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Introduction

Ammonia serves various essential purposes in human society, functioning as a fertilizer, a precursor for chemical production, and a non-carbon fuel for transportation.¹⁻⁴ As the global

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Bias-free solar to ammonia photoelectrochemical conversion using a perovskite-silicon tandem absorber and 1T-MoS₂ integration⁺

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Ammonia, as a non-carbon fuel, is increasingly in demand due to global population growth. Traditional ammonia production *via* the Haber–Bosch process is energy-intensive, requiring high temperatures and pressures, which lead to significant carbon dioxide emissions. This study presents a sustainable alternative through the bias-free photoelectrochemical (PEC) nitrogen reduction reaction (NRR) to realize artificial photosynthesis for solar to ammonia conversion, utilizing a perovskite-silicon tandem absorber integrated with a 1T-MoS₂ catalyst. The experimental results demonstrate a promising solar-to-ammonia conversion efficiency of 1.48% (0.5 M Li₂SO₄ electrolyte) under one sun illumination (100 mW cm⁻², AM 1.5G) without external bias, achieving bias-free artificial photosynthesis of ammonia. This device configuration shows promising direct solar to ammonia conversion and leverages cost-effective and abundant materials, offering a viable solution for large-scale ammonia synthesis. The success of this system underscores the potential of utilizing renewable solar energy for sustainable chemical production, marking a significant advancement in the field of solar-to-fuel conversion and opening new avenues for environmentally friendly ammonia synthesis.

population grows, the demand for ammonia has risen steadily in recent years. Consequently, there is a critical need for costeffective and large-scale ammonia production in the future. The widely adopted method for ammonia production on an industrial scale is the Haber-Bosch process.5 This process, however, requires high temperatures (400-500 °C) and high pressures (150-350 atm), leading to carbon dioxide emissions during production. A more sustainable alternative gaining substantial research attention is the aqueous-based electrocatalytic (EC) nitrogen reduction reaction (NRR) performed at ambient temperature and pressure to reduce carbon dioxide emissions. The electrocatalytic NRR is a process that involves breaking the triple bond of N2 with suitable catalysts to form NH_3 (N₂ + 6H⁺ + 6e⁻ \rightarrow 2NH₃). Thus, developing efficient electrocatalysts for the NRR with high ammonia conversion efficiency is essential. Many electrocatalysts have been reported for efficient NRR, such as precious metals (e.g., Au-based catalyst amorphous Au nanoparticles on CeO_x-RGO support and Au flower microstructures), transition metal-based compound catalysts (e.g., vanadium and cobalt oxynitride, cobalt oxide, and cobalt phosphide), and transition metal dichalcogenides (e.g., $MoSe_2$ and MoS_2). Among them MoS_2 stands out as a cost effective, abundant, and highly tunable material for NRR catalysis. Its high selectivity, stability, and adaptability for integration with advanced systems make it a strong candidate

for sustainable ammonia production compared to other materials. $^{\rm 6-12}$

In contrast to the EC approach, the photoelectrochemical (PEC) techniques integrate photochemical and electrochemical processes in a device, representing a more promising and energy-efficient method to facilitate the NRR using renewable solar energy. The typical device architectures for PEC devices consist of semiconducting light absorbers for light harvesting integrated with catalysts for redox reactions. Utilizing solar energy to convert nitrogen into value-added chemicals provides a promising platform for solar-to-fuel conversion. Various PEC cells have been proposed based on different materials, such as black phosphorus, or metal nanoparticles deposited on a silicon photocathode, that demonstrate promising Faraday efficiencies (FEs).13-15 However, although promising progress in the PEC NRR based on the abovementioned light absorbers or catalysts has been demonstrated, most PEC NRR studies are based on half-cells, and these devices usually require an extra applied voltage to achieve solar-to-ammonia conversion. A selfpowered PEC system, operating without the need for external bias, is essential for mimicking the natural photosynthesis process, where leaves efficiently convert solar energy into chemical energy. Recently, Ho et al. reported an unassisted artificial leaf device using a tandem junction of the InGaP/GaAs/ Ge/Ni photoelectrode integrated with a Au thin film to achieve direct solar to ammonia (STA) conversion.16 The generated photovoltage effectively overcomes the reaction barrier for spontaneous ammonia synthesis, realizing an STA efficiency of 1.1% under 0.2 sun illumination. In this work, we would like to demonstrate a bias-free solar-to-ammonia conversion based on a cost-effective perovskite-silicon tandem absorber system integrated with a 1T-MoS₂ catalyst. We employed a backilluminated p-n junction Si photocathode to decouple lightharvesting from the catalytic surface to maximize photon absorption for efficient PEC NRR. To further accomplish spontaneous NRR solely powered by solar energy, a semitransparent perovskite solar module is paired with a Si photoelectrode to form a tandem light absorber for additional photovoltage to overcome the thermodynamic barrier. Based on this design, we have accomplished unassisted solar NRR and achieved an STA conversion efficiency of 1.48% under one sun illumination (100 mW cm⁻², AM1.5 G) without requiring an extra bias, realizing unassisted artificial photosynthesis of ammonia by harvesting sustainable solar energy.

