

## Supporting Information

### **Interrupted Chemical Reaction-based Tri-Phase Design of the FeMoO<sub>4</sub>/CuFe<sub>2</sub>S<sub>3</sub>/CuSe<sub>2</sub> Electrocatalyst for Enhancing Electrochemical Nitrogen Reduction**

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**Table S1.** Molar content of each precursor chemical for preparing the electrochemical catalysts

No	Catalyst code	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	Cu(NO <sub>3</sub> ) <sub>3</sub>	(NH <sub>4</sub> ) <sub>5</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O	Catalyst load (mg)	Foam size (cm <sup>2</sup> )
1	FeCu (2:2)	2	2	0	2.65	1x1
2	MoCu (3:2)	0	2	3	2.8	1x1
3	FeMo (2:3)	4	0	6	3.7	1x1
4	FeMoCuSe (2:3:2:0)	2	3	2	2.3	1x1
5	FeMoCuSe(2:3:2:0.7)	2	3	2	4.7	1x1
6	FeMoCuSe(2:3:2:1.4)	2	3	2	4.51	1x1
7	FeMoCuSe(2:3:2:2.1)	2	3	2	5.01	1x1

Note: During catalyst labeling, the elemental symbols indicate precursor metal type, and the number shows the ratio (in mmol) used during mixing.

## 1. Quantification of nitrate, nitrite, and hydrazine using colorimetric analyses

### 1.1. Procedure for nitrate (NO<sub>3</sub><sup>-</sup>) detection

For nitrate determination, 2 mL of the diluted electrolyte was mixed thoroughly with 100 µL of 1 M HCl, 10 µL of a 0.8 wt.% sulfamic acid solution, and 2 mL of deionized water. After allowing the mixture to react for 20 minutes, the absorbance at 220 and 275 nm was recorded using UV–visible spectroscopy. The final absorbance value was calculated using the equation  $A = A_{220} - 2A_{275}$ , and the nitrate (NO<sub>3</sub><sup>-</sup>) concentration was determined from a calibration curve.

### 1.2. Detection and analysis of nitrite (NO<sub>2</sub><sup>-</sup>)

Nitrite was quantified using the Griess reagent method<sup>1</sup>. The Griess reagent was prepared by dissolving 0.1 g of N-(1-naphthyl)ethylenediamine dihydrochloride, 1.0 g of sulfanilamide, and 2.94 mL of H<sub>3</sub>PO<sub>4</sub> in 50 mL of deionized water. For analysis, 2 mL of the diluted electrolyte was mixed with 1 mL of Griess reagent and 2 mL of deionized water, then incubated for 15 minutes. The absorbance was then measured at 540 nm using a UV–visible spectrophotometer, and the

nitrite ( $\text{NO}_2^-$ ) concentration was determined from a calibration curve<sup>1,2</sup>.

### **1.3. Procedure for hydrazine ( $\text{N}_2\text{H}_4$ ) determination**

The by-product  $\text{N}_2\text{H}_4$  was determined using the method of Watt and Chrisp<sup>3</sup>. To determine hydrazine ( $\text{N}_2\text{H}_4$ ) production, 150 mL of ethanol was combined with 15 mL of 37 wt.% HCl and 3 g of p-(dimethylamino)benzaldehyde to prepare the detection solution. Then, 1.5 mL of the test electrolyte was mixed with 1.5 mL of this solution. After 20 minutes of reaction, the absorbance of the mixture was measured at 460 nm using UV–visible spectroscopy, and the hydrazine concentration was calculated from a standard calibration curve.

### **1.4. Procedure for $^1\text{H}$ NMR characterization**

Before the nitrogen reduction reaction ( $\text{N}_2\text{RR}$ ), the electrolyte was purged with high-purity Ar for 30 minutes to remove residual gas. Subsequently,  $^{15}\text{N}_2$  bubbled through the electrolyte for 20 minutes. Electrolysis was then performed for 1 hour at  $-0.6$  V versus RHE in  $0.5$  M  $\text{Na}_2\text{SO}_4$ . The resulting  $^{15}\text{NH}_4^+$ -containing  $600$   $\mu\text{L}$  electrolyte was concentrated and mixed with  $\text{D}_2\text{O}$  and  $\text{DMSO-d}_6$  prior to  $^1\text{H}$  NMR measurement. The same procedure was followed for a sample prepared with  $^{14}\text{N}_2$  as the feed gas.

## **2. Outcomes of the control experiments**

The credibility of  $\text{N}_2\text{RR}$  experiments depends strongly on carefully designed control tests. To rule out ammonia contamination from the H-cell, electrodes, and Nafion 211 membrane, which can act as both sources and sinks of  $\text{NH}_3$  during  $\text{N}_2\text{RR}$ , all components were thoroughly cleaned before experimentation. XRD, XPS, and SEM-EDS analyses confirmed that no nitrogen species were present in the as-prepared catalysts, even though nitrogen-containing precursors were used during synthesis. Additional control experiments were conducted to further verify that the detected  $\text{NH}_3$

originated exclusively from the supplied N<sub>2</sub>, and the corresponding results are discussed below.

- a) When Ar was used as the feed gas in the Ar-saturated experiment, no NH<sub>3</sub> was detected, indicating the absence of residual nitrogen from either the feed gas or the components of the H-type electrolytic cell. This result confirms that, even under suitable electrolysis conditions, NH<sub>3</sub> cannot be produced without a nitrogen source, underscoring the essential role of N<sub>2</sub> in ammonia formation.
- b) Electrolyte samples were collected from both the cathodic and anodic compartments to assess potential NH<sub>3</sub> crossover. No NH<sub>3</sub> was detected in the anodic chamber, confirming that ammonia generated at the cathode does not migrate through the membrane in the H-type cell. The Nafion 211 membrane, acting as a proton exchange membrane (PEM), enables selective proton (H<sup>+</sup>) transport from the anode to the cathode while effectively separating the anodic and cathodic products. This separation prevents NH<sub>3</sub> crossover and avoids direct gas mixing between the two compartments.
- c) When the Nafion 211 membrane was removed, only a negligible NH<sub>3</sub> yield was observed. In the absence of the membrane, direct contact and mixing between the anodic and cathodic compartments occur, allowing NH<sub>3</sub> generated at the cathode during N<sub>2</sub>RR to be readily oxidized at the anode. This leads to an underestimation of the actual NH<sub>3</sub> yield and introduces measurement interference. These results underscore the critical role of a membrane-separated reactor configuration in N<sub>2</sub>RR, as it suppresses NH<sub>3</sub> oxidation and ensures reliable quantification. Accordingly, this study emphasizes that electrochemical NH<sub>3</sub> synthesis should be carried out in an H-type cell equipped with a separating membrane. These critical control experiments confirm that the detected NH<sub>3</sub> originates from the electrochemical reduction of feed N<sub>2</sub> using the as-prepared catalyst.

### 3. Faradaic Efficiency, Energy Efficiency, and Energy Consumption Calculation

The Faradaic efficiency (FE) of the N<sub>2</sub>RR was determined according to Equation (1):

$$\%FE = \frac{3 \times F \times C_{NH_4^+} \times V(mL)}{17 \times Q} \dots\dots\dots (1)$$

$$\%FE = \frac{3 \times \frac{96500 C}{mol} \times 136 \frac{\mu g}{mL} \times 90 mL}{17 \times 222.14 A/s} \times 100 = 93.8\%$$

Here, C<sub>NH<sub>4</sub><sup>+</sup></sub> (136 μg/mL) represents the concentration of generated ammonium ions, V (90mL) is the volume of 0.5 M Na<sub>2</sub>SO<sub>4</sub> in the cathode chamber, F is the Faraday constant (96,500 C/mol), and Q denotes the total charge passed during the N<sub>2</sub>RR, obtained from the chronoamperometry (CA) curve using an effective sample area of 1×1 cm<sup>2</sup>. This Faradaic efficiency is a record high.

To evaluate the energy efficiency (EE) of ammonia electrosynthesis relative to the conventional Haber–Bosch process, the specific energy consumption (EC) was calculated in units of kWh per kg of NH<sub>3</sub> produced. This was done using the following equation, which allows a direct comparison of the energy demands between the two methods.

$$EC = \frac{n \times F \times V_{cell}}{3600 \times FE \times M} \dots\dots\dots (2)$$

$$EC = \frac{n \times F \times V_{cell}}{3600 \times FE \times M} = \frac{3 \times 96500 \times 2.0}{3600 \times 50.9 \times 17} = \frac{579000}{3115080} = 18.58 kWh/kgNH_3$$

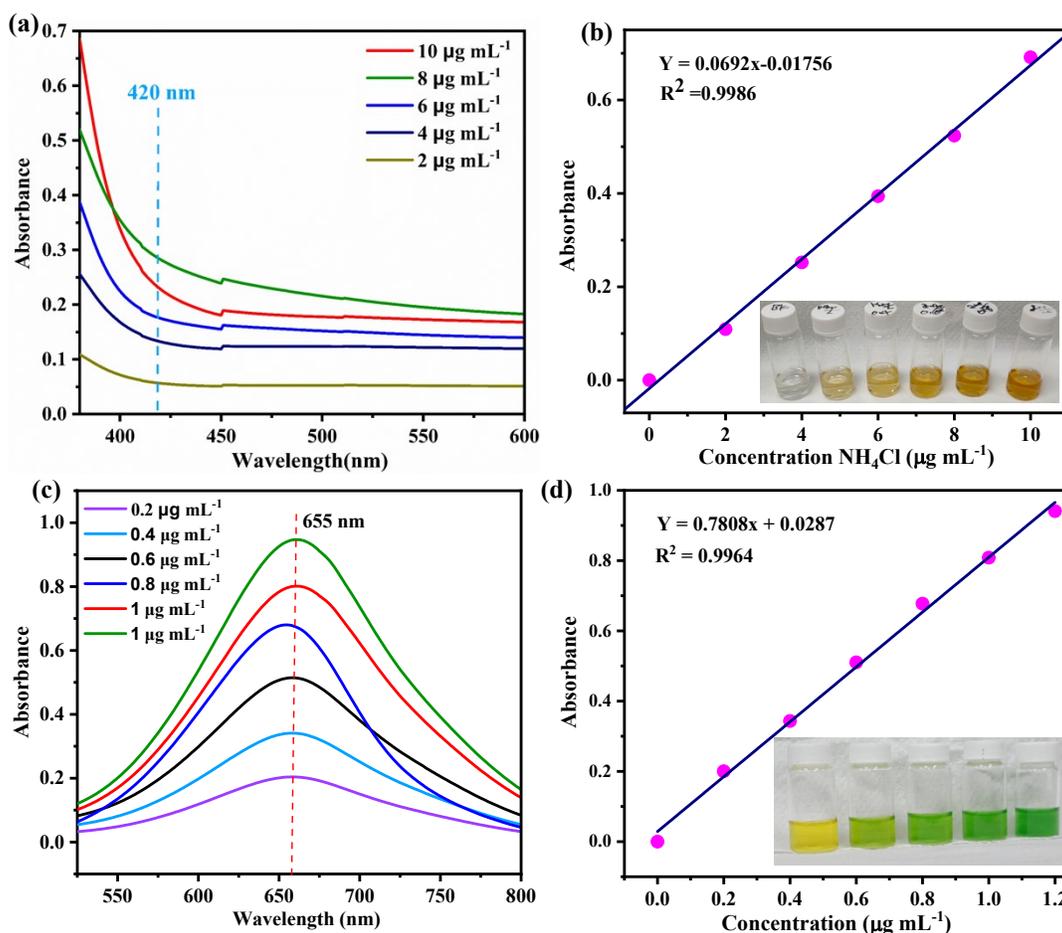
Here n denotes the number of electrons transferred per mole of ammonia produced (3e<sup>-</sup>), F is the Faraday constant (96,500 C/mol), V<sub>cell</sub> represents the applied cell voltage (2.0 V), FE is the Faradaic efficiency (50.9%), and M is the molecular weight of NH<sub>3</sub>(17 g/mol). For calculating energy consumption, an optimized cell voltage of 2.0 V was used to maximize ammonia

production. The electrocatalytic energy efficiency (EE) of the single-stack cell was then evaluated based on this calculation using the corresponding equation.

