

Electronic Supplementary Information

Exploring the Source of Ammonia Generation in Electrochemical Nitrogen Reduction using Niobium Nitride

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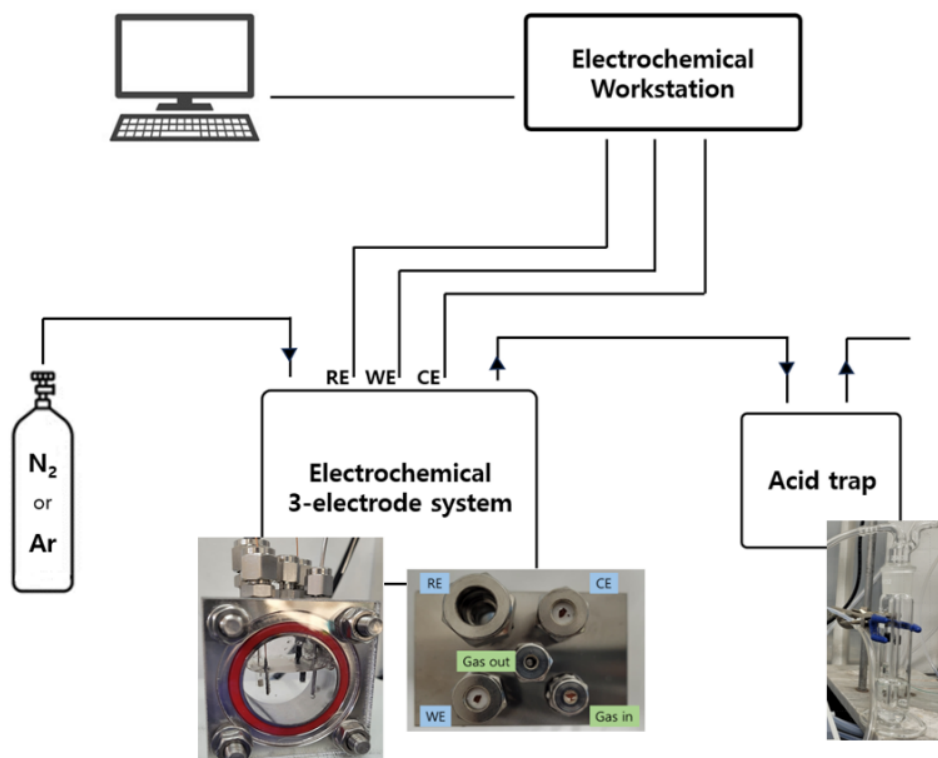


Fig. S1. Schematic illustration and photographs of the electrochemical measurement system.