Results and discussion

1T-MoS₂ has recently received considerable attention as a costeffective and promising catalyst for various electrochemical energy conversions due to its earth abundance and excellent catalytic activities.^{17,18} This is primarily attributed to its intrinsic metallic properties and highly active surface.^{19,20} It exhibits exceptional electronic conductivity, approximately six orders of magnitude higher than that of its 2H-MoS₂ semiconducting counterpart. Recently, Patil *et al.* reported that 1T-MoS₂ was used as an electrocatalyst, and an EC NRR faradaic efficiency of 27.66% was achieved.¹⁰ Furthermore, the EC NRR activity also benefits from the unsaturated coordination sites in the 1T-MoS₂ lattice. These dangling bonds are NRR active sites because they have abundant localized electrons to preserve charge neutrality and weaken the N2 triple bond.20,21 Here, 1T-MoS2 has been synthesized by using a hydrothermal route, which has been demonstrated to enrich the number of active sites and enhance the electrocatalytic activity of 1T-MoS₂ by creating structural disorder in the lattice.^{10,22,23} The experimental details for the hydrothermal synthesis of 1T-MoS₂ are described in the ESI.† Fig. 1(a) shows the electron scanning microscopy (SEM) image of the as-synthesized 1T-MoS₂. It shows a flower-like cluster morphology with an average cluster size of 500 nm to 1 µm, and each cluster comprises numerous 1T-MoS₂ nanosheets. The high resolution transmission electron microscopy (HRTEM) image of the nanosheet in Fig. 1(b) shows that the crystal has an average planar spacing of about 0.95 nm with crystalline expansion compared with the 0.62 nm of the 2H phase (002) plane.24 To further identify the crystalline phase and chemical constituents of 1T-MoS2, X-ray diffraction (XRD), electron paramagnetic resonance spectroscopy (EPR), Raman vibrational spectroscopy, and X-ray photoelectron spectroscopy (XPS) analysis were conducted. The XRD pattern of the MoS₂ powder in Fig. 1(c) confirms that the crystalline structure has 1T phase characteristic (002) and (004) planes with peaks located at 9.18° and 18.35°, respectively.25 The EPR spectrum further revealed the presence of S vacancies in the 1T-MoS₂ lattice as shown in Fig. S1[†] which displayed the a prominent signal at g = 2.004assigned to S vacancies.^{26,27} Pristine MoS₂ is generally not paramagnetic because all electrons are paired in the crystal structure. However, when S vacancies are introduced in the MoS₂ crystal, unpaired electrons become localized near the defect sites which can be detected as paramagnetic centers by EPR. These vacancy sites and dangling bonds are usually active sites for electrochemical reactions to enhance catalytic efficiency.20,28,29 Energy-dispersive X-ray spectroscopy (EDS) in Fig. S2[†] also shows an atomic Mo/S ratio of 1.84, indicating the presence of S vacancies in the1T-MoS₂ lattice. Fig. 1(d) illustrates the Raman vibrational spectrum of the synthesized 1T- MoS_2 , revealing distinct peaks at 156 (J_1), 238 (J_2), and 337 cm⁻¹ (J_3) . These peaks correspond to the longitudinal acoustic phonon modes of 1T-MoS₂.^{30,31} The presence of these three characteristic vibration peaks confirms the successful formation of 1T-MoS₂ through the hydrothermal process. There is an additional peak in Fig. 1(d) that is located at 290 cm⁻¹ (E_{1g}), which corresponds to the in-plane vibration of S atoms. However, E1g can be observed in both the 2H and 1T phases of MoS₂ and cannot be a representative identification for the 1T phase.³² To further verify the composition of hydrothermally synthesized MoS₂, XPS measurements was carried out. Fig. 1(e) shows the Mo 3d spectra with two dominant peaks at 228.3 and 231.5 eV assigned to $Mo^{4+} 3d_{5/2}$ and $Mo^{4+} 3d_{3/2}$ of 1T phase MoS₂, respectively. Two additional minor peaks were also deconvoluted at 229.6 and 233.0 eV allocated to $\mathrm{Mo}^{4+} \, \mathrm{3d}_{5/2}$ and $Mo^{4+} 3d_{3/2}$ of 2H phase MoS₂. For the S 2p spectrum in Fig. 1(f), the $S^{2-} 2p_{3/2}$ and $2p_{1/2}$ peaks are found at 161.1 and 162.3 eV, exhibiting lower binding energy relative than the 2H phase, which has peaks at 161.6 and 163.5 eV. The lowered XPS