$$EE(\%) = \frac{(1.23 - E^0) \times FE}{E} \dots\dots\dots(3)$$

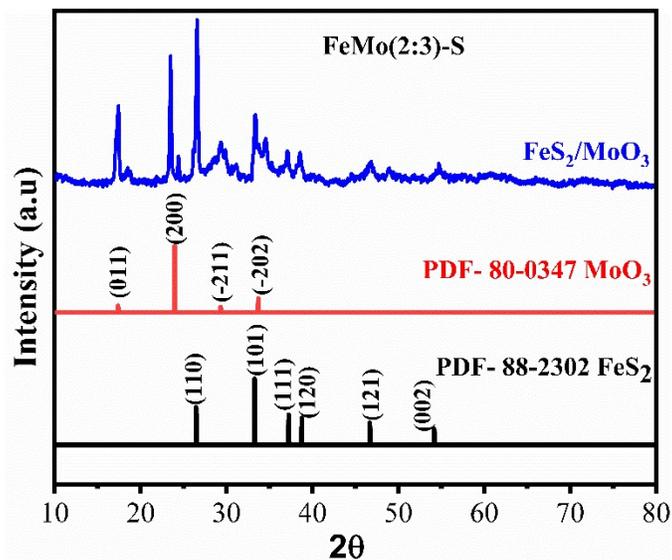
$$EE(\%) = \frac{(1.23 - 0.092) \times 50.9}{2.0} = \frac{57.92}{2} = 28.96$$

where  $E^0$  is the standard potential of  $N_2RR$  to  $NH_3$ , which is 0.092 V vs. RHE; FE is the faradaic efficiency for ammonia, which is 50.9%; E or  $E_{cell}$  is the applied potential, which is 2.0 V; F is the Faraday constant ( $96\,500\text{ C mol}^{-1}$ ).

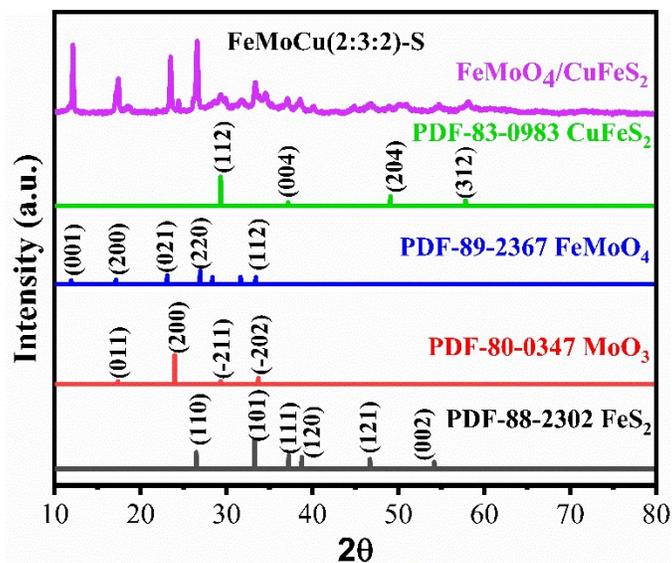


**Figure S1.** (a) The calibration curve at 420 nm is used to determine the  $NH_3$  concentration. (b) UV-vis adsorption curves at different ammonium chloride concentrations, as measured by the

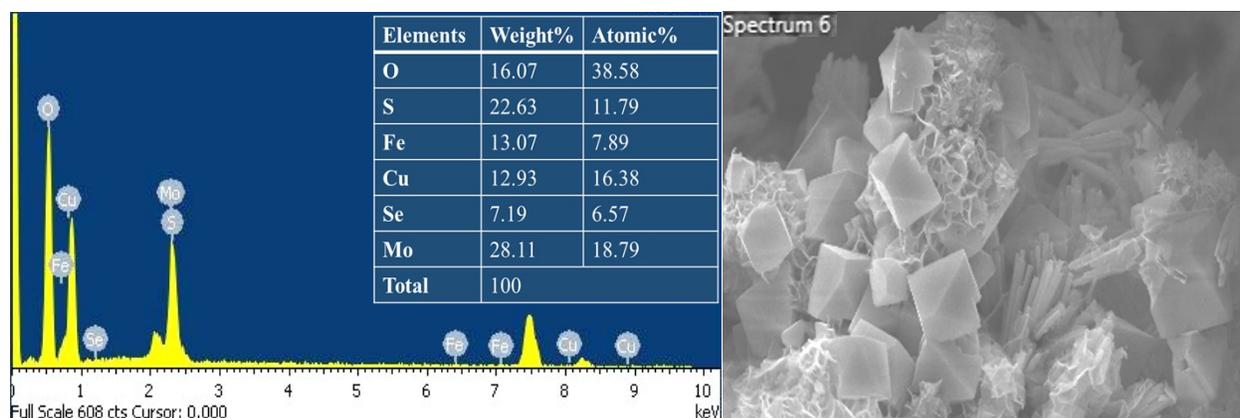
Nessler method, are used for calibration. (c) The calibration curve at 655 nm is used to determine the  $\text{NH}_3$  concentration. (d) UV-vis adsorption curves at different ammonium chloride concentrations.



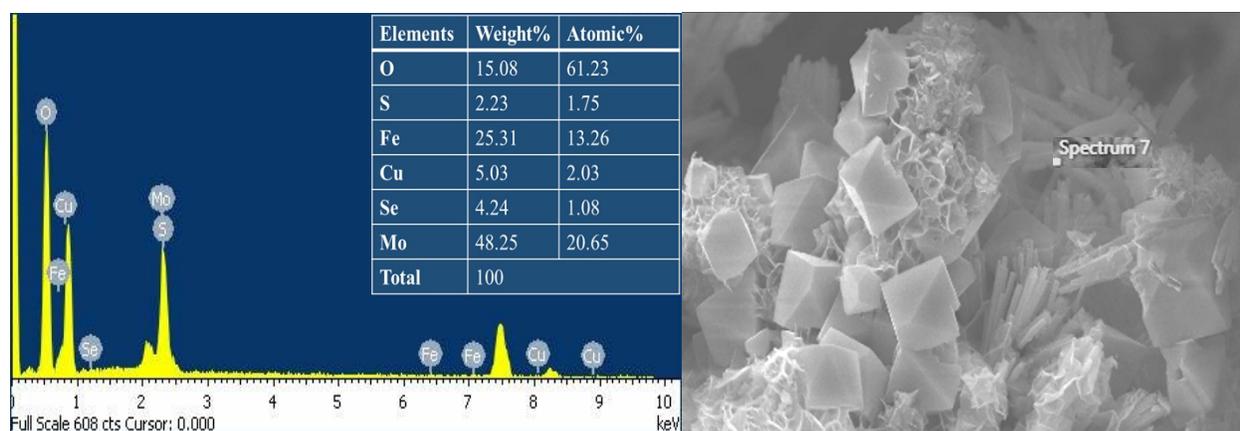
**Figure S2.** XRD patterns of FeS<sub>2</sub> and MoO<sub>3</sub> phases from the FeMo (2:3) bimetal system.



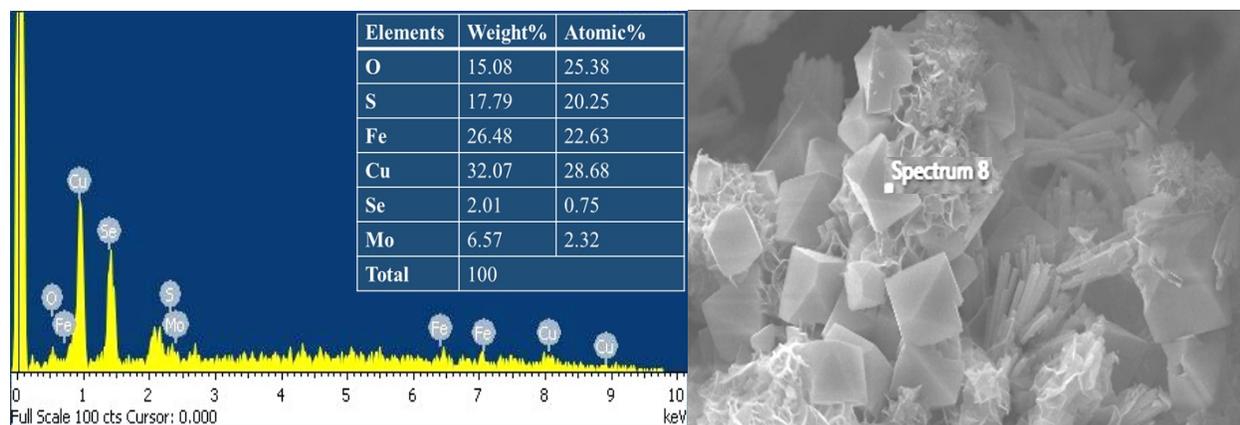
**Figure S3.** XRD patterns of FeMoO<sub>4</sub> and CuFeS<sub>2</sub> phases from the FeMoCu(2:3:2) system.



