

Bias-Free Solar to Ammonia Photoelectrochemical Conversion Using Perovskite-Silicon Tandem Absorber and 1T-MoS₂ Integration

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tandem; 1T-MoS₂

1. Synthesis of 1T-MoS₂

1T-MoS₂ were synthesized using a straightforward hydrothermal method. In a typical synthesis, 2.5 mM of H₂MoO₄ and 6.25 mM of CH₄N₂S were dissolved in 40 mL of distilled water and stirred vigorously for 30 minutes to form a homogeneous solution. This solution was then transferred to a Teflon-lined stainless-steel autoclave, which was subsequently sealed. The autoclave was heated to 180°C for 24 hours, and then allowed to cool to room temperature. The resulting product was washed several times with deionized water and ethanol to remove any residual reactants. Finally, the sample was dried at 60°C to obtain a shiny black powder of 1T-MoS₂. The MoS₂ ink was prepared using the 10 mg of MoS₂ powder mixed with 990 μL IPA and 10 μL Nafion.

2. Indophenol blue test for the quantification of NH₃

The indophenol method coupled with UV-vis spectroscopy is employed to detect and quantify the yield of NH₃ in the solution. First, 1 mL of electrolyte was collected from the cathodic cell. The collected sample was reacted with 100 μL of oxidizing solution containing NaClO (pCl = 6–14) in 1 M NaOH. Then, 100 μL of 0.5 M phenol solution and 50 μL of catalyst solution containing 0.002 M sodium nitroprusside were added. The solution mixture was gently mixed for 30 seconds and then kept in the dark for 30 minutes. The absorbance of the resulting solution was measured at 640 nm using a UV-vis spectrophotometer. The concentration of NH₃ was quantified using a concentration-absorbance calibration curve. Standard NH₄Cl solutions with NH₄⁺ concentrations ranging from 1 to 10 mg/mL in Li₂SO₄ were used to calibrate the concentration-absorbance curve.

3. Isotopic Labeling Studies Using ¹⁴N₂ and ¹⁵N₂

Isotopic labeling studies were conducted using both ¹⁴N₂ and ¹⁵N₂ as feeding gases to investigate the nitrogen reduction reaction (NRR). The ¹⁵N₂ gas, with 99% ¹⁵N₂ enrichment, was supplied by Sigma-Aldrich. To ensure high purity, both ¹⁴N₂ and ¹⁵N₂ gases were passed through a saturator containing 0.05 M H₂SO₄.

The electrocatalytic reaction was carried out at 0.2 V for 4 hours, with continuous purging the electrolyte with saturated ¹⁵N₂ gas. After the reaction, the solution was concentrated to 2.0 mL by heating at 80°C for 3 hours. The pH of the concentrated solution was adjusted to approximately 3 by adding 0.01 M HCl. Finally, 1 mL of the concentrated solution was mixed with 0.2 mL of d₆-DMSO, and this mixture was used for 1H NMR spectroscopy measurement.

4. Electron paramagnetic resonance spectroscopy of hydrothermally synthesized 1T-MoS₂

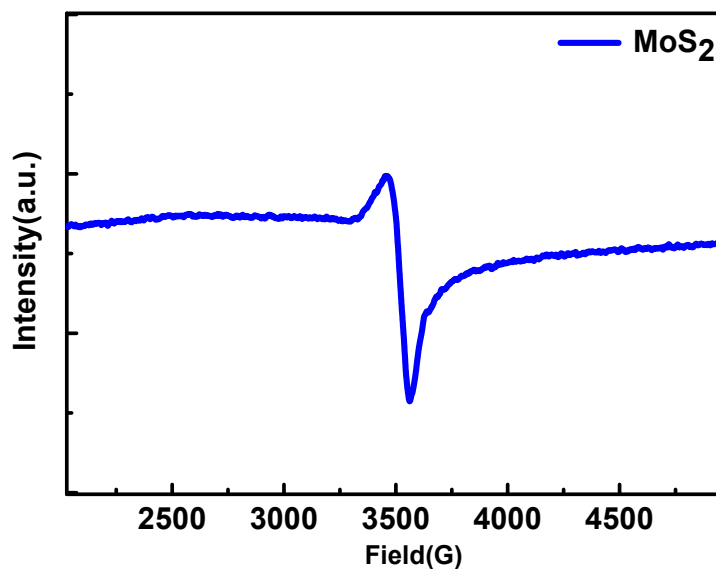


Figure S1. EPR of hydrothermally synthesized 1T-MoS₂ with a predominant signal at $g=2.004$ assigned to S vacancy.¹