Fig. 1 Morphology and crystalline characterization of the as-synthesized $1T-MoS_2$ catalyst. (a) SEM image showing a cluster-like morphology composed of nanosheets. (b) HR-TEM image showing the nanosheets with an average interplanar spacing of 0.95 nm. (c) XRD spectrum displaying characteristic peaks for the (002) and (004) planes of 1T-phase MoS_2 . (d) Typical Raman spectrum of $1T-MoS_2$ with characteristic J_1 , J_2 , and J_3 peaks. (e) and (f) show the XPS spectra of Mo 3d and S 2p, respectively.

binding energy can be attributed to the enriched surrounding electron density of the Mo and S atoms in the 1T phase.^{33,34} Calculations of the peak area ratio from the deconvoluted Mo 3d and S 2p spectrum indicate that the 1T phase constitutes over 80% of the hydrothermally synthesized MoS₂, confirming its dominance in NRR catalysis. Although a small fraction of the 2H phase was detected in the XPS spectrum, no crystallographic diffraction peaks or Raman vibrations associated with the 2H phase were observed in the XRD and Raman spectra. These findings indicate that the hydrothermally synthesized MoS₂ predominantly exhibits the 1T phase, with a nanosheet morphology that offers a large surface area and numerous active sites, enhancing its suitability for electrocatalytic reactions.

Next, the 1T-MoS₂ catalyst was integrated with a Si p-n junction solar cell as the photoelectrode for the PEC NRR. Conventional photoelectrodes integrate catalysts on the same side as light illumination; consequently, solar energy can only be partially utilized for PEC due to the light-blocking properties of opaque catalyst materials. Recently, a photoelectrode that physically separates light absorption and electrocatalyst components was proposed to simultaneously enhance optical and electrical performances.14 As schematically illustrated in Fig. 2(a) for the photoelectrode structure, the 1T-MoS₂ electrocatalyst was coated on one side of the Si photoelectrode while light was harvested from the opposite side. This configuration allows the optimization of electrocatalyst coverage over the photoelectrode surface and simultaneously mitigates undesired light absorption and reflection from the 1T-MoS₂ catalyst. To fabricate this photoelectrode, the 1T-MoS₂ electrocatalyst was

spray-coated onto the Si p-n junction surface using an ink mixture of as-synthesized 1T-MoS₂ powder, isopropyl alcohol and Nafion. Detailed information regarding the MoS₂ ink formulation is provided in the ESI.† This was followed by lowtemperature thermal annealing at 60 °C in an Ar-purged environment in order to prevent the oxidation at the catalyst/Si interface and ensure excellent electrical contact for efficient photocarrier transfer and collection by the MoS₂ catalyst. Fig. 2(b) shows the resulting electrode surface morphology by SEM; 1T-MoS₂ was uniformly dispersed on the pyramid surface of the Si photoelectrode throughout the whole surface area. EDS element mapping shows the presence of Mo, S, and Si, also confirming a homogeneous distribution of the MoS₂ layer over the p-n junction Si surface. It also displays an intact interface between the 1T-MoS₂ catalyst and Si photoelectrode resulting from excellent integration.

