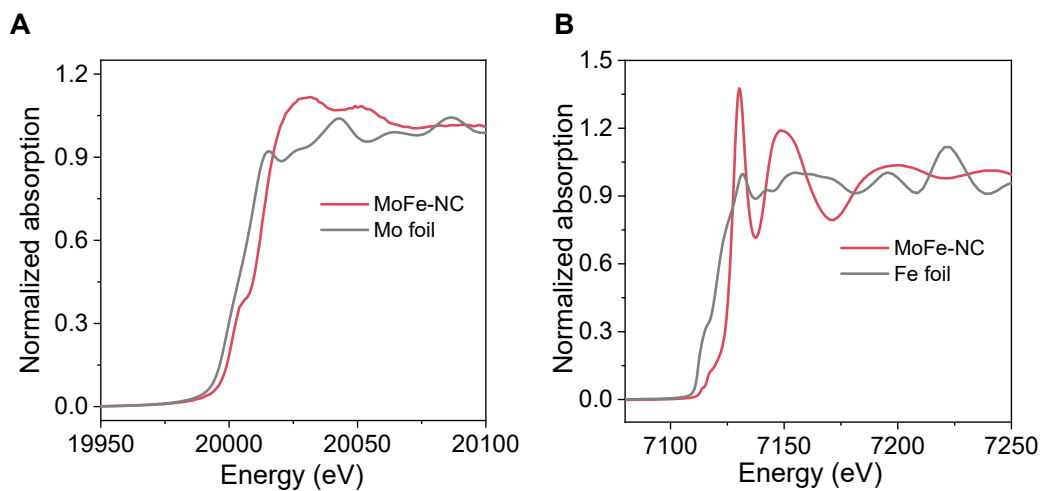

Figure S2. HRTEM image of MoFe-NC

Figure S3. BET measurements MoFe-NC. (A) N_2 adsorption isotherm, and (B) pore size distribution curves.

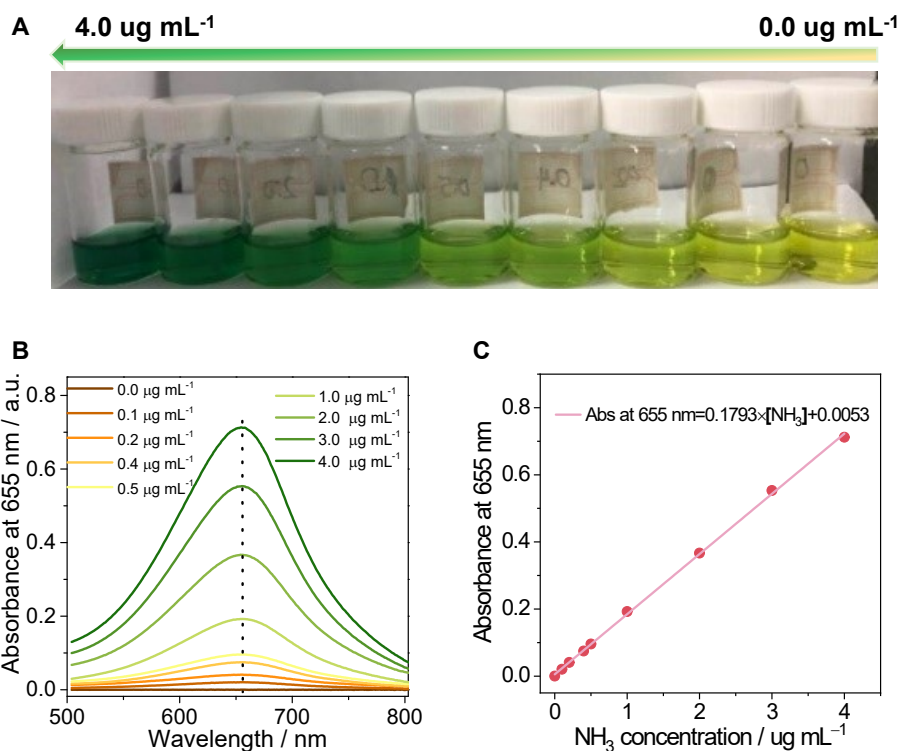**Figure S4.** Raman spectra of Fe-NC, Mo-NC, and MoFe-NC

Figure S5. XPS survey spectrum of Fe-NC, Mo-NC, and MoFe-NC. (A) XPS survey, and (B) C1s spectra.