5. Energy-dispersive X-ray spectroscopy (EDS) of hydrothermally synthesized 1T-MoS₂

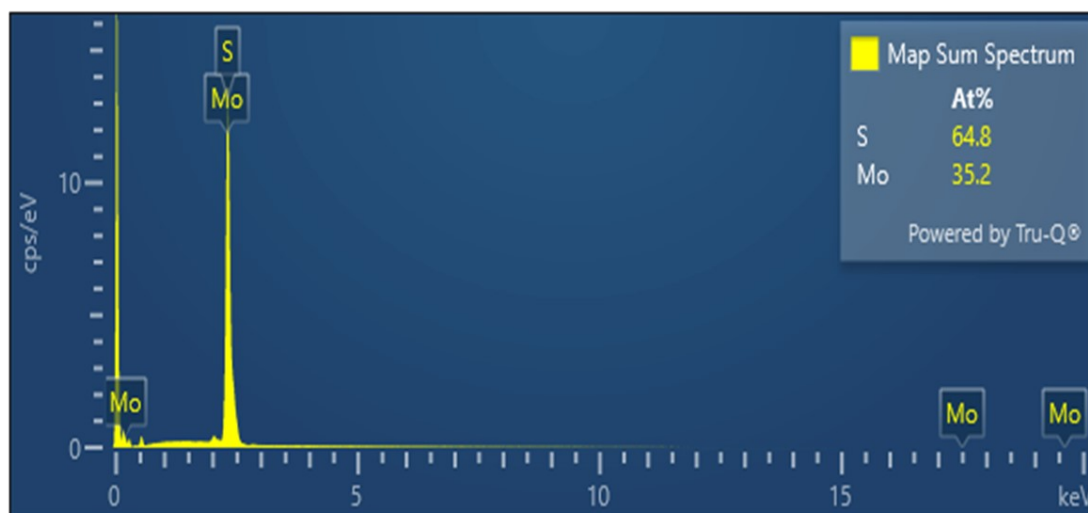


Figure S2. EDS of hydrothermally synthesized 1T-MoS₂ with atomic Mo/S ratio of 1.84