PEC NRR conversion was performed in a standard threeelectrode electrochemical setup in an H-cell configuration with Si p–n junction/1T MoS₂ as the working electrode; a Pt wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Fig. 2(c) presents the PEC NRR linear sweeping voltage (LSV) curves of the Si p–n junction/1T-MoS₂ photoelectrode in the 0.25 M Li₂SO₄ electrolyte under standard one sun illumination. A dark electrode using an n⁺-Si (heavily doped n-Si) substrate coated with 1T-MoS₂ is also included for comparison, representing the catalyst's EC NRR performance. The 1T-MoS₂ exhibits an EC NRR onset potential of -0.15 V vs. the reversible hydrogen electrode (RHE), where the onset potential in this work is defined as the potential at



Fig. 2 (a) Photoelectrode structure with decoupled light absorption and electrocatalytic interface. Light is illuminated from the back side of the 1T-MoS₂ surface. (b) SEM and EDS patterns of spray-coated 1T-MoS₂ on the Si photoelectrode. (c) NRR LSV curves based on the Si photoelectrode (red line) and dark electrode (black line). (d) CA measurements of the PEC NRR at different overpotentials; the inset shows the corresponding UV-Vis absorption spectra stained with indophenol blue test agents. (e) Summary of PEC NRR faradaic efficiency and yield rate. (f) NMR spectra of the isotope experiments using $^{14}N_2$ and $^{15}N_2$ as feeding gases in the PEC NRR.

a current density of -1 mA cm^{-2} . Fig. S3[†] shows the EC NRR performances at various potentials; the highest faradaic efficiency of 22.2% and the highest yield rate of 12.2 $\mu g \ h^{-1} \ cm^{-2}$ were obtained at -0.4 V vs. RHE, similar to the reported EC NRR performance for the 1T-MoS₂ catalyst.¹⁰ On the other hand, the p-n junction Si/1T-MoS₂ photoelectrode demonstrates a PEC onset potential of 0.45 V vs. RHE under one sun illumination, which is positively shifted nearly 600 mV compared to the dark electrode, revealing the high photovoltage contribution by the p-n junction Si solar cell under light illumination. Subsequently, to evaluate the PEC NRR performance, five different potentials beyond the onset potential (0.3, 0.2, 0.1, 0, and -0.1 V RHE) were used for the chronoamperometric (CA) vs. measurement under one sun illumination to determine the optimal faradaic efficiency and yield rate. Fig. 2(d) shows the resulting current density of the PEC NRR at each potential for 2 hours. These reaction currents increased monolithically with the applied overpotential as observed in the LSV curve. However, at higher overpotentials (such as 0.1, 0, and -0.1 V), the parasite HER that produced H₂ microbubbles covering the catalytic active site on the electrode surface gradually decreased

the reaction current density during the CA measurement. The corresponding ammonia production amount was quantified using the indophenol blue method by measuring the absorption intensity at 635 nm. The ultraviolet-visible (UV-Vis) absorption spectra of the samples stained with indophenol blue test agents are shown in the inset of Fig. 2(d). The absorption intensity at 635 nm increased and reached a maximum when the PEC NRR reaction potential was changed from 0.3 to 0.2 V vs. RHE, signifying the increased ammonia formation with higher overpotential. The ammonia concentration decreased on further increasing the overpotential beyond 0.2 V, as revealed by the reduced absorption intensity at potentials of 0.1 to -0.1 V. Additionally, the possible by-product of N₂H₄ during the PEC NRR was also analysed using the Watt and Chrisp test.^{35,36} As shown in ESI Fig. S4,† there was no signal for N₂H₄, highlighting the efficacy of the p-n junction Si/1T-MoS₂ photoelectrode in selectively promoting the PEC NRR. In Fig. 2(e), a similar trend for faradaic efficiency and ammonia yield rate over these potentials was also obtained by analysing the CA and UV-Vis data. The PEC NRR exhibited optimal performance when reaction potential was increased from 0.3 to 0.2 V, with an enhancement in faradaic efficiency from 21.05% to 28.63% and the yield rate from 3.39 to 18.33 $\mu g \ h^{-1} \ cm^{-2}.$ On further increasing the reaction potential to more negative values, the parasite hydrogen evolution reaction became nonnegligible and resulted in an increased current density but with lower absorbance intensity compared to the reaction at 0.2 V as shown in Fig. 2(d). Therefore, the FE significantly decreased to 4.09, 1.43, and 1.98%, and yield rates dropped to 8.08, 5.43, and 9.53 μ g h⁻¹ cm⁻², correspondingly at potentials of 0.1, 0, and -0.1 V. Moreover, at these potentials, H₂ bubbles formed gradually during the catalytic process, blocking the active sites, hindering electron transfer between the electrolyte and photoelectrode and consequently reducing the current density. This phenomenon became more pronounced at higher overpotentials (e.g., 0 and -0.1 V) and caused a sudden drop in current density at 2000 second. The overall results indicated that the p-n junction Si/1T-MoS₂ photoelectrode synergistically enhances light-harvesting efficiency, facilitating photocarrier generation/collection and improving the photoelectrochemical performance for the NRR. To further confirm the generation of NH₃ over 1T-MoS₂ and to eliminate the possibility of environmental contamination in the NRR, the NRR product was further examined through isotope ¹⁵N₂ labelling experiments. Electrolyte solutions obtained from the PEC NRR experiments using ¹⁴N₂ and ¹⁵N₂ as feeding gases, operated at 0.2 V, were subjected to nuclear magnetic resonance (NMR) measurement. The distinct triplets and doublets in the 1H spectra in Fig. 2(f) were identified for the PEC NRR experiments performed with ¹⁴N₂ and ¹⁵N₂, respectively. The results provide conclusive evidence of the PEC NRR when the p-n junction Si/1T-MoS₂ photoelectrode is employed under light illumination.