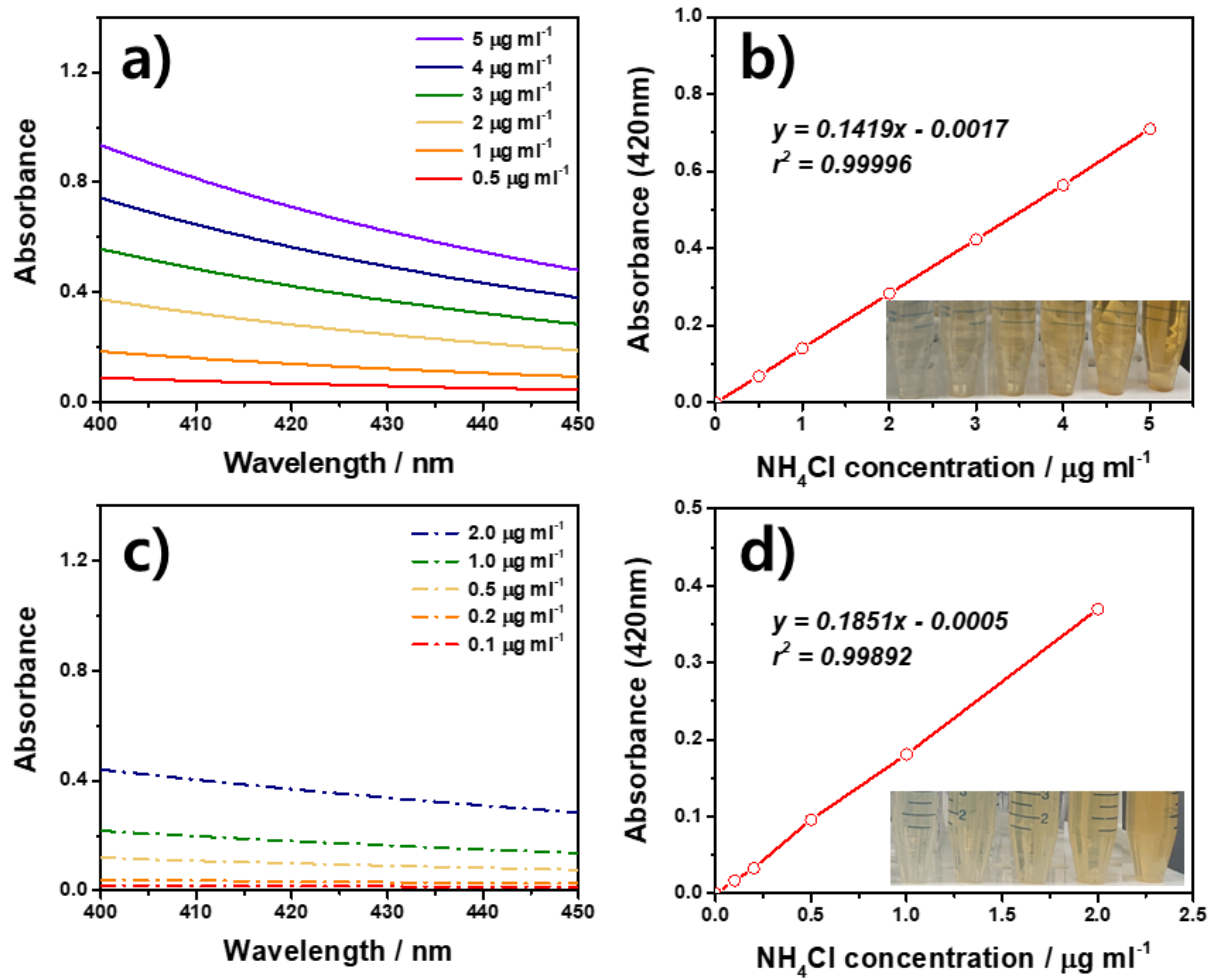


Fig. S2. Ammonia detection method and calibration curves for Nessler's method a) in alkaline electrolyte, b) its calibration curve ($y = 0.1419x - 0.0017$, $r^2 = 0.99996$) and c) in acid trap, d) its calibration curve ($y = 0.1851x - 0.0005$, $r^2 = 0.99892$).

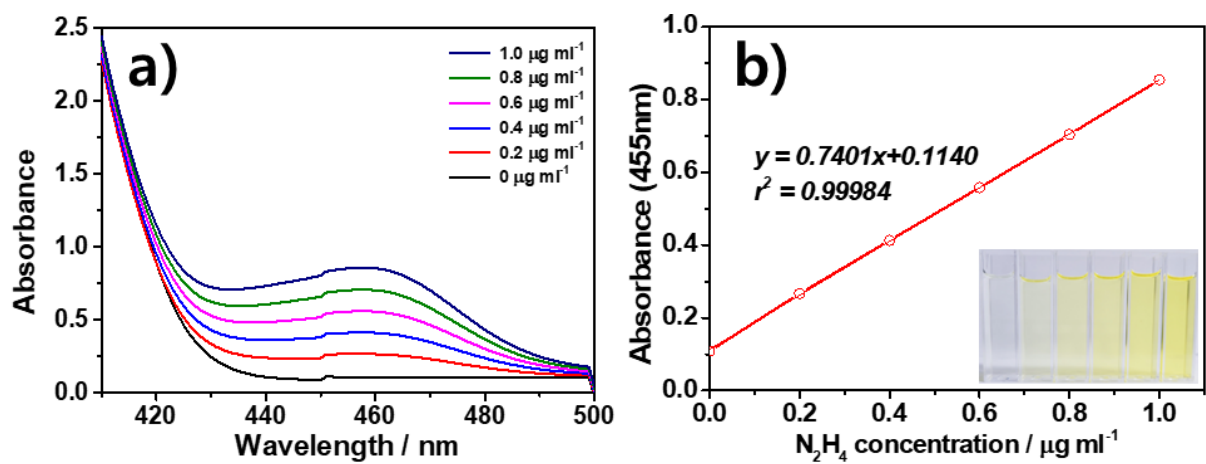


Fig. S3. Hydrazine detection method using a) Watt and Chrisp method and b) calibration curve ($y = 0.7401x + 0.1140$, $r^2 = 0.99984$) of Watt and Chrisp method.