6. Electrochemical (EC) performance of 1T-MoS₂

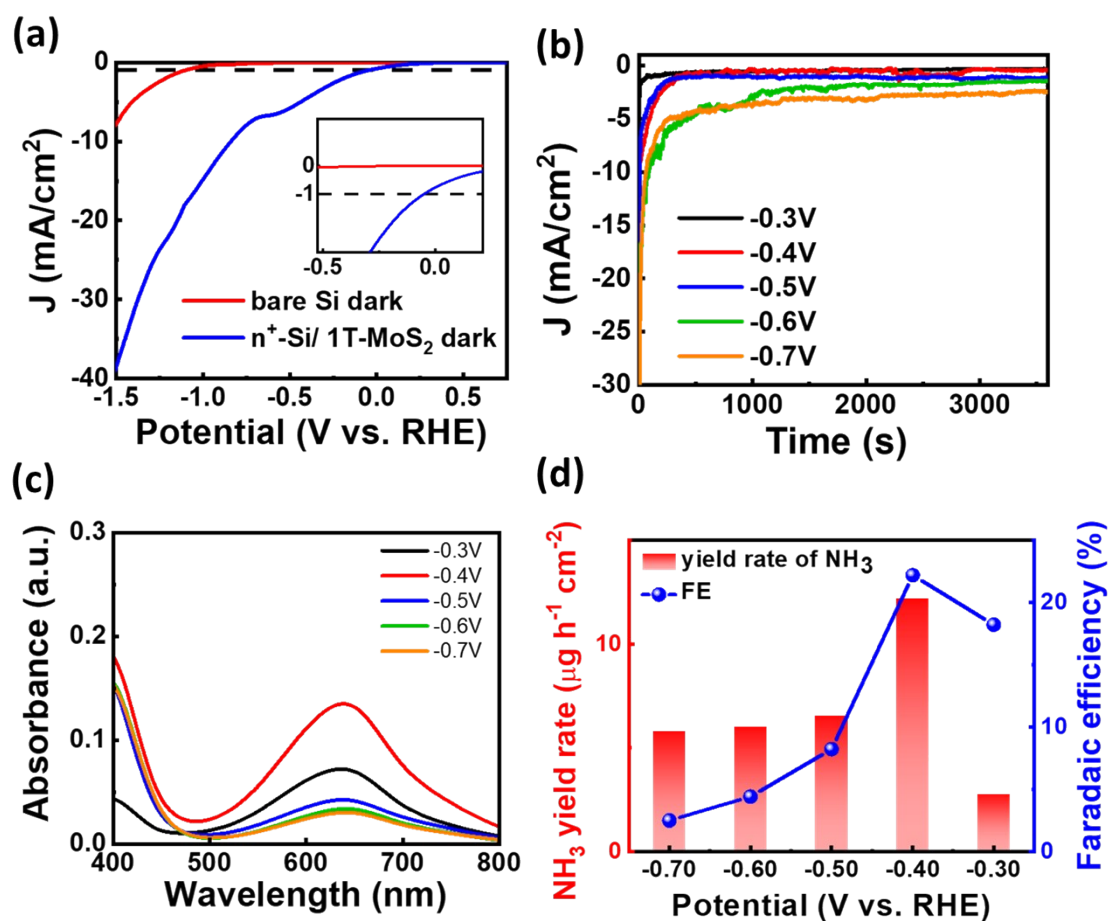


Figure S3. (a) LSV of EC NRR using bare Si (red line) and n⁺-Si/1T-MoS₂ (blue line) as dark electrodes. (b) EC NRR chronoamperometric (CA) measurement based on n⁺-Si/1T-MoS₂ at various potentials and (c) the corresponding absorption by using UV-Vis spectra measurement. (d) Faradaic efficiency and yield rate of EC NRR production.

7. Watt and Chrisp test for N₂H₄ identification²

The coloring agent was prepared by mixing 5.99 g of para-(dimethylamino) benzaldehyde with 30 mL of HCl and 300 mL of ethanol. 9 mL of 1.0 M HCl was added to 1 mL of electrolyte (after the reaction) and was followed by the addition of 5 mL of coloring agent. The UV-Vis spectrum was recorded after incubating for 30 min to measure the absorbance at 455 nm.³

The result that obtained in this work was presented in Fig. S4, where no hydrazine is detectable in the electrolyte.

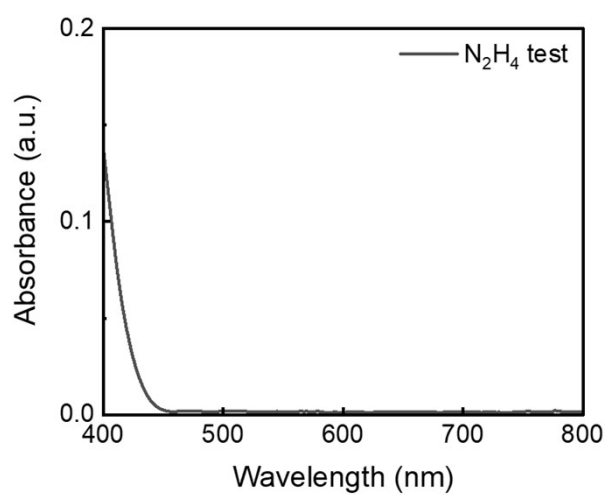


Figure S4. UV-Vis spectrum for hydrazine test by the Watt and Chrisp method.

8. Fabrication of semi-transparent perovskite solar cell (ST-PSC) and 2-series semi-transparent perovskite solar module (ST-PSM)

Preparation of Cs_{0.4}FA_{0.6}Pb(I_{0.8}Br_{0.2})₃ precursor

29.99 mg formamidinium bromide (FABr), 82.55 mg formamidinium iodide (FAI), 102.15 mg cesium bromide (CsBr) and 580.87 mg lead iodide (PbI₂) are dissolved in the mixture solvent of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) in the glovebox to form 1.2 M Cs_{0.4}FA_{0.6}Pb(I_{0.8}Br_{0.2})₃ precursor.

Fabrication of p-i-n semi-transparent perovskite solar cell

Sol-gel NiO_x solution is spin coated on to the pre-clean ITO substrate at 4000 rpm for 20 seconds and then thermal annealed at 300°C for 5 minutes in an ambient environment, forming a hole transport layer (HTL). It is subsequently transferred to a N₂-filled glovebox for depositing perovskite layer. The perovskite precursor is filtered through a 0.45 μm PTFE filter and deposited on the HTL by a 2-step spin coating process. It begins at a rate of 1000 rpm for 5 s and followed by 5000 rpm for 30 s. During the process, an antisolvent ethyl acetate is dripped on to the sample. The

resulting film was thermally annealed at 140°C for 10 minutes for the conversion of perovskite thin film. Then electron transport layer of PCBM is spin coated at 1000 rpm for 20 s. Next, as-synthesized SnO₂ solution is freshly used, and spin coated on to PCBM at 1500 rpm for 30 s. A mild heat treatment at 70°C for 1 minute is carried out to dry the solvent. Top ITO electrode is sputtered at a working pressure of 3 mTorr with a sputtering power of 50 W for 7200 s..