Although the Si p–n junction/1T-MoS₂ photoelectrode exhibits promising PEC NRR conversion, it still requires external electrical power to convert solar energy to ammonia. Aiming for a system similar to natural photosynthesis for a biasfree NRR conversion, an artificial leaf device that operates solely

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powered by light without an external bias is crucial. To achieve the bias-free PEC NRR, this device must supply the necessary thermodynamic potential for the NRR at the cathode and the concurrent anodic reaction, such as water oxidation (OER). In addition, it must also account for any overpotentials and voltage losses occurring within the cell during operation. It has been reported that for a photoelectrochemical system involving cathodic NRR and anodic OER, a photoelectrode that provides a photovoltage of at least 1.80 V is necessary.16 However, a single p-n junction Si photoelectrode in this work can only provide a photovoltage of up to 0.6 V; therefore, it is necessary to integrate the p-n junction Si photoelectrode with an additional component to form a multi-absorbing system that generates sufficient photovoltage to meet the minimum requirement of 1.80 V to resemble artificial leaves. Given the back-illumination configuration of the p-n junction Si photoelectrode, it is ideally suited for integration with a light absorber featuring a larger optical bandgap, such as a semi-transparent organohalide perovskite solar cell. This configuration enables the formation of a tandem absorber system to maximize solar spectrum utilization, with the large-bandgap perovskite solar cell positioned at the front to capture high-energy photons and the Si photoelectrode placed behind it to utilize lower-energy photons. Solution-processable perovskite solar cells have emerged as a promising candidate for the next generation of solar cells due to their cost-effective fabrication process and high-power conversion efficiency.37 They are also excellent candidates for tandem configurations because of their relatively high opencircuit voltage and optical transparency.38,39 Herein, we developed a tandem absorber system by integrating a p-n junction Si/1T-MoS₂ photoelectrode with a semi-transparent perovskite solar cell (ST-PSC) positioned at the front. This configuration provides additional photovoltage, effectively enhancing the spontaneous NRR performance under solar illumination.

To fabricate a perovskite solar cell (PSC) that achieves high power conversion efficiency (PCE) and high optical transparency, a p-i-n PSC utilizing Cs_{0.4}FA_{0.6}Pb(I_{0.8}Br_{0.2})₃ as the photo-active layer and ITO as bottom and top electrodes was constructed. The detailed p-i-n device structure is shown in the cross-sectional SEM image in Fig. 3(a). PSCs based on the mixed cation composition $Cs_{0.4}FA_{0.6}Pb(I_{0.8}Br_{0.2})_3$ leverage the benefits of mixed-cation and mixed-halide compositions to enhance stability and efficiency, as well as enhance the resistance to humidity and thermal degradation.⁴⁰ However, providing a high PCE and ambient stability while maintaining high optical transparency is challenging. These challenges are primarily associated with the fabrication of top transparent electrodes. So far, ITO has been the most widely used transparent electrode material due to its high optical transparency and excellent electrical conductivity. It is commonly deposited using the sputtering process where high-energy ions (typically Ar⁺) are used to eject ITO particles from a target material and then deposit onto the substrate. However, these high-energy ions can physically impact the soft and thermally sensitive perovskite layer, leading to decreased film quality and performance. Therefore, in this work, a thin SnO₂ layer was introduced as a protective layer between the active layer and the top ITO