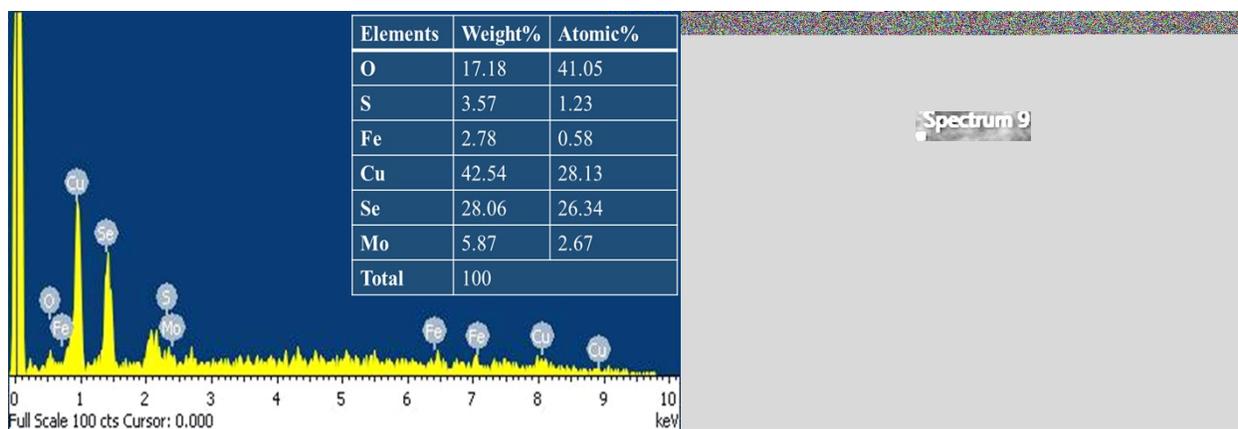
**Figure S4.** Large-area SEM-EDS compositional analysis of the  $\text{FeMoO}_4/\text{CuFe}_2\text{S}_3/\text{CuSe}_2$  catalyst.



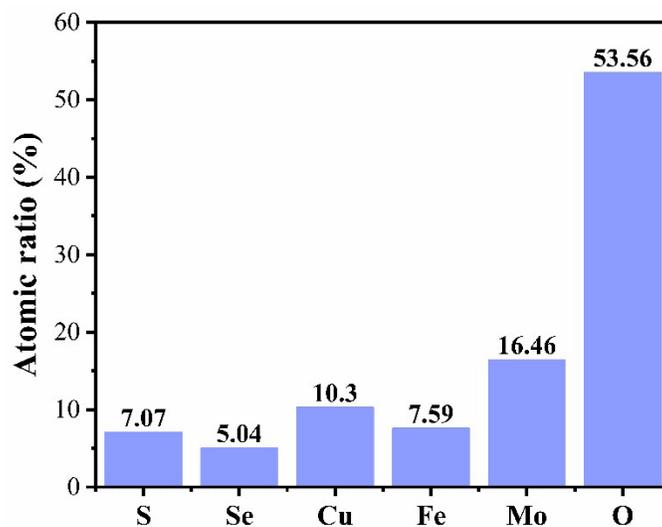
**Figure S5.** Small-area SEM-EDS compositional analysis of the  $\text{FeMoO}_4$  phase in the  $\text{FeMoO}_4/\text{CuFe}_2\text{S}_3/\text{CuSe}_2$  catalyst.



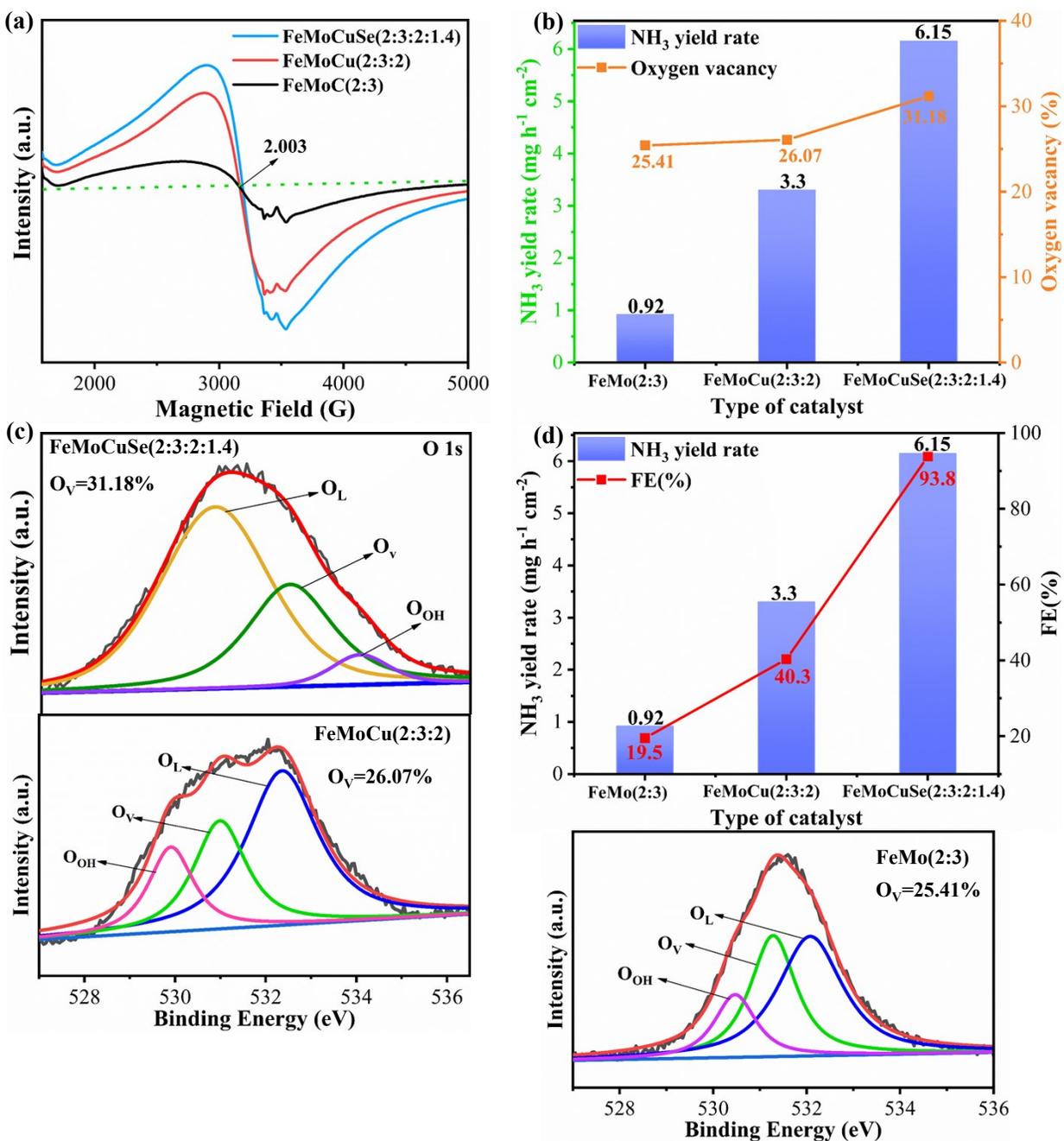
**Figure S6.** Small-area SEM-EDS compositional analyses of the  $\text{CuFe}_2\text{S}_3$  phase in the the  $\text{FeMoO}_4/\text{CuFe}_2\text{S}_3/\text{CuSe}_2$  catalyst.



**Figure S7.** Small-area SEM-EDS compositional analyses of the CuSe<sub>2</sub> phase in the the FeMoO<sub>4</sub>/CuFe<sub>2</sub>S<sub>3</sub>/CuSe<sub>2</sub> catalyst.



**Figure S8.** Atomic ratios of the Fe(MoO<sub>4</sub>)/CuFe<sub>2</sub>S<sub>3</sub>/CuSe<sub>2</sub> tri-phase.



**Figure S9.** (a) EPR spectra of bimetal FeMo (2:3), FeMoCu (2:3:2), and FeMoCuSe (2:3:2:1.4) catalysts. (b) Quantitative comparison between oxygen vacancy and N<sub>2</sub>RR performance of FeMo (2:3), FeMoCu (2:3:2), and FeMoCuSe (2:3:2:1.4). (c) Comparison of oxygen vacancy concentrations in FeMo (2:3), FeMoCu (2:3:2), and FeMoCuSe (2:3:2:1.4). (d) NH<sub>3</sub> yields for FeMo (2:3), FeMoCu (2:3:2), and FeMoCuSe (2:3:2:1.4) catalysts for a 2 h test.

**Table S2.** ICP-MS elemental analyses in FeMoO<sub>4</sub>/CuFe<sub>2</sub>S<sub>3</sub>/CuSe<sub>2</sub> catalyst.

Element	Atomic %	RSD (%)
Fe	18.69	0.25%
Mo	27.10	0.25%
Cu	25.89	0.54%
Se	15.17	0.39%
S	13.15	-

**Table S3.** XPS atomic concentration of Fe, Mo, Cu, Se, S, and O in the FeMoO<sub>4</sub>/CuFe<sub>2</sub>S<sub>3</sub>/CuSe<sub>2</sub> electrocatalysts, obtained from the Fe 2p, Mo 3d, Cu 2p, Se 3d, S 2p, and O 1s spectra, respectively.

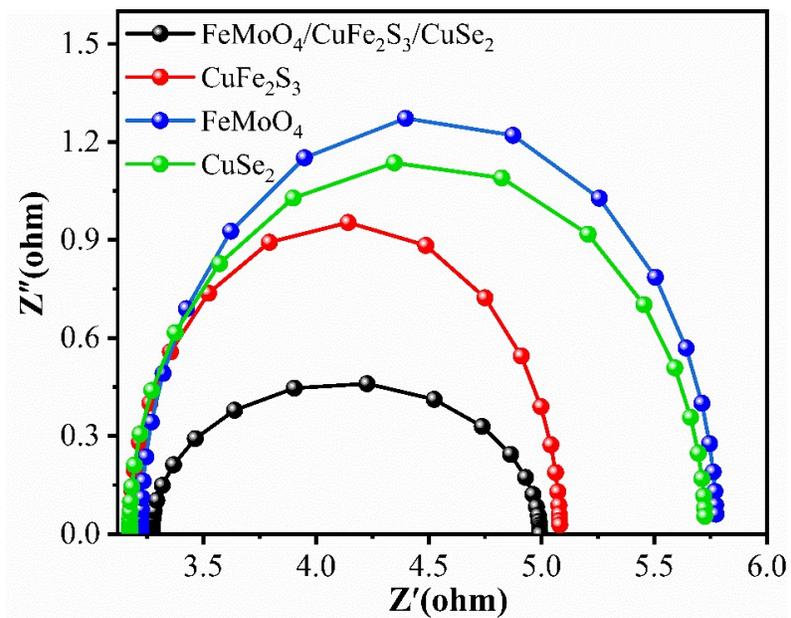
Catalyst	Element	Peak area (%)		
FeMoO <sub>4</sub> /CuFe <sub>2</sub> S <sub>3</sub> /CuSe <sub>2</sub>	Fe	3.96	Fe <sup>3+</sup>	59.9%
			Fe <sup>2+</sup>	40.1%
	S	4.87	S <sup>2-</sup>	100%
	Mo	8.59	Mo <sup>4+</sup>	66%
			Mo <sup>6+</sup>	34%
	Cu	6.14	Cu <sup>2+</sup>	100%
	Se	5.95	Se <sup>2-</sup>	100%
O	70.48	O <sub>L</sub>	63.16%	
		O <sub>V</sub>	31.18%	
		O <sub>H</sub>	5.64%	

$$\begin{aligned}
 \%Mo &= \left( \frac{\text{peak area of } \frac{Mo}{ASF}}{\text{Peak area of } \frac{Mo}{ASF} + \text{paek area of } \frac{Fe}{ASF} + \text{Peak area of } \frac{Cu}{ASF} + \text{peak area of } \frac{O}{ASF} + \text{peak area of } \frac{S}{ASF}} \right) \times 100 \\
 \% &
 \end{aligned}$$

