Supporting Information for

Electrocatalytic reduction of nitrogen to ammonia under ambient conditions using nanorod-structured MoN catalyst

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Table S1. A summary of the recently reported Mo-based NRR electrocatalysts.

Catalyst	*Conditions*	*FE (%)*	*NH_3 Yield Rate*	*Ref.*
Mo nanofilm	0.01 M H_2SO_4	0.72	3.09×10^{-11} mol s^{-1} cm^{-2}	1
Mo_2C/C	0.5 Li_2SO_4	7.8	11.3 μg h^{-1} mg^{-1}_{Mo2C}	2
MoS_2/C_3N_4	0.1 M $LiClO_4$	17.8	18.5 μg h^{-1} mg^{-1}	3
MoO_2/graphene	0.1 M Na_2SO4	6.6	37.4 μg h^{-1} mg^{-1}	4
defect-rich MoS_2	0.1 M Na_2SO_4	8.34	29.28 μg h^{-1} $mg^{-1}_{cat.}$	5
MoS_2	0.1 M Na_2SO_4	1.17	8.08×10^{-11} mol s^{-1} cm^{-1}	6
MoS_2/RGO	0.1 M Na_2SO_4	27.93	16.41 μg h^{-1} $mg_{cat.}^{-1}$	7
MoN	0.1 M HCl	1.15	3.01×10^{-10}mo1 s^{-1} cm^{-2}	8
Mo_2N	0.1 M HCl	4.5	78.4 μg h^{-1} $mg_{cat.}^{-1}$	9
Bi_2MoO_6	0.1 M HCl	8.17	20.46 μg h^{-1} $mg^{-1}_{cat.}$	10
MoO_3	0.1 M HCl	1.9	29.43 mg h^{-1} $mg_{cat.}^{-1}$	11
MoO_{3-x}	0.1 M KOH	12.01	35.83 ug h^{-1} mg^{-1}_{cat}	12
MoN	0.1 M KOH	12.84	6.31 μmoL h^{-1} cm^{-2} 107.3 μg h^{-1} cm^{-2}	This Work

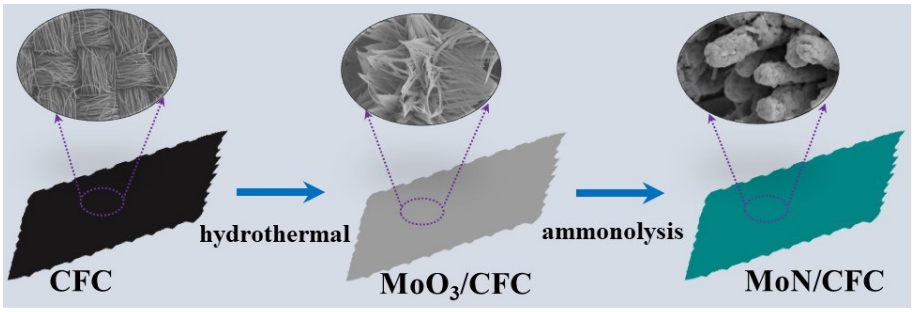

Fig. S1 Schematic illustration for preparing of MoN/CFC electrocatalyst

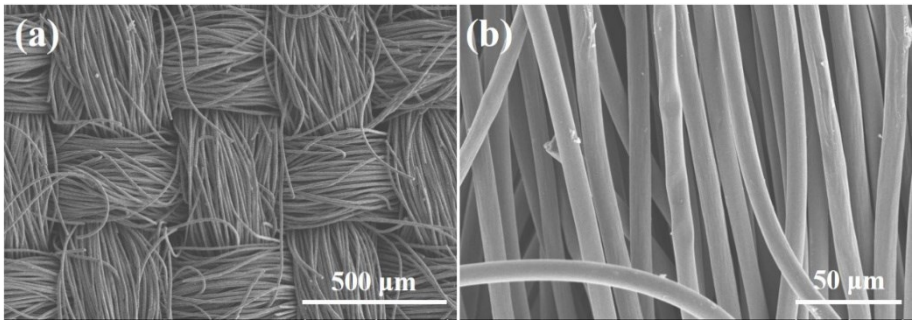

Fig. S2 (a) Low- and (b) high-magnification SEM images of CFC.