Fig. 3 (a) ST-PSC cross-sectional SEM image showing the detailed pi-n structure. (b) Characteristic J-V curves for the single ST-PSC and 2-series ST-PSC module. (c) Optical transmission spectrum of the ST-PSC. And (d) EQE spectra for the ST-PSC and Si photoelectrode.

electrode to prevent damage from high-energy ion bombardments during the sputtering process.41 As shown in the crosssectional SEM image, SnO2 formed a sharp and intact interface with ITO and helped to protect the underlayers of PSCs. Moreover, the presence of SnO₂ also aligns the work function between PCBM and the top ITO electrode, establishing an ohmic contact for efficient photocarrier transport.42 The utilization of a SnO₂ protective layer represents an effective strategy to enhance the durability and performance of the ST-PSCs. More detailed device fabrication processes are described in the experimental section. Fig. 3(b) exhibits a PCE of 14.62% for a single ST-PSC under one sun illumination, with an opencircuit voltage (Voc) of 1.05 V, a short-circuit current density $(I_{\rm sc})$ of 20.80 mA cm⁻², and a fill factor (FF) of 67.6%. In addition, as shown in the transmission spectrum in Fig. 3(c), the perovskite solar cell based on the proposed device structure is semi-transparent with an optical transmission of nearly 70% beyond the wavelength of 700 nm due to the high transparency of both top and bottom ITO electrodes. This allows low-energy photons to transmit through the PSC and be harvested by the Si photoelectrode behind as displayed in external quantum efficiency (EQE) spectra in Fig. 3(d). Nevertheless, a single ST-PSC with a Voc of 1.05 V fails to provide sufficient photovoltage for the bias-free PEC NRR. A module that contains two series-connected ST-PSCs was thus fabricated to generate a sufficient photovoltage to meet the minimum requirement for the bias-free PEC NRR. Two ST-PSCs were configured planarly and connected in a series circuit by metal connections as schematically presented in Fig. S4.[†] The planar configuration ensured that both ST-PSC modules were illuminated with the same light intensity, leading to a module PCE of 13.43% with a $V_{\rm oc}$ of 2.02 V and a $J_{\rm sc}$ of 10.20 mA cm⁻² as shown in the J-V characteristics in Fig. 3(b), matching the photovoltage requirement for a bias-free NRR conversion. Another advantage of the planar configuration in the 2-series ST-PSC module is the

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retained high optical transparency for constructing a tandemabsorber system. Fig. 3(d) exhibits the EQE of the ST-PSC and p-n junction Si photoelectrode in a tandem-absorber configuration, where the ST-PSC serves as the front absorber and p-n junction Si solar cell is positioned behind. The EQE spectrum shows that the ST-PSC generates photocurrent by harvesting the solar spectrum from 300 to 700 nm, consistent with its optical transmission spectrum, with a max EQE of approximately 80%. The Si p-n junction solar cell subsequently absorbs the transmitted light in the 700 to 1200 nm range and exhibits a maximum EQE of around 65%. The result reveals that the tandem absorber containing an ST-PSC module and a Si p-n junction photoelectrode could provide sufficiently high photovoltage to overcome the required thermodynamic potential for overall bias-free NRR. The high transparency of the ST-PSC module also allows wide range spectral harvesting from 300 to 1200 nm to boost significant photo-electrochemical catalytic reactions.

To resemble an artificial leaf that operates as an unassisted solar NRR system, we used a two-electrode electrochemical configuration in an H-type cell containing Li_2SO_4 electrolyte (pH \sim 7.6) for the bias-free PEC NRR under light illumination as shown schematically in Fig. 4(a). Si p–n junction/1T-MoS₂ is



Fig. 4 (a) Schematics of the unassisted solar NRR system operating in a two-electrode configuration with a ST-PSC module. (b) Photocurrents of the front absorber ST-PSC and the PEC NRR at different Li_2SO_4 concentrations. (c) The corresponding CA currents. (d) The faradaic efficiency, yield rate, and (e) STA efficiency of the unassisted solar NRR system at various concentrations.

