Supporting Information

Fe,Mo-N/C hollow porous nitrogen doped carbon nanorods

as an effective electrocatalyst for N₂ reduction reaction

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Table S3. Summary of the NRR activity of electrocatalysts under ambient conditions.

Experimental Section

Materials: Zinc oxide (nanorods), dopamine hydrochloride (DA), sodium molybdate dihydrate (Na₂MoO₄·2H₂O), ferric chloride (FeCl₃), Tris base, sodium citrate, salicylic acid, sodium hypochlorite solution (NaClO), sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O), N₂H₄·H₂O, and para-dimethylaminobenzaldehyde (p-C₉H₁₁NO) were acquired from Macklin. All chemical reagents were used without any pretreatment. During the whole experimentation, deionized water has been used.

Preparation of ZnO–Fe,Mo/PDA: Typically, 0.2 g of ZnO nanorods were first spread in 100 mL of Tris buffer solution (10 mM, pH = 8.5) through ultrasonication. After that, 0.1g of DA, 0.1g of FeCl₃, and 0.1g of Na₂MoO₄·2H₂O were slowly added to maintain Fe/Mo = 1:1. The as-prepared solution was further stirred for 24 hours so that the dopamine polymerizes onto ZnO nanorods to form Fe,Mo co-doped ZnO–PDA composite. The mixture was then centrifuged, washed, and dried in vacuum at 60 °C for 8 hours. At the end, black powder of composite material can be obtained.

Preparation of Fe,Mo-N/C: Pyrolysis of ZnO–Fe,Mo/PDA was performed at 800 °C for two hours under the nitrogen atmosphere at a heating rate of 5 °C/min. Then, the products of pyrolysis were rinsed with 1 M HCl under ultrasound for two hours to eliminate the ZnO nanorods templates from ZnO–Fe,Mo/PDA. Subsequently, centrifugation, rinsing, and freeze-drying processes, the black color product of Fe,Mo–N/C (1:1) was finally obtained. In order to synthesize Fe,Mo–N/C (2:1) and Fe,Mo–N/C (1:2) systems, only the mass of Mo was changed to 0.05 and 0.2 g, respectively, and the corresponding initial Fe/Mo mass ratios were 2 and 0.5. For

comparison, a similar procedure (as discussed in the synthesis of ZnO–Fe,Mo/PDA) was repeated for preparing Fe containing N-doped porous carbon (Fe–N/C) without using of Na₂MoO₄·2H₂O. Also, Mo based N-doped porous carbon (Mo–N/C) was prepared without using of FeCl₃. N–C was prepared without the addition of both salts Na₂MoO₄·2H₂O and FeCl₃ in the synthesis step.

Electrochemical Measurements: Catalyst drop-casted carbon paper was used as the cathode (working electrode) throughout electrocatalytic NRR experimentation. In general, 1.1 mL of water and 0.375 mL of isopropanol solution, 5 mg of catalyst, and 30 µL of Nafion are distributed and sonicated for 1 hour to obtain a uniform solution. The catalyst suspension solution (200 μ L) was drop-cast onto carbon paper (1 cm \times 1 cm) and dried in vacuum at 60 °C. Electrochemical measurements were performed by using CHI 760E electrochemical workstation with two-chamber H-type cell separated by Nafion 211 membrane at room temperature and pressure. The Nafion membrane was heated in an aqueous H₂O₂ solution and deionized water at 80 °C for 1 h respectively. A Pt mesh (1 cm \times 1 cm) was used as the counter electrode and Ag/AgCl electrode was used as the reference electrode. All potentials measured in this work were calibrated to the reversible hydrogen electrode (RHE) using the Nernst equation: $E_{RHE} = E_{Ag/AgCl} +$ 0.197 + 0.059 pH. Linear sweep voltammetry (LSV) curves were collected at a scan rate of 10 mV/s. For NRR experiments, potentiostatic tests were conducted in 80 mL of a N_2 -saturated 0.1 M Na_2SO_4 solution (the electrolyte was purged with N_2 for 0.5 hour before the measurement). During NRR process (NH $_3$ synthesis), pure N $_2$ was continuously fed into the cathode compartment.