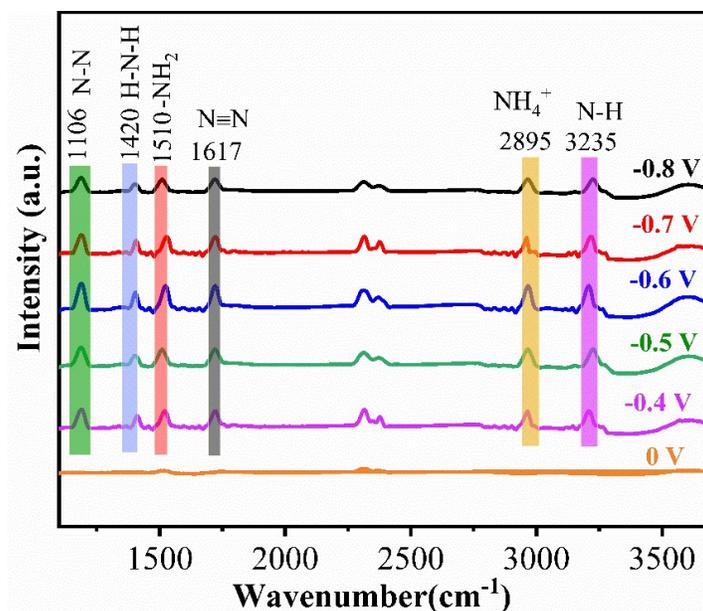
**Table S4.** Calculation of elemental composition by EDS analysis of FeMoO<sub>4</sub>/CuFe<sub>2</sub>S<sub>3</sub>/CuSe<sub>2</sub> combined with the XPS data.

EDS from point area	Fe	Mo	O	Cu	Se	S
The CuFe <sub>2</sub> S <sub>3</sub> phase		<p>Combining the Cu and Fe valence states and the data from the bulk CuFe<sub>2</sub>S<sub>3</sub> cubic-like nanostructures with the basis of valence charge balance for an ionic compound. The elemental composition for the cube-like crystals, as determined by analysis (<b>Figure S6</b>), revealed 28.68% Cu, 22.63% Fe, 25.38% O, 20.63% S, and trace amounts of Se and Mo. The CuFe<sub>2</sub>S<sub>3</sub> phase can be viewed:</p> <p>→ <math>Cu_{28.68}^{2+}(Fe_{0.40}^{2+}Fe_{0.60}^{3+})_{28.68}(O_{25.38}S_{20.63})</math> ---Valence charge balance</p> <p>→ <math>28.68 Cu_1^{2+}(Fe_{0.4}^{2+}Fe_{0.6}^{3+})_{1.39}(O_{1.23}S_{1.64})</math></p> <p>→ <math>28.68Cu_1^{2+}(Fe_{0.4}^{2+}\square_{0.3}Fe_{0.6}^{3+})_{1.39}(O,S)_3</math>--Charge balance of defects</p> <p>→ <math>28.68 Cu_1^{2+}(Fe_{0.308}^{2+}\square_{0.231}Fe_{0.462}^{3+})_{1.39}(O_{0.773}S_{0.227})_3</math></p> <p>→ <math>28.68 Cu_1^{2+}(Fe_{0.308}^{2+}\square_{0.231}Fe_{0.462}^{3+})_{2-1.39}(O_{0.773}S_{0.227})_3</math></p> <p>→ <math>28.68CuFe_{2-x}(O,S)_3</math></p>				
	Theoretical	CuFe <sub>2</sub> S <sub>3</sub> = CuS·2FeS				
	Defects	$Fe^{3+}$ to $Fe^{2+}$ defect ( $Fe_{Fe}^{1+}$ ); $Fe^{2+}$ vacancy ( $V_{Fe}^{2-}$ )				
<b>30.5% iron vacancies in CuFe<sub>2-x</sub>S<sub>3</sub></b>						
The FeMoO <sub>4</sub> phase		<p>For the smaller rod-like crystals (<b>Figure S5</b>), the components have 13.26% Fe, with 40.05% Fe<sup>2+</sup> and 59.9% Fe<sup>3+</sup>, and 20.65% Mo, with 66% Mo<sup>4+</sup> and 33.99% Mo<sup>6+</sup>. The FeMoO<sub>4</sub> phase can</p>				

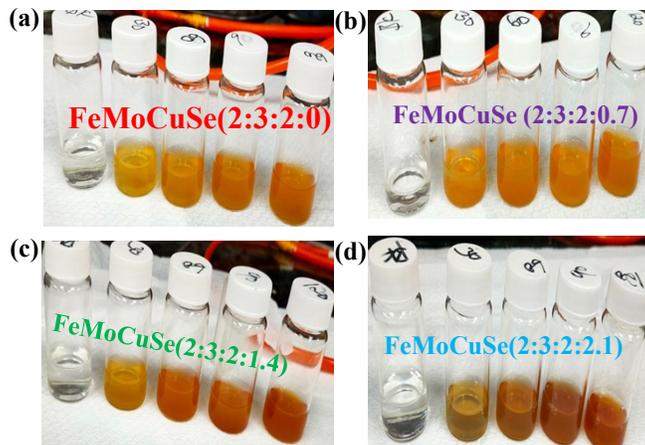
		<p>be viewed as:</p> $\rightarrow (Fe_{0.401}^{2+} Fe_{0.599}^{3+})_{13.26} [Mo_{0.660}^{4+} Mo_{0.339}^{6+}]_{20} O_{61.23}$ $\rightarrow 13.26 (Fe_{0.401}^{2+} Fe_{0.599}^{3+}) [Mo_{0.660}^{4+} Mo_{0.339}^{6+}]_{1.5} O_{5.46}$ $\rightarrow 8.84 (Fe_{0.401}^{2+} Fe_{0.599}^{3+})_{0.666} [Mo_{0.660}^{4+} Mo_{0.339}^{6+}]_1 O_{3.07}$ $\rightarrow 8.84 [(Fe_{0.401}^{2+} Fe_{0.599}^{3+})_{1-0.34} [Mo_{0.55}^{4+} Mo_{0.45}^{6+}]_1 O_{4-0.93}$ $\rightarrow 8.84 Fe_{1-x} (MoO_{4-y})$
	Theoretical	$FeMoO_4 = FeO \cdot MoO_3$
	Defects	$Fe^{2+}$ vacancy ( $V_{Fe}^{2-}$ ); $Fe^{3+}$ -to- $Fe^{2+}$ defect ( $Fe_{Fe}^{1+}$ ); $Mo^{4+}$ -to- $Mo^{6+}$ defect ( $Mo_{Mo}^{2-}$ )
<b>23.25% oxygen vacancies in <math>Fe_{1-x} MoO_{4-y}</math></b>		
The $CuSe_2$ phase		<p>For the highly porous, or sponge-like crystals, the components have 28.13% Cu, and 26.34% Se. From Table S3, Se is in the form of <math>Se^{2-}</math> instead of a diselenide ion <math>(Se_2)^{2-}</math>, so overall neutrality can hold with <math>Cu^{2+}</math>: The <math>CuSe_2</math> phase can be viewed as:</p> $\rightarrow Cu_{28.13}^{2+} Se_{26.34}^{2-} = 28.13 Cu_1^{2+} (Se_{0.94}^{2-}) \sim 28.13 Cu_1^{2+} (Se_1^{2-})$ $Cu^{2+} (Se_{1.0}^{2-}) (V_{Se}^{1+})$
	Theoretical	$CuSe_2 = Cu^{2+} (Se_2)^{2-}$
	Defects	$Se^{2-}$ -to- $Se^{1-}$ defect ( $Se_{Se}^{1-}$ ) $Se^{1-}$ vacancy ( $V_{Se}^{1+}$ )
<b>50 % <math>Se^{1-}</math> vacancies in <math>CuSe_{2-z}</math></b>		



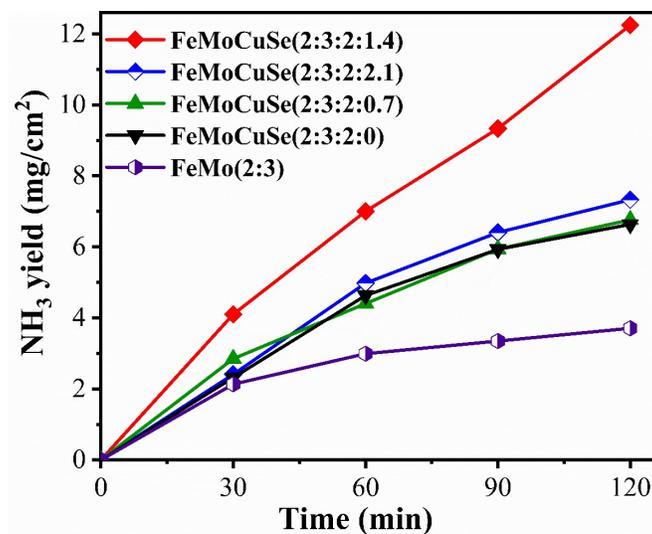
**Figure S10.** Nyquist plots comparing the electrochemical impedance behavior of FeMoO<sub>4</sub>, CuFe<sub>2</sub>S<sub>3</sub>, CuSe<sub>2</sub>, and the FeMoO<sub>4</sub>/CuFe<sub>2</sub>S<sub>3</sub>/CuSe<sub>2</sub> electrocatalysts in an aqueous electrolyte containing 0.5 M Na<sub>2</sub>SO<sub>4</sub>.