Fabrication of 2-series module

To fabricate 2-series module, two ST-PSCs are fabricated following the abovementioned procedures on the same ITO substrate. Then a 120 nm Ag connection is deposited to connect the top and bottom ITO of individual ST-PSC in a series circuit, as shown in the Fig. S5. Each cell has an active area of 0.16 cm².

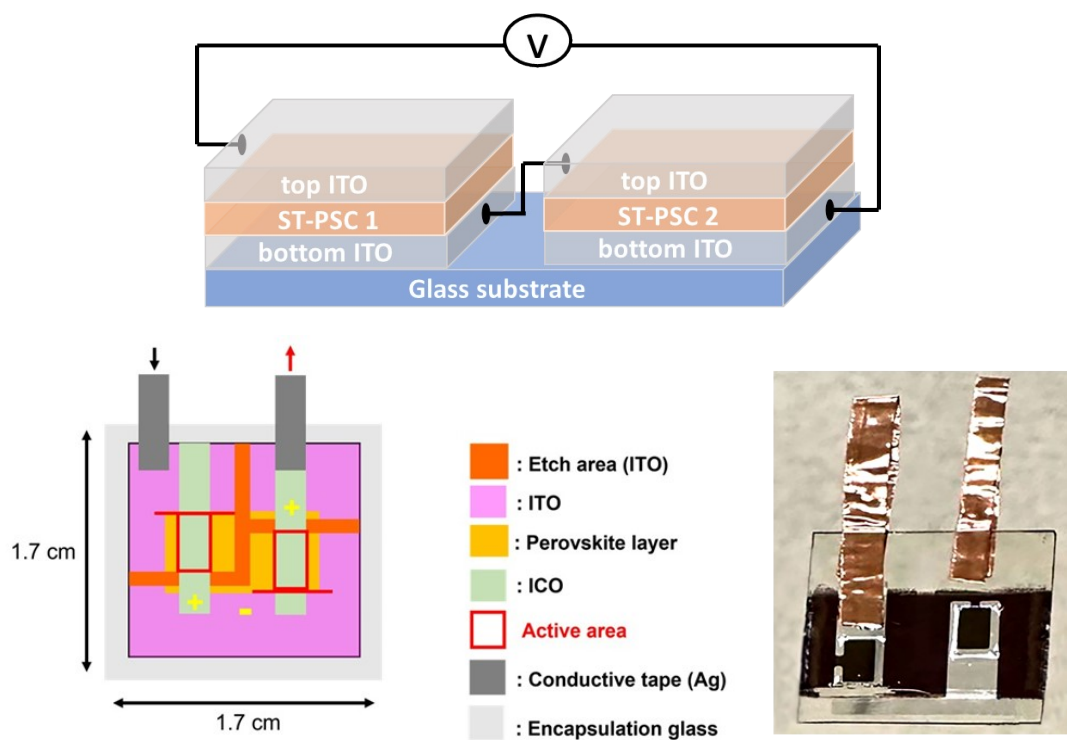


Figure S5. Planar configuration of 2-series ST-PSM. Individual ST-PSCs are connected by depositing an Ag connection.

9. Tafel analysis of PEC NRR in various Li_2SO_4 concentrations.

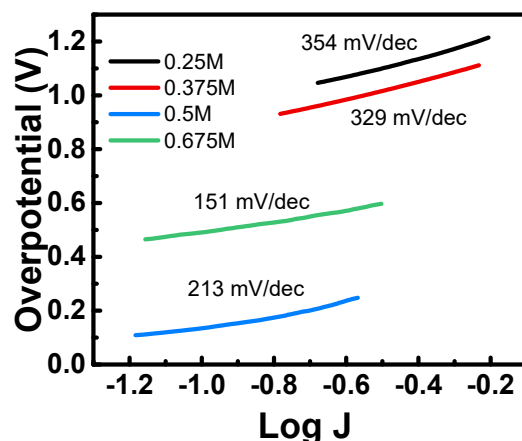


Fig. S6. Tafel slopes of PEC NRR of Si photoelectrode with 1T- MoS_2 in various Li_2SO_4 concentrations.