Determination of ammonia: The concentration of produced NH₃ was determined by the indophenol blue method.^{1,2} Typically, 2 mL of the electrolyte was taken out from the electrochemical reaction vessel. Afterwards, 2 mL of 1 M NaOH solution containing salicylic acid (5 wt%) and sodium citrate (5 wt%) was added, followed by the addition of 1 mL of 0.05 M NaClO and 0.2 mL of C₅FeN₆Na₂O (1 wt%). After keeping at room temperature for 2 hours, the absorption spectrum of the resulting solution was measured using a UV-vis spectrophotometer. All samples for UV-vis spectrophotometer were prepared by following the same previous procedure. The concentration of indophenol blue was measured using the absorbance at $\lambda = 655$ nm. To quantify the generated NH₃, a calibration curve was constructed using a series of standard ammonium chloride (NH₄Cl) solutions in 0.1 M Na₂SO₄, 0.05 M H₂SO₄ and 0.1 M KOH, respectively. Fitting curves (Na₂SO₄: y = 6.694x + 0.005, R² = 0.999; H_2SO_4 : y = 6.123x + 0.006, $R^2 = 0.999$; KOH: y = 4.448x + 0.008, $R^2 = 0.999$, in which x and y stand for absorbance and concentration) of the three independent calibrations show a good linear relationship between the absorbance value and the NH₃ concentration.

Determination of hydrazine: As reported early,² hydrazine (N₂H₄) present in 0.1 M Na₂SO₄ was estimated via method developed by Watt and Chrisp. A mixture of 5.99 g p-C₉H₁₁NO, 30 mL concentrated HCl and 300 mL C₂H₅OH was used as color reagent. Typically, 5 mL of the electrolyte was removed from the reaction cell and mixed with 5 mL of the aforementioned color reagent. The absorbance of the resulting solution was measured at $\lambda = 458$ nm. Calibration curve was constructed using standard hydrazine hydrate solutions with series of concentrations, a curve fit (y = 0.083x + 0.062, $R^2 = 0.998$) of three independent calibrations shows a good linear relationship between the absorbance value and the N₂H₄ concentration.

Determination of yield rate and Faradaic efficiency: The yield rate of NH₃ formation can be calculated using the following equation:

$$Yieldrate = (C_{NH_3} \times V)/(t \times A), \tag{S1}$$

where C_{NH_3} is NH₃ concentration, V is the volume of electrolyte, t is the reaction time and A is the surface area of the working electrode. Assuming that three electrons are needed to produce one NH₃ molecule, the Faradaic efficiency (FE) can be calculated using the following equation:

Faradaicef ficiency =
$$(3F \times C_{NH_3} \times V)/Q$$
, (S2)

where F is the Faraday constant and Q is the total charge passed through the electrode during the reduction reaction.

Characterizations: Powder X-ray diffraction (XRD) patterns of all of the samples were carried out using graphite-filtered Cu K α radiation operating at 40 kV and 30 mA, λ = 0.15418 nm (Shimadzu XRD-6000 diffractometer). Scanning electron microscope (SEM) with an accelerating voltage of 20 kV (SEM, Zeiss SUPRA 55) was applied for detailed morphology analysis. X-ray photoelectron spectrometry (XPS) spectra were recorded using Al K α radiation (Thermo VG ESCALAB MK II). The positions of all BEs were calibrated by using the C 1s line at 284.8 eV. Transmission electron microscope (TEM) images and energy dispersive X-ray spectroscopy (EDS) mappings were taken using a JEOL JEM-2010F combined with EDX (Oxford X-MaxN 80-TLE)

spectroscopy.



Figure S1. XRD patterns of pure ZnO.



Figure S2. SEM images of (a) Fe–N/C and (b) Mo–N/C catalysts.



Figure S3. NH₃ yield rates and Faradaic efficiencies in the three electrolytes.



Figure S4. UV-vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp after NRR reaction at a series of potentials.



Figure S5. Controlled NMR analysis of Fe,Mo–N/C at the potential of -0.1 V vs. RHE.



Figure S6. Chronoamperometry (CA) tests of the stability of Fe,Mo–N/C catalyst at the potential of -0.1 V vs. RHE.



Figure S7. TEM image for post-NRR Fe,Mo-N/C.