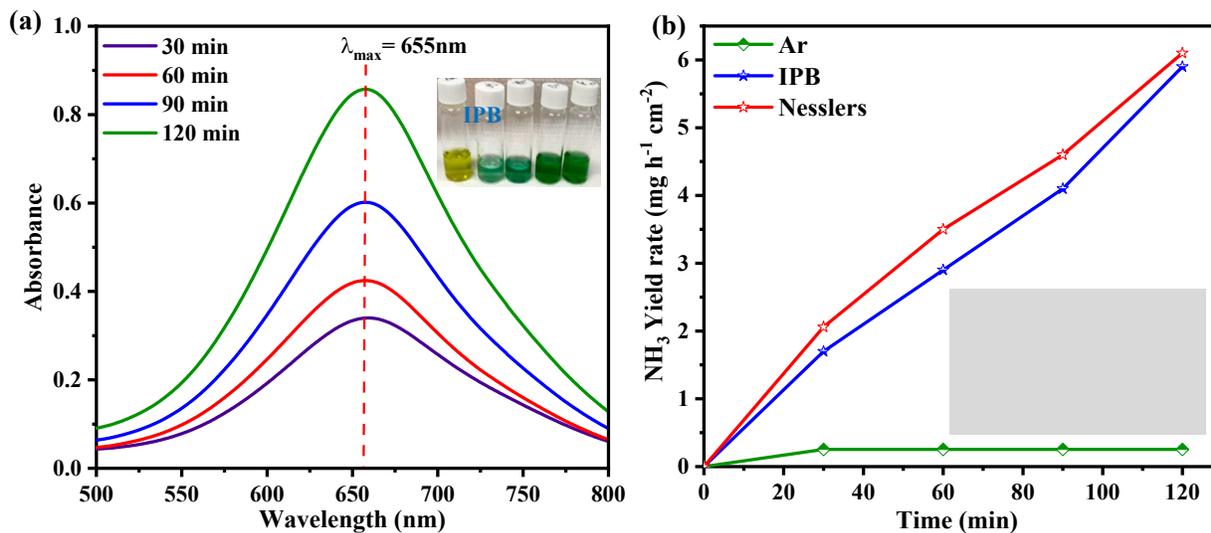
**Figure S11.** In situ FT-IR spectra of FeMoCuSe (2:3:2:1.4) recorded in 0.5 M Na<sub>2</sub>SO<sub>4</sub> under cathodic polarization at potentials from -0.4 to -0.8 V vs. RHE.



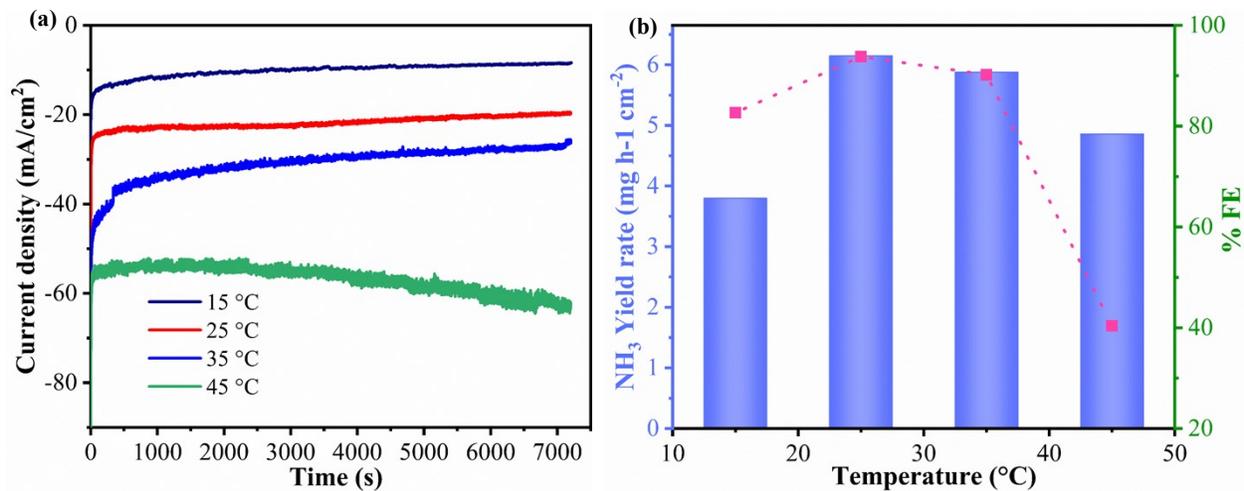
**Figure S12.** Changes in the color of solutions with the reaction time after adding Nessler reagent at 30 min intervals for (a) FeMoCuSe (2:3:2:0), (b) FeMoCuSe (2:3:2:0.7), (c) FeMoCuSe (2:3:2:1.4), and (d) FeMoCuSe (2:3:2:2.1).



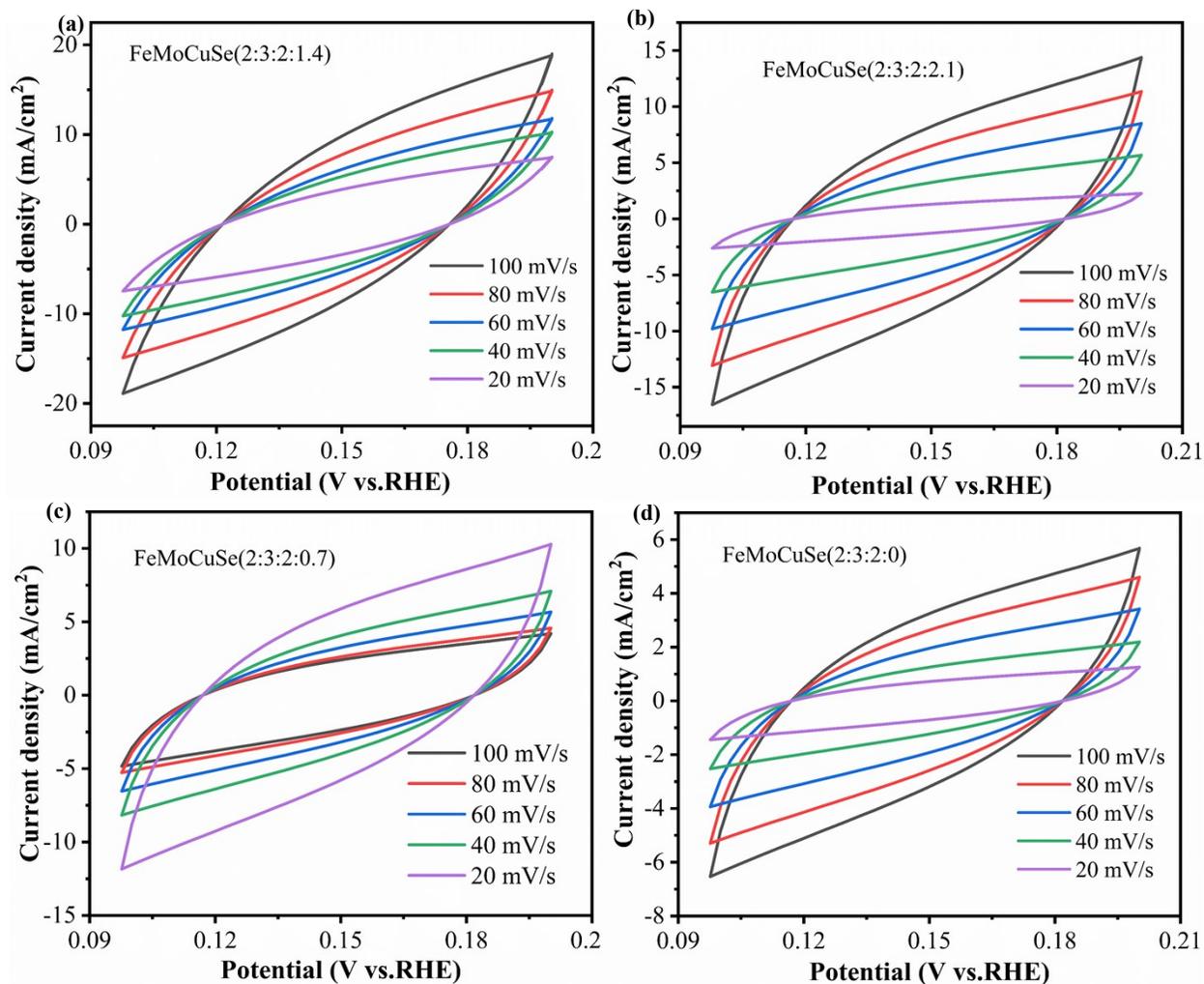
**Figure S13.** NH<sub>3</sub> yield data production at 30-minute intervals after adding Nessler reagent.



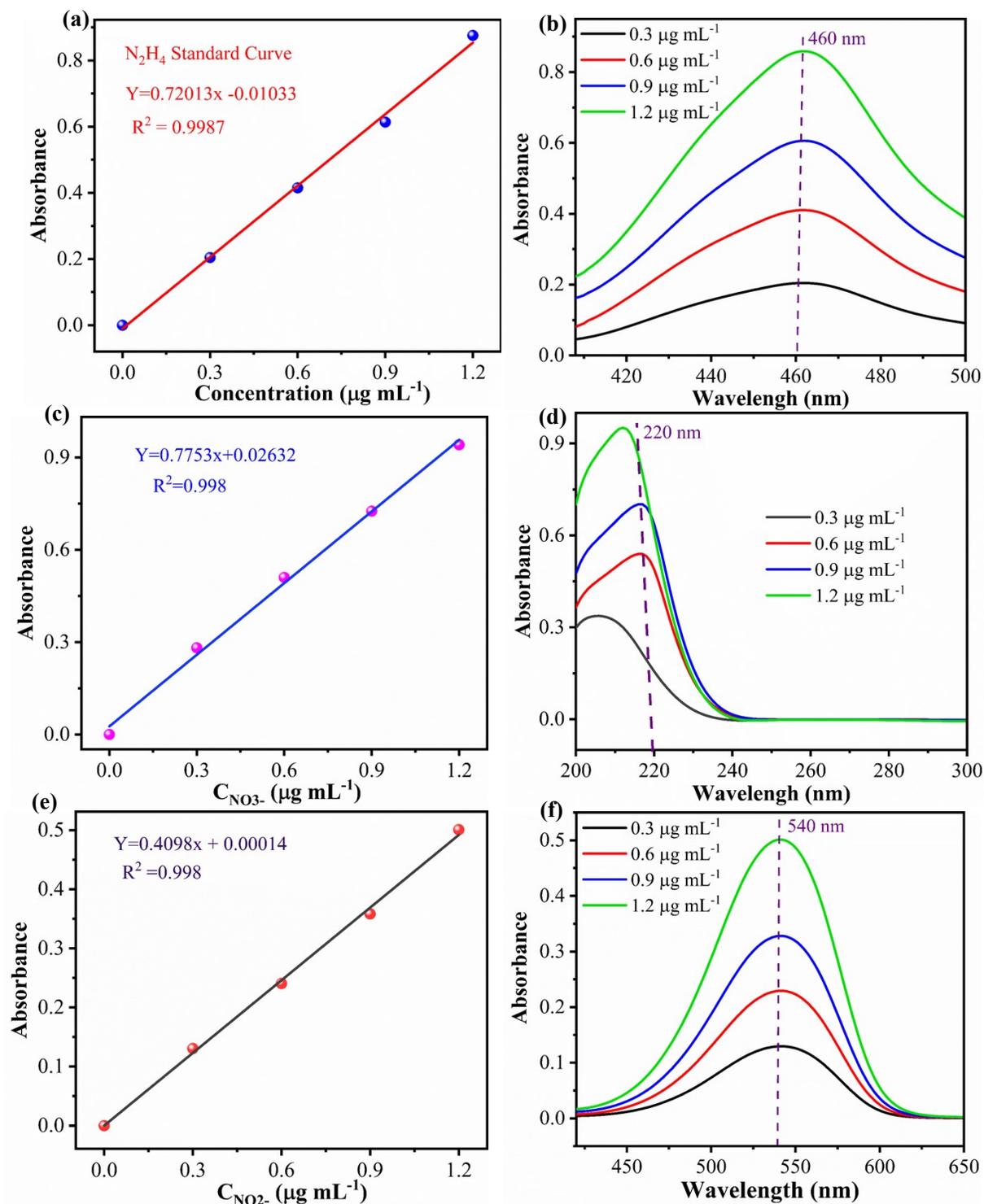
**Figure S14.** (a) UV-vis spectra of NH<sub>3</sub>, confirmed by the Indophenol blue method, with 30 min interval electrolysis. (b) Comparison between Nessler and IPB methods for ammonia detection of FeMoCuSe (2:3:2:1.4) in 0.5M Na<sub>2</sub>SO<sub>4</sub> at -0.6V vs. RHE.