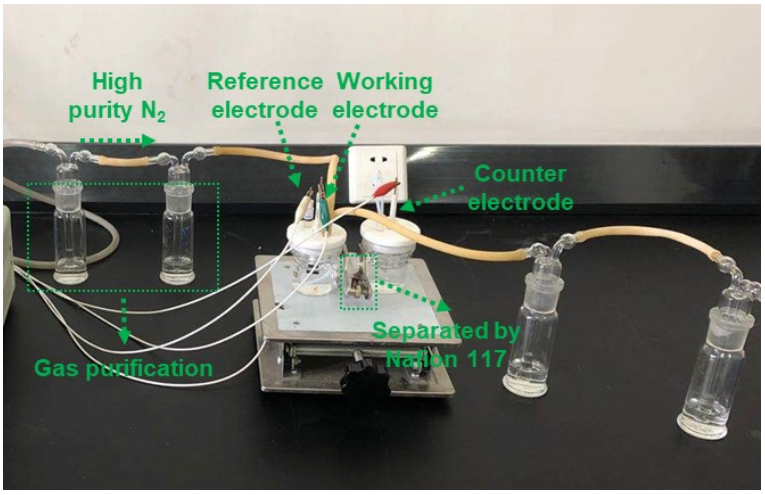

Fig. S3 Schematic diagram for electrocatalytic NRR.

A representative digital photo of NRR device is provided in Fig. S3, which includes gas-tight two-compartment cell and gas purification system. The gas-tight two-compartment is separated by Nafion 117 and integrated with a three-electrode system. In addition, the experiment is implemented under 0.1 M KOH electrolyte after depurating feedstock of Ar or N_2 to eliminate the potentially mixed NH_3 and NO_x through 0.05 M H_2SO_4 and deionized water successively.

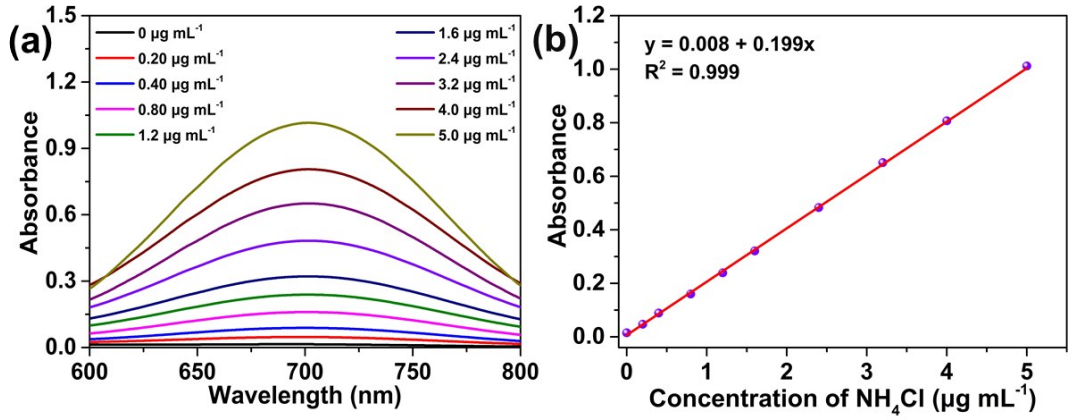

Fig. S4 (a) UV-Vis absorbance spectra of the indophenol blue indicator under different concentrations of NH_4^+ ions after incubating for 1 h at room temperature in 0.02 M of KOH, (b) Calibration curve derived from the absorbance at wavelength of 700 nm as a function of the various concentrations of NH_4^+.