Figure S8. (a) Chronoamperometric results of Fe–N/C at different potentials and (b) corresponding NH_3 yield rates and Faradaic efficiencies.



Figure S9. (a) Chronoamperometric results of Mo–N/C at different potentials and (b) corresponding NH_3 yield rates and Faradaic efficiencies.



Figure S10. (a) Chronoamperometric results of N–C at different potentials and (b) corresponding NH_3 yield rates and Faradaic efficiencies.



Figure S11. Faradaic efficiency of HER at different potentials.



Figure S12. High-resolution XPS spectra of N 1s regions in (a) Fe,Mo–N/C (1:2) and (b) Fe,Mo–N/C (2:1) catalysts.



Figure S13. Different UV-vis absorption spectra of (a) Fe–N/C and (b) Mo–N/C catalysts before and after the addition of 10 mM KSCN at -0.1 V vs. RHE in 0.1 M Na_2SO_4 .



Scheme S1. Schematic illustrations of the proposed reaction pathway for NRR on the Fe,Mo-N/C surface.

Table S1. Summary of elemental quantification determined by using XPS as a function of different catalysts.

Catalyst	Fe	Мо	С	N	0	Relative concentrations of different N species (area%)				
	atom %					Pyridinic N	N-Fe/Mo	Pyrrolic N	Graphitic N	N-oxide
Fe,Mo-N/C (1:1)	0.248	0.29	85.593	7.532	6.337	30.86	21.74	19.72	16.73	11.39
Fe,Mo-N/C (1:2)	0.311	0.532	86.039	4.583	8.535	12.56	15.25	33.22	31.79	7.18
Fe,Mo-N/C (2:1)	0.358	0.323	87.379	5.637	6.303	16.3	18.22	28.94	25.14	11.4

Applied Potential vs. RHE	R _{NH3} (mol h ⁻¹ cm ⁻²)	FE %
-0.05 V	9.71 ×10 ⁻⁷	10.8
-0.1 V	1.52 ×10 ⁻⁶	14.2
-0.2 V	8.81 ×10 ⁻⁷	7.51
-0.3 V	8.37 ×10 ⁻⁷	5.49
-0.4 V	7.69 ×10 ⁻⁷	3.27

Table S2. The average NH_3 yields (mol h⁻¹cm⁻²) and corresponding Faradaic efficiencies (%) under different applied potentials.

Table S3. Summary of the NRR activity of electrocatalysts under ambient conditions.

NRR Catalyst	R _{NH3} (mol h⁻¹ cm⁻²)	FE (%)	Reference	
Fe,Mo-N/C	1.52 × 10 ⁻⁶	14.2	This work	
CrO _{0.66} N _{0.56}	3.22 × 10 ⁻⁷	6.7	3	
TiO ₂ -Au	1.26 × 10 ⁻⁶	8.11	4	
Li-PEBCD	1.18 × 10 ⁻⁷	2.91	5	
γ -Fe ₂ O ₃	5.58 × 10 ⁻⁸	1.9	6	
Mo-D-R-5h	1.11 × 10 ⁻⁷	0.72	7	
Ir/C	7.63 × 10 ⁻⁸	0.017	8	
Fe ₂ O ₃ /CNT	1.32 × 10 ⁻⁷	0.02	9	
Rh nano-sheet	4.46 × 10 ⁻⁷	0.2	10	
MoS ₂	3.05 × 10 ⁻⁷	0.096	11	
Vo-rich NiCo ₂ O ₄ @HNCP	2.4 × 10 ⁻⁷	5.3	12	
Fe ₃ O ₄ nanorod	2.01 × 10 ⁻⁷	2.6	13	
TiO ₂ /Ti	3.30 × 10 ⁻⁷	2.5	14	
AuHNCs	2.29 × 10 ⁻⁷	30.2	15	
ZIF-derived carbon	3.4 × 10 ⁻⁶	10.2	16	
VN/TM	3.02 × 10 ⁻⁷	2.25	17	
MoN NA	1.08 × 10 ⁻⁶	1.15	18	
MnO	4.00 × 10 ⁻⁷	8.02	19	
SnO ₂	5.29 × 10 ⁻⁷	2.17	20	
Ag nanosheet	1.66 × 10 ⁻⁷	4.8	21	

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