Figure S6. XAS measurements of MoFe-NC and metal foil references. (A) XANES curves at (A) Mo and (B) Fe K-edge

Figure S7. (A) Photographs of a series of standard solutions of NH_4^+ at different concentrations mixed with chromogenic agent, (B) UV-vis curves of indophenol assays with NH_4^+ ions after incubated for 2 h, and (C) calibration curve used for estimation of NH_3 by NH_4^+ ion concentration.
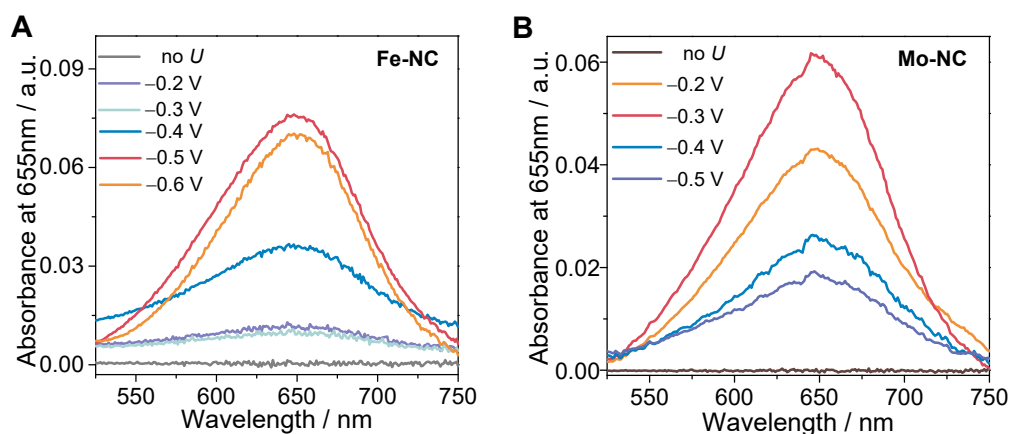
Figure S8. Electrocatalytic NRR on Mo-NC and Fe-NC catalyst in 0.1 M Li_2SO_4 electrolyte. (A) UV-vis absorption spectra of the electrolytes colored with an indophenol indicator after charging for Fe-NC at different potentials for 1 h, and (B) UV-vis absorption spectra of the electrolytes colored with an indophenol indicator after charging for Mo-NC at different potentials for 1 h.
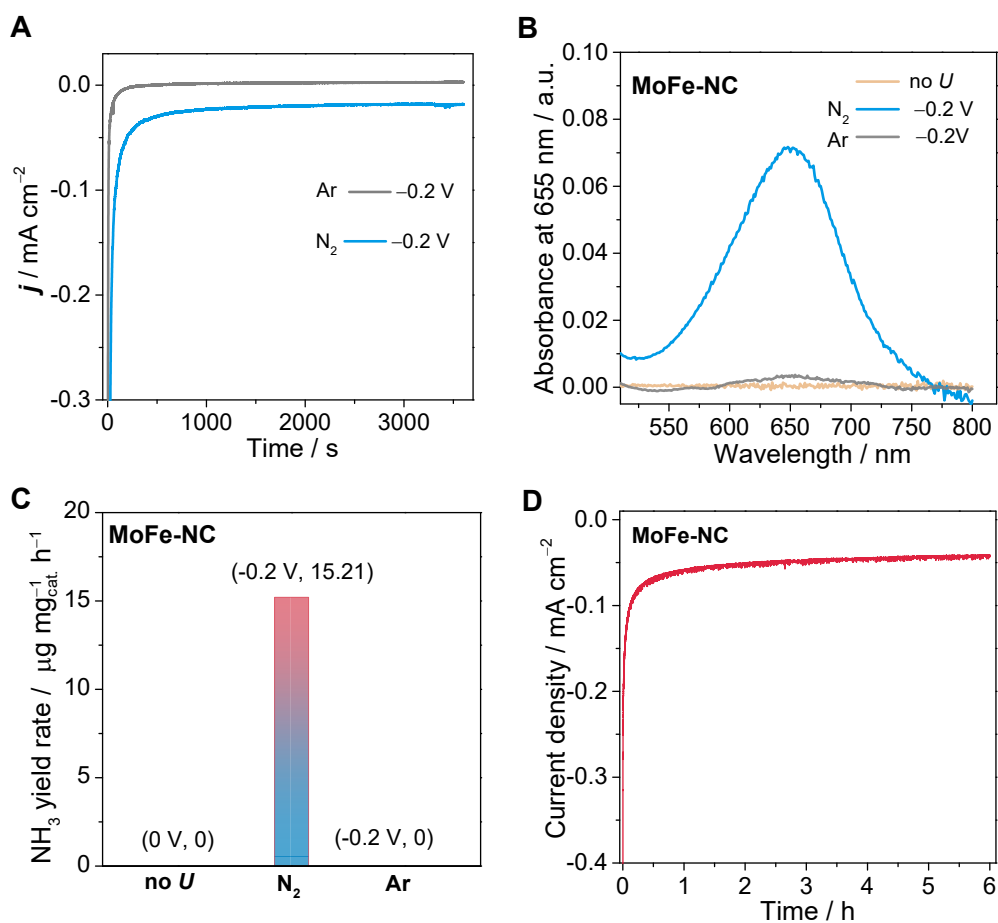
Figure S9. (A) Time-dependent current density curves for MoFe-NC under different atmospheres, (B) UV-vis absorption spectra of the electrolytes colored with an indophenol indicator after charging for 1 h, and (C) Comparison of NH_3 yields of MoFe-NC catalysts under different test conditions. (D) Time-dependent current density curves of the MoFe-NC electrode for 6 h at –0.3 V.