**Figure S15.** Influence of temperature on the electrocatalytic  $N_2$  reduction reaction (N<sub>2</sub>RR): (a) chronoamperometric responses at various temperatures, and (b) corresponding  $NH_3$  yield rates and FE.

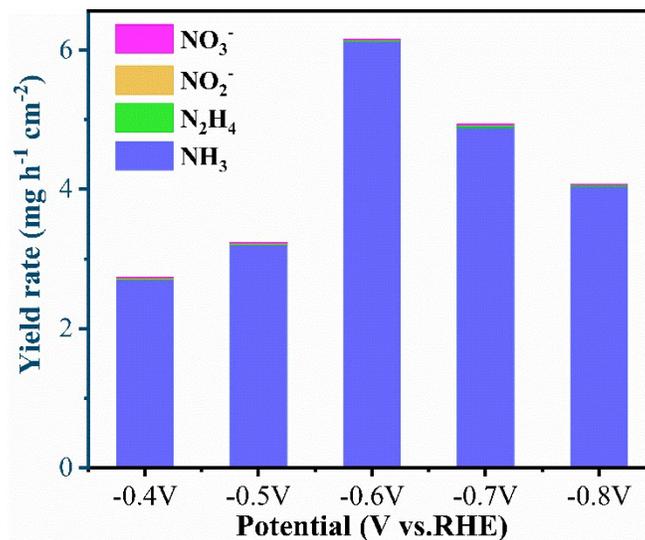


**Figure S16.** CV tests for (a) FeMoCuSe (2:3:2:1.4), (b) FeMoCuSe (2:3:2:2.1), (c) FeMoCuSe (2:3:2:0.7), and (d) FeMoCuSe (2:3:2:0).

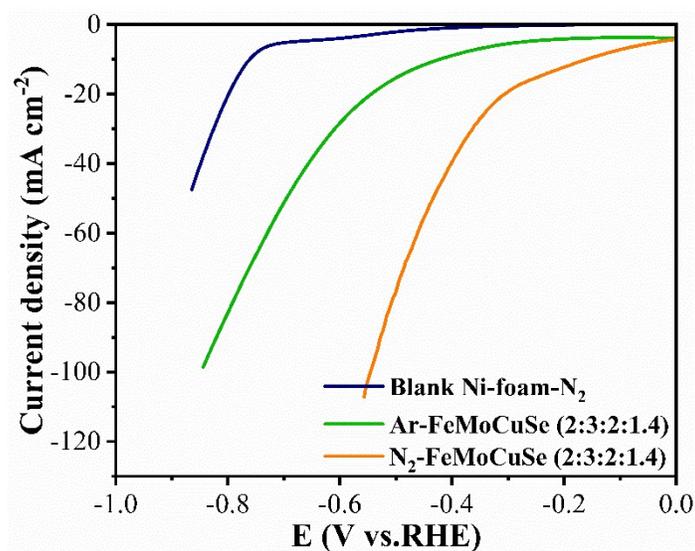


**Figure S17.** (a) UV-Vis absorption spectra of  $N_2H_4$  solutions measured after 20 minutes of incubation at room temperature. (b) Calibration curve used to determine the  $N_2H_4$  concentrations. (c) Calibration for  $NO_3^-$  quantification. (d) UV-Vis absorption spectra of  $NaNO_3$  solutions with

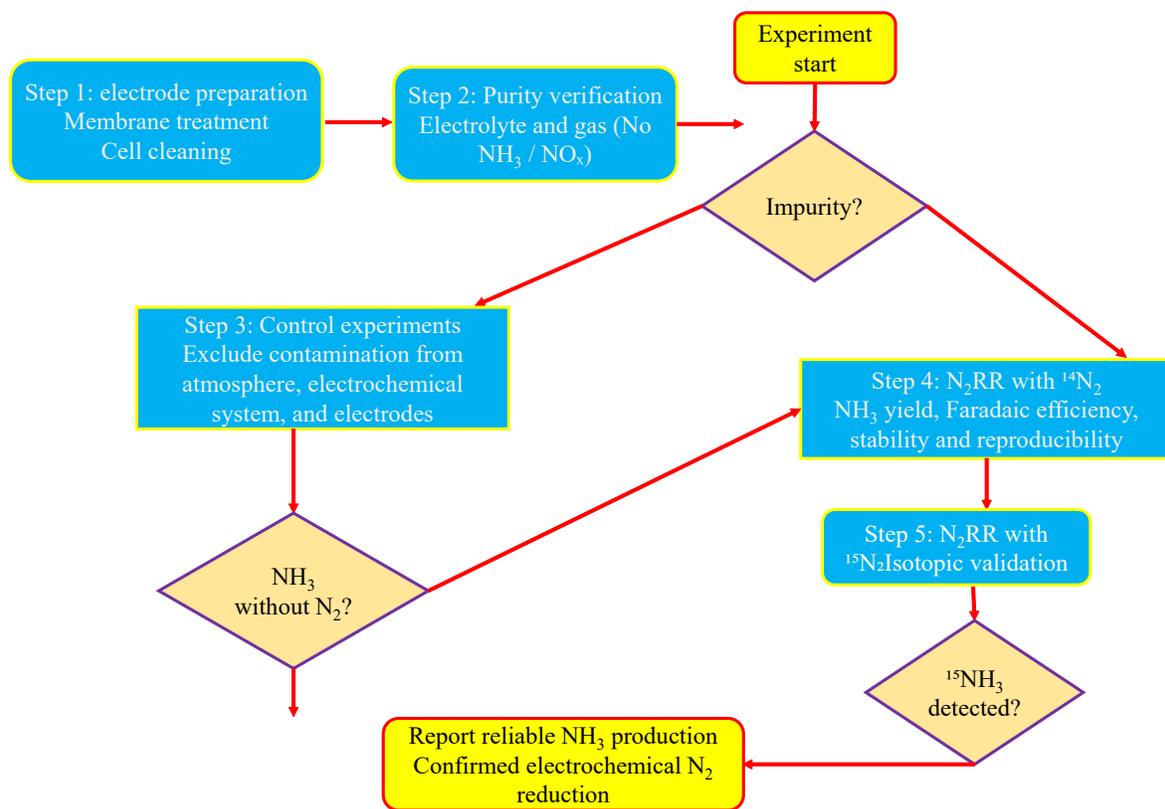
known concentrations. (d) Calibration curve to show the relationship between  $\text{NaNO}_3$  concentration and absorbance. (e) UV–Vis absorption spectra of  $\text{NaNO}_2$  solutions with known concentrations. (f) Calibration curve depicting the relationship between  $\text{NaNO}_2$  concentration and absorbance.



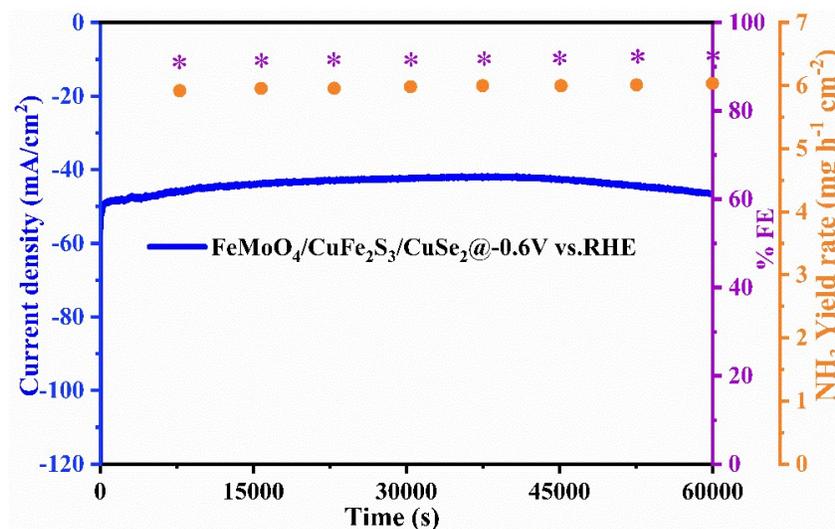
**Figure S18.** Yield rates of  $\text{NH}_3$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{N}_2\text{H}_4$  produced by the  $\text{FeMoCuSe}$  (2:3:2:1.4) catalyst at different applied potentials after catalytic reaction for 2h in the cell system.