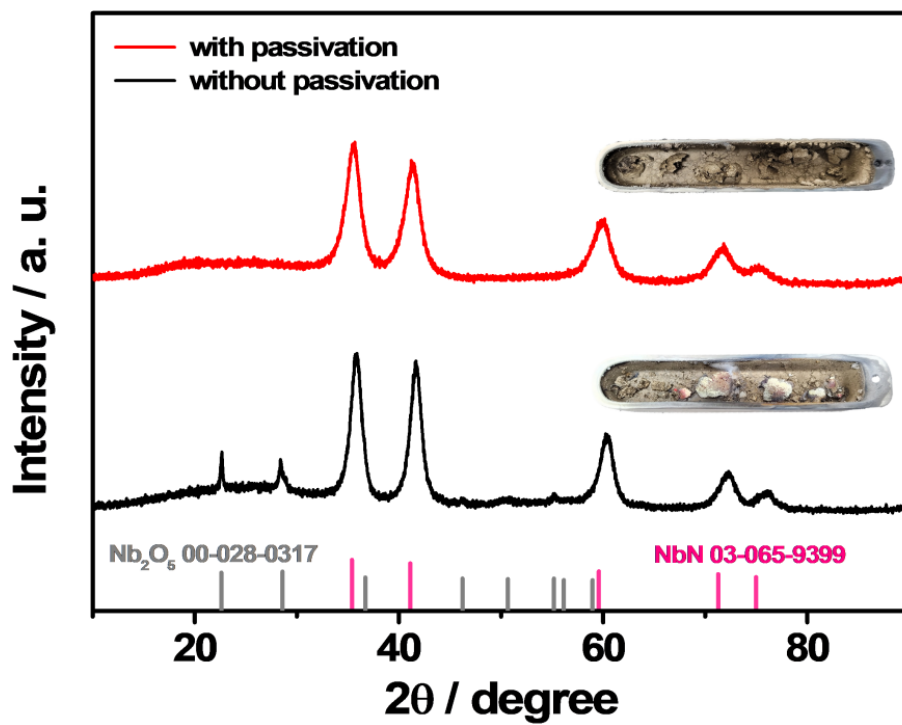


Fig. S4. XRD patterns of prepared catalysts with/without passivation.

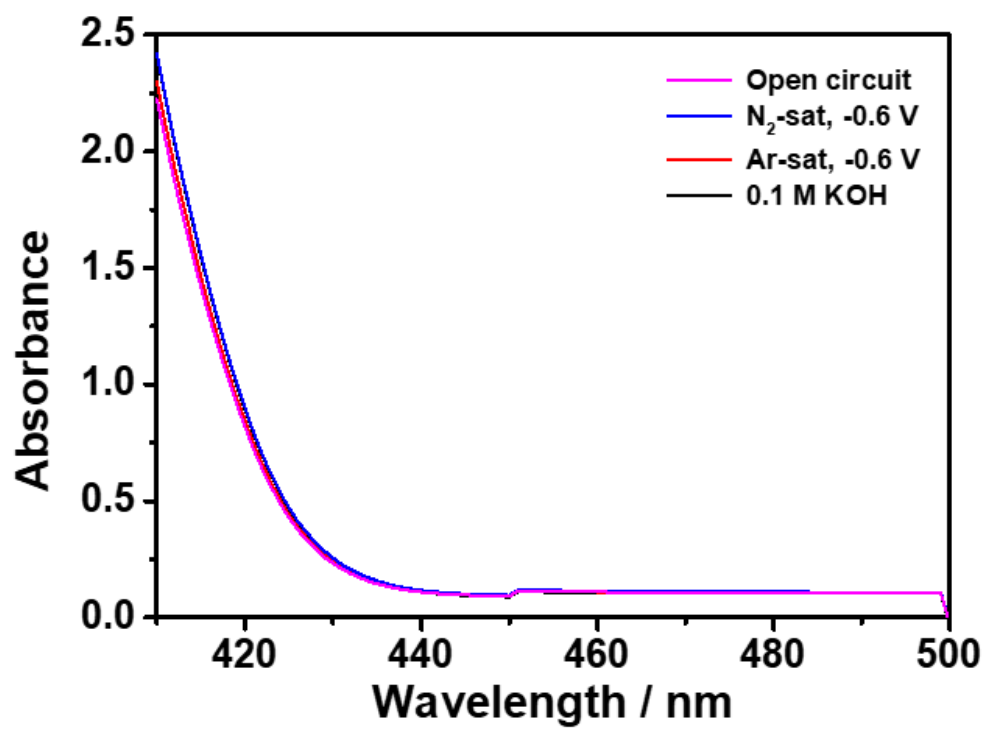


Fig. S5. Hydrazine detection in control experiments.

Table. S1. Employed characterization methods for leaching of TMN-based catalysts in NRR.

Catalyst	Electrolyte	Methods			Ref.
		¹⁵ N ₂ isotope & NMR	Detection of leached atoms	Acid trap	
NbN	0.1 M KOH	O	ICP-OES (Nb) UV-vis (N)	O	This work
Mo ₂ N	0.1 M HCl	O	—	—	ACS Energy Lett. 2019, 4, 1053-1054
VN	0.05 M H ₂ SO ₄	O	—	O	ACS Sustain. Chem. Eng. 2019, 7, 6839-6850
CrN	0.05 M H ₂ SO ₄	O	ICP-MS (Cr) CHN-EA (N)	O	J. Mater. Chem. A 2021, 9, 8568-8575

Table. S2. The detected amount of Nb, N and Nb/N molar ratio at various potentials.

Potentials (vs RHE)	Nb (ICP-OES)	NH₃-N (UV-vis)	Molar Ratio (Nb : N)
-0.3V	2.79 μmol	2.90 μmol	0.96 : 1
-0.4V	3.26 μmol	2.73 μmol	1.19 : 1
-0.5V	3.29 μmol	2.79 μmol	1.18 : 1
-0.6V	3.84 μmol	3.82 μmol	1.00 : 1
OCP	3.20 μmol	2.88 μmol	1.11 : 1