10. NRR performance metrics of reported studies using MoS_2 as catalyst.

Catalyst	Reaction type*	Yield rate	FE (%)	Ref.
$\text{MoS}_2/\text{C}_3\text{N}_4$	EC	$18.5 \mu\text{g h}^{-1} \text{mg}^{-1}$	17.8	4
Ru- MoS_2	EC	$0.11 \text{ nmol s}^{-1} \text{cm}^{-2}$	17.6	5
Co- MoS_2	EC	$0.63 \text{ mmol h}^{-1} \text{g}^{-1}$	~10	6
1T- MoS_2-Ni	EC	$1.05 \mu\text{g min}^{-1} \text{cm}^{-2}$	27.66	7
$\text{MoS}_2/\text{TiO}_2$	PEC	$24.1 \mu\text{g h}^{-1} \text{cm}^{-2}$	65.52	8
1T- $\text{MoS}_2@/\text{Ti}_3\text{C}_2$	EC	$30.33 \mu\text{g h}^{-1} \text{mg}^{-1}$	10.94	9
g-C_3N_4/1T- MoS_2	EC	$71.07 \mu\text{g h}^{-1} \text{mg}^{-1}$	21.01	10
S vacancy 1T- $\text{MoS}_2@/\text{MoO}_3$	EC	$116.1 \mu\text{g h}^{-1} \text{mg}^{-1}$	18.9	11
CoS_2/1T- MoS_2	EC	$59.3 \mu\text{g h}^{-1} \text{mg}^{-1}$	26.6	12
1T- MoS_2	EC	$12.2 \text{ mg h}^{-1} \text{cm}^{-2}$	22.2	This work
1T- MoS_2	PEC	$18.3 \text{ mg h}^{-1} \text{cm}^{-2}$	28.6	This work
1T- MoS_2	Unbiased PEC	$167.7 \text{ mg h}^{-1} \text{cm}^{-2}$	22.5	This work

*EC: electrochemical reaction, PEC: photoelectrochemical reaction

Reference

1. M. Pan, X. Zhang, C. Pan, J. Wang and B. Pan, *ACS Applied Materials & Interfaces*, 2023, **15**, 19695-19704.
2. G. W. Watt and J. D. Chrisp, *Analytical Chemistry*, 1952, **24**, 2006-2008.
3. C. Lv, C. Lee, L. Zhong, H. Liu, J. Liu, L. Yang, C. Yan, W. Yu, H. H. Hng and Z. Qi, *ACS nano*, 2022, **16**, 8213-8222.
4. K. Chu, Y.-p. Liu, Y.-b. Li, Y.-l. Guo and Y. Tian, *ACS applied materials & interfaces*, 2020, **12**, 7081-7090.
5. B. H. Suryanto, D. Wang, L. M. Azofra, M. Harb, L. Cavallo, R. Jalili, D. R. Mitchell, M. Chatti and D. R. MacFarlane, *ACS Energy Letters*, 2018, **4**, 430-435.
6. J. Zhang, X. Tian, M. Liu, H. Guo, J. Zhou, Q. Fang, Z. Liu, Q. Wu and J. Lou, *Journal of the American Chemical Society*, 2019, **141**, 19269-19275.
7. S. B. Patil, H.-L. Chou, Y.-M. Chen, S.-H. Hsieh, C.-H. Chen, C.-C. Chang, S.-R. Li, Y.-C. Lee, Y.-S. Lin and H. Li, *Journal of Materials Chemistry A*, 2021, **9**, 1230-1239.
8. W. Ye, M. Arif, X. Fang, M. A. Mushtaq, X. Chen and D. Yan, *ACS Applied Materials & Interfaces*, 2019, **11**, 28809-28817.
9. X. Xu, B. Sun, Z. Liang, H. Cui and J. Tian, *ACS Applied Materials & Interfaces*, 2020, **12**, 26060-26067.
10. R. Liu, T. Guo, H. Fei, Z. Wu, D. Wang and F. Liu, *Advanced Science*, 2022, **9**, 2103583.
11. X. Zi, J. Wan, X. Yang, W. Tian, H. Zhang and Y. Wang, *Applied Catalysis B: Environmental*, 2021, **286**, 119870.
12. S. Liu, G. Yang, L. Zhao, Z. Liu, K. Wang, X. Li and N. Li, *Inorganic Chemistry*, 2022, **61**, 7608-7616.