Table S1. Comparison of the NRR performance of MoFe-NC with previously reported catalysts

Catalysts	Potential /vs. RHE	Electrolyte	NH$_3$ Rate / $\mu g\ mg_{cat.}^{-1}\ h^{-1}$	Maximum FE / %	Reference
Cu SAC	-0.3	0.1 M HCl	49.3	11.7	*ACS Catal.* 2019, 9, 10166−10173
P-NV-C$_3$N$_4$	-0.3	0.1 M Na$_2$SO$_4$	28.6	22.1	*Chem. Eng. J.* 2022, 430, 132682
Fe$_2$Mo$_3$O$_8$/X C-72	-0.3	0.1 M Na$_2$SO$_4$	30.4	8.2	*Nano Res.* 2022, 15, 5940–5945
Pd-TiO$_2$	-0.5	0.1 M Na$_2$SO$_4$	17.4	12.7	*Chem. Commun.* 2022,58, 3214
Fe–doped Mo/NC	-0.3	0.1 M PBS	26.5	11.8 (-0.25V)	*Nano Energy*, 2020, 77, 105078
Fe-MoS$_2$	-0.3	0.5 M Na$_2$SO$_4$	8.63	18.8	*Angew. Chem. Int. Ed.* 2020, 49, 20411-20416
Mo/MoC/ Mo$_2$C	-0.3	0.1 M Na$_2$SO$_4$	20.4	18.9 (-0.2V)	*J. Mater. Chem. A* 2020, 18, 8920–8926
Mo/CC@ CN	0.0	0.1 M KOH	7.02	22.3	*ACS Catal.* 2019, 9, 6, 5302–5307
Fe$_2$(MoO$_4$)$_3$	-0.7	0.1 M Na$_2$SO$_4$	7.5	1.0	*Eur. J. Inorg. Chem.* 2020, 34, 3236-3241
MoS$_2$/C$_3$N$_4$	-0.3	0.1 M LiClO$_4$	18.5	17.8	*ACS Appl. Mater. Interfaces* 2020, 12, 6, 7081–7090
MoFe-NC	**-0.3**	**0.1 M Na$_2$SO$_4$**	**28.5**	**39.9**	**This work**