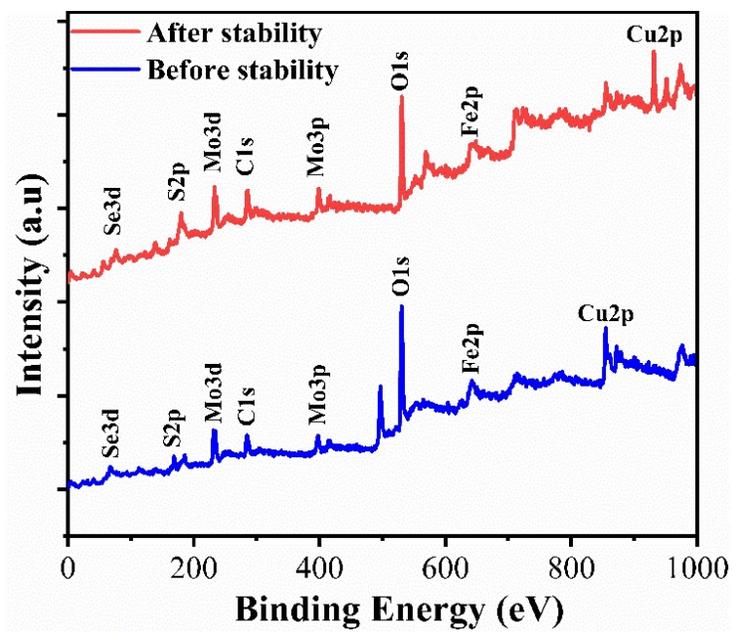
**Figure S19.** LSV curve comparison between blank Ni-foam (catalyst-free) and  $\text{FeMoCuSe}$  (2:3:2:1.4) in a  $\text{N}_2$ -saturated 0.5 M  $\text{Na}_2\text{SO}_4$  electrolyte at  $-0.6$  V vs. RHE.



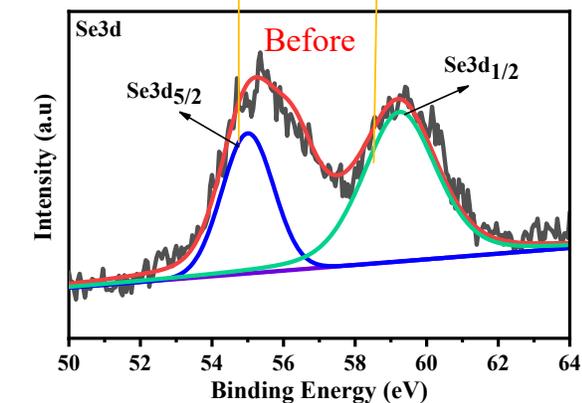
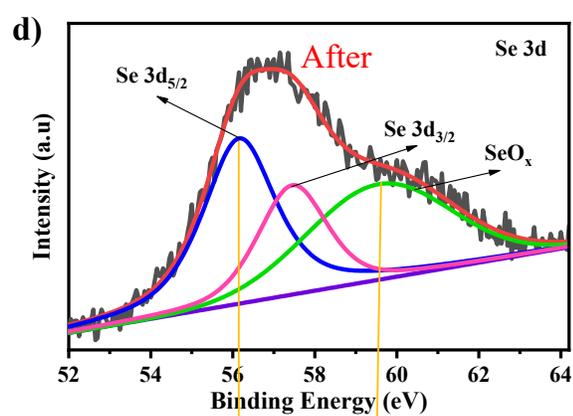
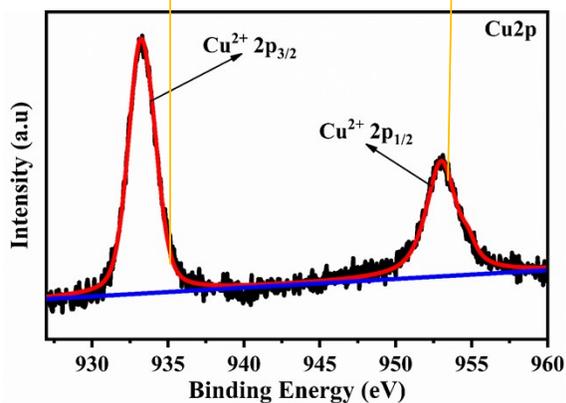
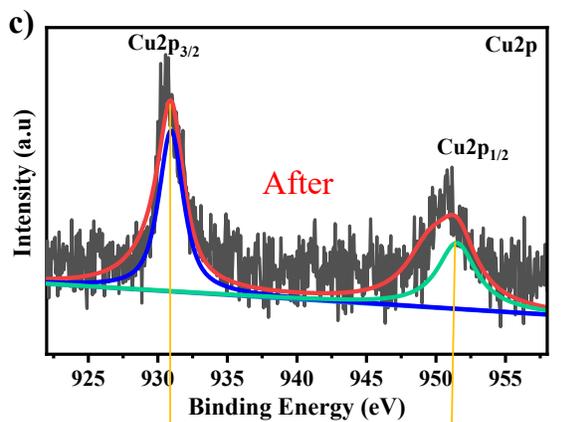
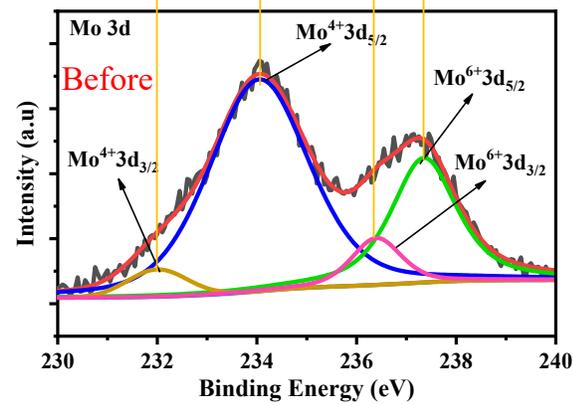
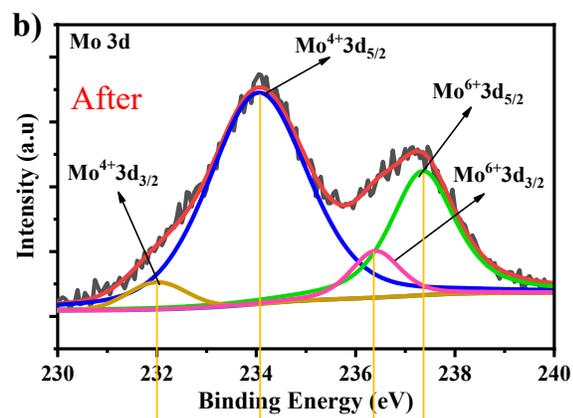
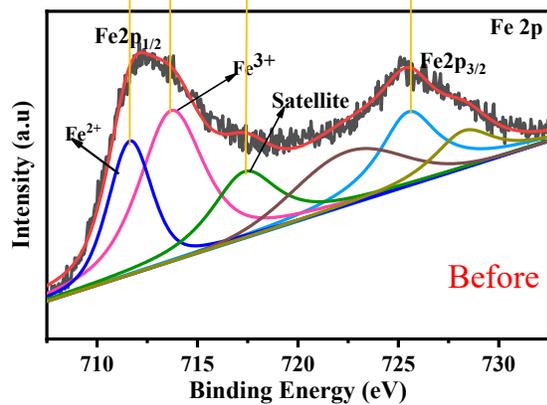
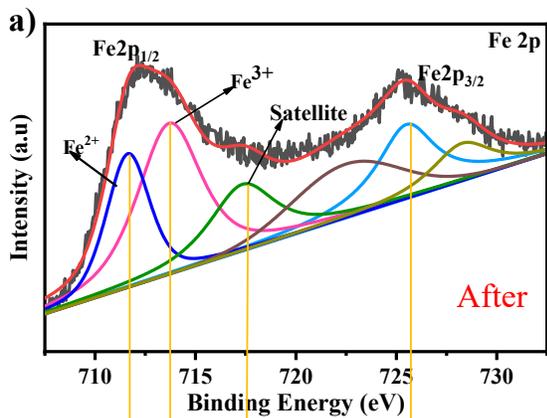
**Figure S20.** Experimental work flow used to reliably verify the nitrogen reduction reaction ( $N_2RR$ ).

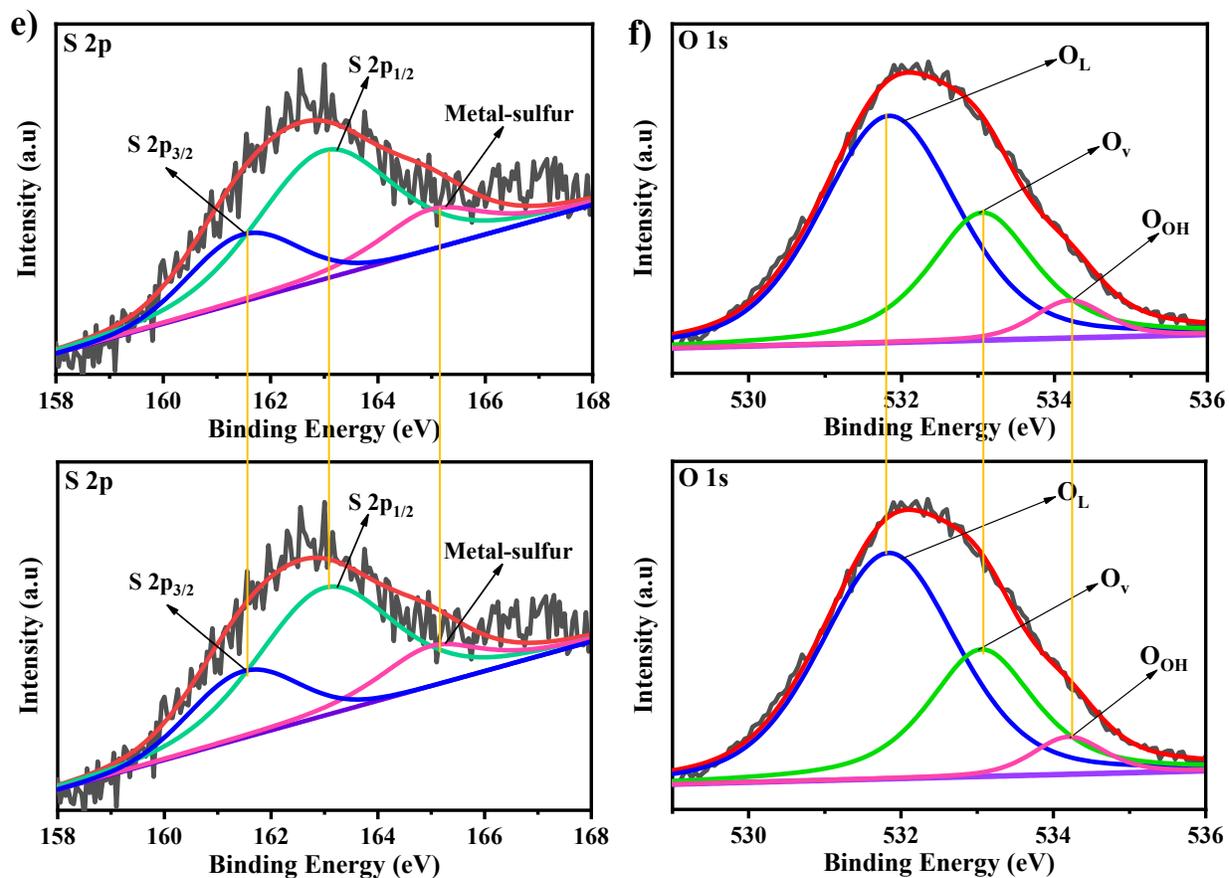


**Figure S21.** The catalysis curves for  $FeMoO_4/CuFe_2S_3/CuSe_2$  in a  $N_2$ -saturated 0.5 M  $Na_2SO_4$  electrolyte solution at -0.6 V vs. RHE over 16 hours in an H-cell.