used as a photocathode for the NRR and Ni-Fe layer double hydroxide (LDH) coated on carbon fiber paper is used as an anode for the OER. Transition-metal-based LDHs have demonstrated their promising performance for electrocatalytic reactions in many types of research,43,44 with Ni-Fe LDH being an excellent anode material for the OER.45-47 An ST-PSC module is further attached to the photocathode side and electrically integrated into the two-electrode electrochemical system in a series configuration, creating a bias-free solar-driven NRR system. Fig. 4(b) displays the current-voltage characteristics of the ST-PSC module along with the two-electrode PEC NRR LSV curves under one sun illumination. To simulate the tandem absorber system where the photoelectrode primarily harvests low-energy photons positioned behind the ST-PSC, LSV measurements were conducted with the ST-PSC serving as an optical filter. Comparisons of the current-voltage characteristics in Fig. 4(b) revealed that the open circuit voltage of the ST-PSC module under one sun illumination is significantly higher than the onset potential of the Si photoelectrode. This indicates that the photovoltage generated by solar power is sufficient to overcome the thermodynamic energy barrier for the NRR. Furthermore, as the ST-PSC and Si photoelectrode are connected in a series circuit, the operating current of the solardriven NRR system is determined by the matching current of the individual devices. Thus, the overall performance of the unassisted solar NRR can be estimated from the intersection of the photocurrent of the ST-PSC module and the LSV curves of the Si photoelectrode. As shown in Fig. 4(b), the photocurrent of the ST-PSC module intersects with the LSV curves at 3.10, 4.16, 5.64, and 6.57 mA cm^{-2} for various electrolyte concentrations, indicating that the photovoltage generated by the ST-PSC module is sufficient to drive the unassisted solar NRR with significantly enhanced reaction kinetics, as predicted by these intersection currents. Therefore, chronoamperometry (CA) measurements that operated solely under one sun illumination were subsequently conducted to determine the unassisted (zero-bias) solar NRR performance. Fig. 4(c) shows the photocurrents operated for 1800 seconds and the corresponding FE and yield rate under light illumination are displayed in Fig. 4(d). When operated in the electrolyte containing $0.25 \text{ M Li}_2\text{SO}_4$, the zero-bias reaction under one sun illumination exhibits an average reaction current of around 3.08 mA cm^{-2} , which gave rise to a faradaic efficiency of 15.9% and an ammonia yield rate of 97.2 μ g h⁻¹ cm⁻², aligning well with the anticipated operating current density (J_{op}) of 3.10 mA cm⁻² (current intersection in Fig. 4(b)). Notably, the results indicated the successful realization of the unassisted solar NRR where ammonia production is entirely powered by solar energy using the ST-PSC module and Si photoelectrode tandem light absorbers integrated with the 1T-MoS₂ catalyst. It exhibited a solar-to-ammonia (STA) efficiency η_{STA} of 0.57% in the 0.25 M electrolyte, estimated by using the following equation:

$$\eta_{\mathrm{STA}} = rac{J_{\mathrm{op}} imes E_{\mathrm{overall}} imes \mathrm{FE}}{P_{\mathrm{in}}} imes 100\%,$$

where J_{op} is the operating current density, $E_{overall}$ is the NRR thermodynamic potential of 1.17 V,^{48,49}, FE is the faradaic

efficiency, and P_{in} is the illumination power of 100 mW cm⁻². The STA efficiency shows a significant correlation with the operating current density and the NRR faradaic efficiency. This connection highlights the critical need for fine-tuning the operating parameters and enhancing the NRR kinetics and selectivity to elevate the efficiency of solar energy conversion into ammonia. To further optimize the unassisted solar NRR performance, various concentrations of Li₂SO₄ electrolyte were investigated. The electrolyte concentration not only influences ionic conductivity but also modulates the intercalation of Li⁺ ions into 1T-MoS₂, forming Li-S bonds. These bonds effectively weaken the N=N triple bond by reducing its bond distance and facilitating electron transfer to the nitrogen molecule, ultimately lowering the activation energy required for ammonia synthesis.¹⁰ Consequently, as the electrolyte concentration increased, the NRR overpotential decreased as shown in Fig. 4(b). This also improved NRR kinetics as evidenced by the reduced Tafel slopes in ESI Fig. S6.† Overall, it leads to increased operating current densities from 3.10 to 4.22, 5.61, and 6.56 mA cm⁻² for concentrations ranging from 0.25 to 0.375 M, as well as 0.5, and 0.625 M. The unassisted solar NRR under one sun illumination at various concentrations, as shown in Fig. 4(c), showed good agreement with the operating current densities predicted by the current intersections in Fig. 4(b). The concentration-dependent faradaic efficiencies, yield rates, and STA efficiencies are presented in Fig. 4(d) and (e). The detailed performance metrics of the tandem-light-absorber system for the unassisted solar NRR are summarized in Table 1. The unassisted solar NRR performance improved with increasing electrolyte concentration, reaching optimal performance in 0.5 M Li₂SO₄ electrolyte. At this concentration, the system achieved a faradaic efficiency of 22.5%, an ammonia yield rate of 167.7 $\mu g~h^{-1}~cm^{-2},$ and an STA efficiency of 1.48%. This superior performance is attributed to the excellent matching of photocurrents between the ST-PSC and Si photoelectrode, as well as the high NRR catalytic activity of the 1T-MoS₂ electrocatalyst. However, further increasing the electrolyte concentration to 0.625 M resulted in reduced overall performance, primarily due to a decline in faradaic efficiency under these operating conditions. Notably, as compared to PEC NRR results, the unassisted solar NRR exhibited higher yield due to the additional photovoltage and current provided by the ST-PSC, which enhances nitrogen reduction kinetics. The unbiased solar NRR system integrates a PEC cell (comprising a Si/MoS₂ photocathode and a Ni/Fe LDH anode) and a ST-PSC module connected in a series circuit. In this setup, ammonia production occurs within the PEC cell, while the ST-PSC module serves as

