Supporting Information

Aqueous N₂ Electrochemical Reduction at Low Overpotential on (110)-oriented

Mo Nanofilm

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1. Experimental section

All chemical reagents in this work were of analytical grade and used without further purification, ultrapure water (18.2 M Ω ·cm at 25 °C) was used throughout the experiment.

1.1 Preparation of molybdenum-based electrodes

The commercial molybdenum foils (Mo-foil, Alfa-Aesar) were polished with 1500 SiC paper for few minutes and washed with isopropyl alcohol and water in ultrasonic cleaner for 5 min, and thoroughly rinsed with water.

Sample of Mo-A-R was prepared by combining electrochemical anodization and reduction process. Firstly, commercial Mo-foil was anodized in 0.5 M H_2SO_4 with a potential of 0.40 V against Pt wire for 1 h.¹ Then, electrochemical reduction by cyclic voltammetry (CV) was performed from 0 to -2.0 V against Ag/AgCl with the scan rate of 50 mV s⁻¹ for 200 cycles in an Ar-degassed H_2SO_4 (0.01 M) at the cathodic compartment.

Sample of Mo-D-R-1h was prepared by electro-deposition of Mo-Fe bimetallic layer and then rinsed in HCl to remove the Fe. It was carried out on commercial Mo-foil at a potential of -2.0 V against Pt wire for 1 h using electrolyte containing the following components: 0.0175 M Fe₂(SO₄)₃ (Sinopharm), 0.005 M (NH₄)₆Mo₇O₂₄ (Alfa-Aesar), 0.05 M sodium citrate (Alfa-Aesar),² then rinsed it in 0.05 M HCl for 2 h to remove Fe completely.

Sample of Mo-D-R-5h was prepared with the procedures same with that of Mo-D-R-1h except the electro-deposition time prolonged as 5 h.

1.2 Characterization

Grazing incidence X-ray diffraction (XRD) patterns of samples were recorded using an automatic Xray diffractometer (Empyrean, Panalytical), with Cu K α radiation (λ =1.5405Å), and employed 2° beam incidence angle. The surface morphologies of the Mo-based samples were characterized by scanning electron microscopy (SEM) (Helios NanoLab 600i, FEI). An energy dispersive spectroscope (EDS) attached to the Helios NanoLab 600i SEM machine provided *in situ* determinations of the composition of the samples. X-ray photoelectron spectroscopy (XPS) of samples was measured using a PHI 5700 X-ray photoelectron spectrometer equipped with a monochromatic Al K α X-ray source.

1.3 Fabrication of electrochemical cell for ammonia synthesis

Anion membrane could avoid the products entering into the anodic chamber and reoxidizing on the anode. Nafion membrane was protonated by first boiling in water for 1 h, then in H_2O_2 for 1 h, then in water for another hour, followed by 3 h in 0.5 M H_2SO_4 , and finally for 6 h in water. All steps were performed at 80°C.³ The membrane was then stored in water for cell fabrication.

Metal foil with work area of 1 cm² was used as work electrode. A Pt plate was used as counter electrode. An Ag/AgCl electrode was used as a reference electrode. The electrolyte was 0.01 M H₂SO₄, the 25 ml electrolyte in the cathodic chamber was stirred with a magnetic stir bar at 400 rpm thorough the electrolysis. All potentials were measured against an Ag/AgCl reference electrode (3.0 M KCl) and converted to the reversible hydrogen electrode (RHE) reference scale using

 $E(vs. RHE) = E(vs. Ag/AgCl) + 0.210 + 0.0591 \times pH$ (1)

 N_2 was purged into the cathodic chamber of the cell at rate of 10 ml min⁻¹ before the electrocatalysis for 30 min. As the electrolysis started, the N_2 was supplied with a rate of 10 sccm, the constant potential was applied by an Autolab Potentiostat. The order for applied potential was from low values to high values.

1.4 ammonia detection

Initially, an absorber contains the electrolyte was used to probe the ammonia in the outer gas. But it was found that all the ammonia was collected by the solution in cathodic chamber and no ammonia was measured in the absorber. So only the solution in cathodic chamber after electrochemical catalysis was detected in the remaining experiments.