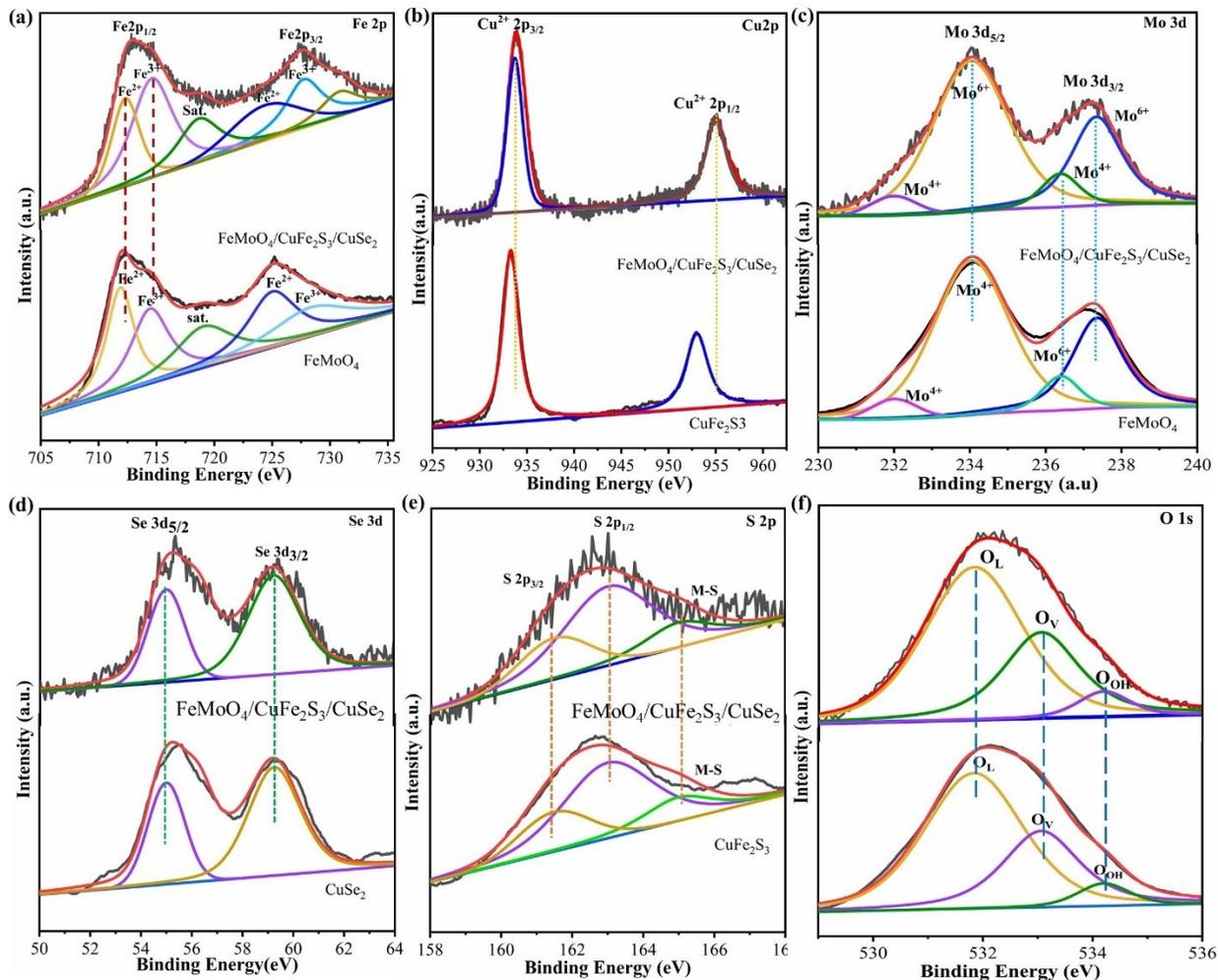


**Figure S22.** XPS survey spectrum of  $\text{FeMoO}_4/\text{CuFe}_2\text{S}_3/\text{CuSe}_2$  before and after stability test.





**Figure S23.** XPS spectra of (a) Fe 2p, (b) Mo 3d, (c) Cu 2p, (d) Se 3d, (e) S 2p, and (f) O 1s for the FeMoO<sub>4</sub>/CuFe<sub>2</sub>S<sub>3</sub>/CuSe<sub>2</sub> catalyst before and after stability tests.



**Figure S24.** XPS analyses of  $\text{FeMoO}_4$ ,  $\text{CuFe}_2\text{S}_3$ , and  $\text{CuSe}_2$  alongside the  $\text{FeMoO}_4/\text{CuFe}_2\text{S}_3/\text{CuSe}_2$  electrocatalyst, highlighting the differences in their surface chemical states.

**Table S5.** Comparison of the  $\text{N}_2\text{RR}$  activity for  $\text{FeMoO}_4/\text{CuFe}_2\text{S}_3/\text{CuSe}_2$  with other recently reported catalysts.

No.	Catalyst	Synthesis method	Potential vs. RHE (V)	Electrolyte	$\text{NH}_3$ yield rate	FE (%)	Ref.
1	$\text{FeMoO}_4/\text{CuFe}_2\text{S}_3/\text{CuSe}_2$	Hydrothermal	-0.6	0.5M $\text{Na}_2\text{SO}_4$	$6.15 \text{ mg h}^{-1} \text{ cm}^{-2}$	93.8	This work
2	$\text{Bi}_2\text{MoO}_6/\text{Cu}_8\text{S}_5$	Hydrothermal	-0.6	0.5M $\text{Na}_2\text{SO}_4$	$6.75 \text{ mg h}^{-1} \text{ cm}^{-2}$	57.9	4
3	$\text{Cu}_2\text{Mn}_3\text{O}_8/\text{CeS}_2$	Hydrothermal	-0.689	0.5M $\text{Na}_2\text{SO}_4$	$4.60 \text{ mg h}^{-1} \text{ cm}^{-2}$	47.2	5
4	$\text{Fe}_2\text{V}_4\text{O}_{13}/\text{Mo}_2\text{S}_3$	Hydrothermal	-0.7	0.5M $\text{Na}_2\text{SO}_4$	$5.46 \text{ mg h}^{-1} \text{ cm}^{-2}$	47.6	6

5	Cu <sub>4</sub> Bi <sub>5</sub> S <sub>10</sub> /Mn <sub>4</sub> V <sub>2</sub> O <sub>9</sub>	Hydrothermal	-0.6	0.5M KOH	4.36 mg h <sup>-1</sup> cm <sup>-2</sup>	46.1	7
6	(V, Ni, Mn) <sub>3</sub> O <sub>4-x</sub> /Nb <sub>2</sub> O <sub>5-y</sub>	Hydrothermal	-0.5	0.1M Na <sub>2</sub> SO <sub>4</sub>	3.19 mg h <sup>-1</sup> cm <sup>-2</sup>	22.7	8
7	(Fe,Mn,Ga) <sub>3</sub> O <sub>4-x</sub> / (Mn,Fe) <sub>2</sub> O <sub>3-y</sub>	Hydrothermal	-0.6	0.1M Na <sub>2</sub> SO <sub>4</sub>	2.04 mg h <sup>-1</sup> cm <sup>-2</sup>	5.77	9
8	Cu <sub>3</sub> BiS <sub>3</sub> /MnO <sub>2</sub>	Hydrothermal	-0.75	0.5M Na <sub>2</sub> SO <sub>4</sub>	3.60 mg h <sup>-1</sup> cm <sup>-2</sup>	31.4	10
9	CoFeB	Chemical reduction method	-0.2	0.05 M H <sub>2</sub> SO <sub>4</sub>	3.5×10 <sup>-2</sup> mg h <sup>-1</sup> cm <sup>-2</sup>	31.6	11
10	NiS <sub>x</sub> /MoS <sub>2</sub>	Hydrothermal	-0.60	0.1 M Na <sub>2</sub> SO <sub>4</sub>	3.43×10 <sup>-2</sup> mg h <sup>-1</sup> cm <sup>-2</sup>	48.53	12
11	Bi <sub>2</sub> S <sub>3</sub> /MoS <sub>2</sub>	Hydrothermal	-0.40	0.1 M Na <sub>2</sub> SO <sub>4</sub>	5.46×10 <sup>-2</sup> mg h <sup>-1</sup> cm <sup>-2</sup>	58.56	13
12	MoSe <sub>2</sub>	Chemical etching &CVD process	-0.3	0.1 M Na <sub>2</sub> SO <sub>4</sub>	6.16×10 <sup>-3</sup> mg h <sup>-1</sup> cm <sup>-2</sup>	37.82	14
13	(Vr-ReSe <sub>2</sub> @CBC)	Combining hydrothermal, heat treatment	-0.25	0.1M Na <sub>2</sub> SO <sub>4</sub>	28.3 mg h <sup>-1</sup> cm <sup>-2</sup>	42.5	15
14	TiO <sub>2</sub> /Ag/Cu <sub>7</sub> S <sub>4</sub> @Se	Electrodeposition	-0.20	0.1 M KOH	39.16 mg h <sup>-1</sup> cm <sup>-2</sup>	51.05	16
15	FeCuS <sub>x</sub>	-	-0.1	0.1 M KOH.	1.37×10 <sup>-2</sup> mgh <sup>1</sup> cm <sup>-2</sup>	53.78	17
16	B <sub>4</sub> C/CNTs	-	-0.6	0.1M Na <sub>2</sub> SO <sub>4</sub>	3.36×10 <sup>-2</sup> mgh <sup>1</sup> cm <sup>-2</sup>	78.2	18
17	B-TiO <sub>1.8</sub>	Hydrothermal	-0.1	0.1 M Li <sub>2</sub> SO <sub>4</sub>	3.16×10 <sup>-2</sup> mgh <sup>1</sup> cm <sup>-2</sup>	47.7	19
18	V <sub>Pd</sub> -PdH <sub>0.41</sub>	Facile wet-chemical way	-0.05	0.1 M Li <sub>2</sub> SO <sub>4</sub>	6.58 mg h <sup>1</sup> cm <sup>-2</sup>	46.5	20

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