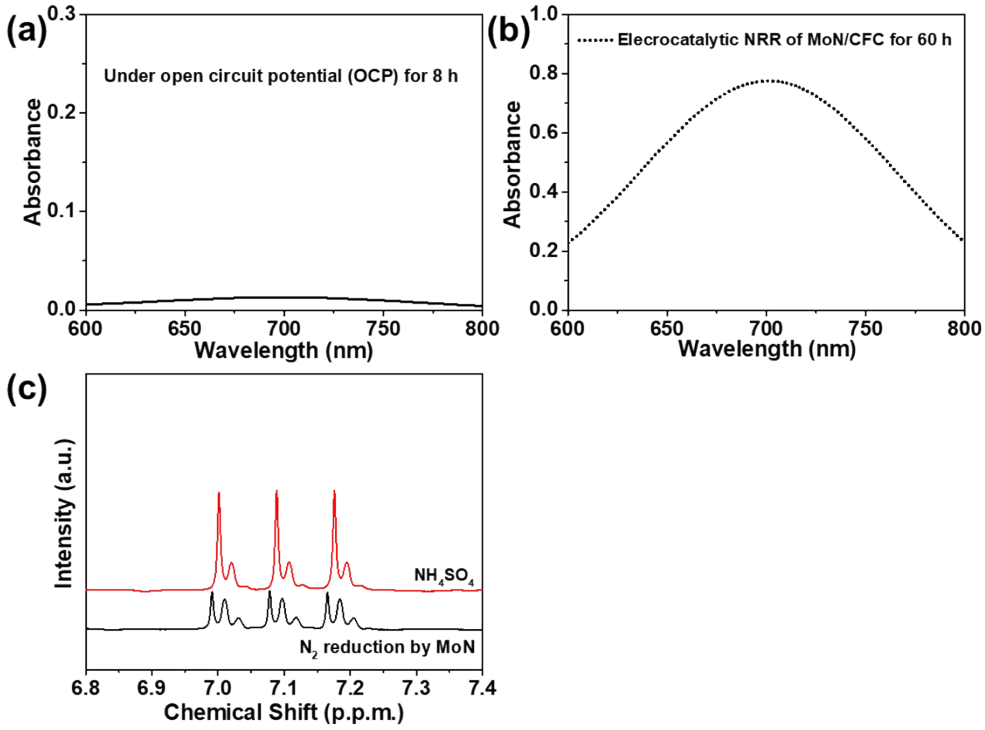

Fig. S5 (a) UV-Vis absorption spectra of electrochemical NRR under OCP for 8 h, (b) UV-Vis absorption spectra of electrocatalysis toward NRR for 60 h, (c) NMR (nuclear magnetic resonance) spectra of electrocatalytic NRR with MoN/CFC as working electrode.

For indophenol blue indicator to detect the product from NRR, 0.1 ml of electrolyte was firstly diluted to 10 ml by deionized water and then successively mixed with 0.5 ml of 0.55 M NaOH solution (containing 5.0 wt% of $C_7H_6O_3$ and 5.0 wt% of sodium citrate), 100 μL of $C_5FeN_6Na_2O$ (10 g L^{-1}), and 100 μL of 0.05 M NaClO. After aging for 1 h at room temperature, absorbance of the above mixture was reported at wavelength of 700 nm. Based on calibration curve in Fig. S4, the yield of the NH_3 was calculated to be 216.2 μmoL，suggesting the accumulation of the generation NH_3.

For NMR to evaluate the product of NRR, the original electrolyte (30 ml of 0.1 M KOH) was acidified by adding of 0.2 M of H_2SO_4 (30 ml) and next concentrated to 2 ml *via* evaporation of water in an oven. Then 0.6 ml of the electrolyte and 0.2 ml of D_2O were mixed and shaken to obtain homogeneous solution. The acidified electrolyte with abundant hydrogen ions results in the splitting of NMR spectra.

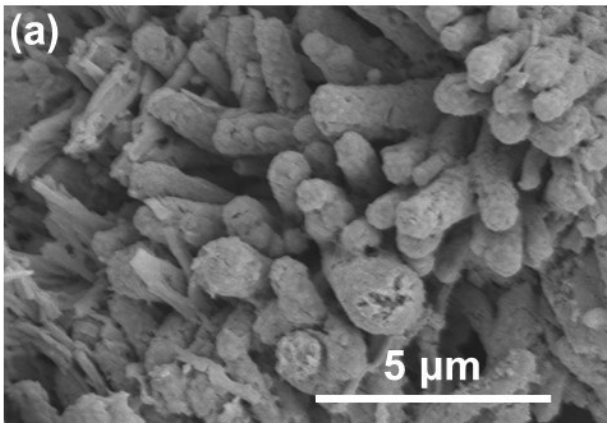

Fig. S6 SEM image of MoN/CFC electrode after long-term electrolysis toward NRR.

Reference

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