Table 1	PFC NRR	performance	at various	electrolyte	e concentrations
Tuble 1		periornance	ut vunous	cicculotyte	, concentrations

Li ₂ SO ₄ concentration (M)	Yield rate (µg h ⁻¹ cm ⁻²)	Faradaic efficiency (%)	STA (%)
0.25	97.2	15.9	0.57
0.375	128.3	19.8	0.96
0.5	167.7	22.5	1.48
0.625	63.3	13.3	1.02

a booster for reaction kinetics, providing the essential photovoltage and photocurrent. According to the principle of series circuit design, the overall reaction current must remain consistent across both components during operation. This current value is determined by the intersection point of the working curves for the ST-PSC module and the PEC NRR system when operated independently, as shown in Fig. 4(b). As a result, under one sun illumination, the unbiased solar NRR system operates at current densities ranging from 3 to 6 mA cm^{-2} for ammonia production under the given conditions of this work. In contrast, the PEC NRR system, lacking the current enhancement from the ST-PSC module, achieves a significantly lower reaction current of only 0.3 mA cm⁻², as indicated in Fig. 2(d). This disparity in reaction currents directly results in a notable difference in production yields, with the unbiased solar NRR achieving 167.7 μ g h⁻¹ cm⁻², compared to 18.3 μ g h⁻¹ cm⁻² for the PEC NRR. A table containing NRR performance metrics from reported studies is provided in the ESI[†] for quantitative comparison. Our results demonstrate the realization of an artificial leaf for solar-to-ammonia conversion based on a cost-effective perovskite-silicon absorber system integrated with a 1T-MoS₂ catalyst, presenting a promising approach to achieve sustainable NRR production directly from renewable solar energy.

Conclusion

This study demonstrates a bias-free solar-to-ammonia conversion system using a perovskite-silicon tandem absorber integrated with a 1T-MoS₂ catalyst. By employing a backilluminated p-n junction Si photocathode, we effectively decoupled light harvesting from the catalytic interface, maximizing photon absorption and photocarrier utilization. This results in a significant improvement in the onset potential for the PEC NRR by 600 mV compared to the EC NRR with a dark electrode. The integration of an ST-PSC module further provided the necessary photovoltage to drive the spontaneous NRR under solar illumination. The system achieved a solar-toammonia conversion efficiency of 1.48% under one sun illumination, showcasing its potential for sustainable ammonia production. This advancement highlights the feasibility of using cost-effective, abundant materials to achieve efficient, self-powered NRR, paving the way for future developments in solar-driven chemical synthesis.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

Tsung-Hsin Liu: data curation, formal analysis, investigation, validation; Yu-Hsiang Huang: investigation, validation; Yu-Xuan Huang: investigation, resources; Yang-Sheng Lu: data curation, formal analysis, resources; Tsung-Min Tsai: formal analysis, resources; Chen Chang: investigation; Pai-Chia Kuo:

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resources; Jessie Shiue: resources; Yu-Ching Huang: funding acquisition, resources, writing – original draft preparation; Chun-Wei Chen: conceptualization, funding acquisition, project administration, supervision, writing – original draft preparation, writing – review & editing; Chia-Chun Chen: funding acquisition; Shao-Sian Li: conceptualization, funding acquisition, formal analysis, project administration, supervision, writing – original draft preparation, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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