1.4.1 Apparatus:

An ultraviolet–visible spectrophotometer (HITACHI U-3900H) was used with a light path of 1 cm, and the wavelength was from 800–400 nm, the scanning rate was 60 nm min⁻¹.

1.4.2 Regents used:

a. Coloring solution: 1 M NaOH solution containing 5% salicylic acid and 5% sodium citrate (by weight);

b. Oxidation solution: 0.05 M sodium hypochlorite;

c. Catalyst solution: aqueous solution of 1% (by weight) $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ (sodium nitroferricyanide);

d. Standard ammonium solution.

1.4.3 Procedure:

A 2 ml aliquot of solution was taken from the cathodic chamber. Then, 0.10 ml of a 1 M NaOH solution containing 5% salicylic acid and 5% sodium citrate (by weight) was added into this solution, followed by addition of 20 ml of 0.05M NaClO and 20 ml of an aqueous solution of 1% (by weight) Na₂[Fe(NO)(CN)₅]•2H₂O (sodium nitroferricyanide).^{4, 5} After 1 h, the absorption spectrum was measured using a HITACHI U-3900H ultraviolet–visible spectrophotometer. The formation of indophenol blue was determined using the absorbance at a wavelength of 700 nm. Absolute calibration of the method was achieved using ammonium chloride solutions of known concentration as standards. Ammonia formation was calculated using the following equation.^{6, 7}

Ammonia formation rate =
$$\frac{[NH_{4}^{+}] \times V}{A \times t}$$
 (2)

Faraday efficiency =
$$\frac{3 \times [NH_4^+] \times V \times N_A}{Q}$$
 (3)

Where $[NH_4^+]$ is the measured NH_4^+ ion concentration, V is the volume of the cathodic chamber, t is the potential applied time, N_A is the Avogadro's constant, Q is the quantity of applied electricity and A is the effective area of the cathode.

1.4.4 Wavenumber selectivity and Calibrations:

The maximum absorbance is centered at 700 nm (Fig. S1). Comparing with the curves in the same conditions, these give similar value on different calibration ammonia concentration sets (Fig. S2). According to the calibrated relationship, the concentration of NH_3 in different electrolyte can be determined.



Fig. S1 Wave scan of the solution to select the detection wavenumber of the light.



Fig. S2 Spectrophotometry calibrations line at 700 nm.

2. Supporting Figures

2.1 The energy dispersive spectrum (EDS) of electrochemical deposited Mo samples.

The electro-deposition film composition profiles obtained by energy dispersive spectrum (EDS) analysis are shown in the Fig. S3 and Fig. S4, and the corresponding composition is given as an inset in the spectrum picture. The results show that both the two surfaces are Mo, and contain almost no Fe, these indicate that the Fe on the electro-deposition films surface was efficiently removed by HCl.



Fig. S3 Energy dispersive spectrum of the electro-deposition film on the Mo-D-R-5h.

	-						Spectrum 57	
	T		Element.	Weight%.	Atomic%.	P		
			Mo L.	100.00.1	100.00.1	ę		
			Totals.,	100.00.1	. a	ę		
				ļ.				
Ι.								
0	2	4	6 8	10	12 14	4 16	18	20
Full S	Scale 619	8 cts Cu	rsor: 0.000					keV.

Fig. S4 Energy dispersive spectrum of the electro-deposition film on the Mo-D-R-1h.

2.2 XPS spectra of the Mo-based samples



Fig. S5 XPS patterns of the top layers of the electrodes. (a) survey spectra, (b) high-resolution Mo 3d spectra, (c) high-resolution O 1s spectra.

2.3 The partial current density for NH₃ formation on different Mo-based samples.



Fig. S6 Comparison of the partial current density for NH₃ on different Mo-based catalysts *vs* applied potential.

2.4 Stability measurement of the Mo-based catalysts.



Fig. S7 Total current density *vs* time at -0.39 V *vs*. RHE for four Mo-based electrodes. This figure indicates the Mo-based electrodes have a good stability for electrolysis.

2.4 Stability of the Mo-D-R-5h catalyst.



Fig. S8 Long-term performance of current and ammonia yield of Mo-D-R-5h at -0.49 V vs RHE for 9-hour electrolysis.



Fig. S9 SEM images of Mo-D-R-5h before (a) and after (b) the electrolysis reaction.

3. References

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