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Construction of a BiVO₄/V_S-MoS₂ S-scheme heterojunction for efficient photocatalytic nitrogen fixation†

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Photocatalytic nitrogen (N_2) reduction to ammonia (N_3), adopting H_2O as the electron source, suffers from low efficiency owing to the sluggish kinetics of N_2 reduction and the requirement of a substantial thermodynamic driving force. Herein, we present a straightforward approach for the construction of an S-scheme heterojunction of $BiVO_4/V_S$ - MOS_2 to successfully achieve photocatalytic N_2 fixation, which is manufactured by coupling an N_2 -activation component (V_S - MOS_2 nanosheet) and water-oxidation module ($BiVO_4$ nanocrystal) through electrostatic self-assembly. The V_S - MOS_2 nanosheet, enriched with sulfur vacancies, plays a pivotal role in facilitating N_2 adsorption and activation. Additionally, the construction of the S-scheme heterojunction enhances the driving force for water oxidation and improves charge separation. Under simulated sunlight irradiation (100 mW cm⁻²), $BiVO_4/V_S$ - MOS_2 exhibits efficient photocatalytic N_2 reduction activity with H_2O as the proton source, yielding NH_3 at a rate of 132.8 μ mol g^{-1} h^{-1} , nearly 7 times higher than that of pure V_S - MOS_2 . This study serves as a noteworthy example of efficient N_2 reduction to NH_3 under mild conditions.

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1. Introduction

Ammonia (NH₃) serves as both a promising energy storage intermediary and an essential raw material affecting agricultural and industrial production. ^{1,2} However, given the molecular inertness of N₂ (dissociation energy of 945 kJ mol⁻¹), the current industrial synthesis of NH₃ predominantly relies on the Haber–Bosch process. ^{3,4} This traditional method requires high temperature and pressure (300–550 °C and 15–25 MPa), resulting in significant investment costs and high energy consumption. ^{5,6} Therefore, the pursuit of synthetic processes under mild conditions has become a paramount objective. Photocatalytic N₂ fixation, employing semiconductor photocatalysts that harness sunlight as the energy source while utilizing N₂ and H₂O as reactants, stands out as a sustainable approach for NH₃ production. ⁷⁻¹⁰ Nonetheless, because of the poor N₂ adsorption–activation and carrier separation in

semiconductor photocatalysts, achieving efficient photocatalytic conversion of $\rm N_2$ to $\rm NH_3$ remains a scientific challenge. $\rm ^{11-13}$

Efficient N2 adsorption-activation and good light absorption of photocatalysts are the fundamental prerequisites for realizing the efficient photoreduction of N2 to produce NH3.14 Consequently, the initial step involves the selection of potential semiconductor materials to reasonably design photocatalysts with suitable energy levels for N2 reduction and favorable properties for N2 adsorption-activation.15-17 Schrauzer and coworkers conducted the pioneering systematic investigation into the photocatalytic NH₃ synthesis using TiO₂-based materials.18 In recent years, numerous studies have explored traditional metal oxides, carbonaceous materials, and layered double hydroxide semiconductors as photocatalysts for N2 photofixation.19-22 However, these semiconductor materials often exhibit wide band gaps and narrow spectral absorption characteristics, which are not conducive for efficient photon utilization in photocatalytic reactions. Inspired by the MoFecofactor in natural nitrogenase, molybdenum disulfide (MoS₂) has garnered significant attention in the field of N2 fixation due to its structural resemblance to nitrogenase with a Mo-S configuration.23,24 As a two-dimensional direct bandgap semiconductor material, MoS2 not only possesses good photon capture ability but also can be used as a carrier to construct composite catalysts to achieve more efficient catalytic conversion. Nonetheless, MoS₂ exhibits poor activity in photocatalytic N₂ reduction systems using water as the electron source due to

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its lack of water oxidation capacity.²⁵ In addition, akin to other semiconductor photocatalysts, its weak photogenerated carrier separation ability also hinders the progress of photocatalytic N2 reduction.26,27 To improve the photocatalytic activity of semiconductor photocatalysts, extensive research efforts have focused on bolstering charge separation through the construction of p-n, II-type, and S-scheme heterojunctions. 28-31 Mimicking natural photosynthesis, the S-scheme charge transfer system has received special attention, which can simultaneously facilitate spatial carrier separation and improve redox ability.32,33 Additionally, monoclinic BiVO4 as a "star" material has a broad range of visible light utilization and excellent photoelectric stability, and has been widely used in the study of photoanodic water oxidation.34 Based on this, BiVO4 has potential to serve as a water oxidation unit for MoS₂ to construct heterojunctions, further enhancing the efficiency of photocatalytic N2 fixation.

Herein, we present an innovative S-scheme heterojunction prepared by coupling sulfur vacancy enriched MoS2 nanosheets (V_S-MoS₂) with BiVO₄ nanocrystals through electrostatic selfassembly for photocatalytic N2 reduction. Under simulated sunlight irradiation (100 mW cm⁻²), BiVO₄/V_S-MoS₂ exhibits efficient photocatalytic N2 reduction activity, with a NH3 yield of 132.8 μ mol g⁻¹ h⁻¹, nearly 7 times that of pure V_S-MoS₂ (20 μ mol g⁻¹ h⁻¹). In addition, the experimental results from in situ X-ray photoelectron spectroscopy and electron spin resonance spectroscopy verify the presence of sulfur-rich vacancies on the surface of V_S-MoS₂ nanosheets and the successful formation of an S-scheme heterojunction, which are conducive to the improvement of N2 adsorption-activation and driving force of water oxidation as well as charge separation. The mechanism of the N2 reduction reaction is speculated using in situ diffuse reflectance infrared Fourier transform spectroscopy.

2. Experimental

2.1. Sample preparation

2.1.1. Preparation of V_S-MoS₂ **nanosheets.** $Na_2MoO_4 \cdot 2H_2O$ (243 mg) and CH_4N_2S (304 mg) were dissolved in ultrapure water (35 mL). After 30 min of stirring, the mixture was transferred to a 50 mL Teflon autoclave and heated at 180 °C for 48 h. Subsequently, the products were washed 3 times with a 0.1 M HCl solution to eliminate any residual nitrogen in the sample. The V_S -MoS₂ nanosheet powder can be obtained after vacuum drying at 60 °C for 12 h.

2.1.2. Preparation of BiVO₄ **nanocrystals.** In a three-neck flask, a mixture containing 484 mg of Bi(NO₃)₃·5H₂O, 20 mL of octadecene, 3 mL of oleylamine, and 3 mL of oleic acid was heated to 170 °C until it became transparent, and then stored at 100 °C. NaVO₃ (242 mg) was dissolved in ultrapure water (20 mL) at 100 °C, and added to the above three-neck flask. The resulting mixture was poured into ethanol to induce precipitation. Afterward, it was subjected to three rounds of washing with a hexane and ethanol mixture, followed by vacuum drying at 60 °C for 12 h to obtain a yellow-green BiVO₄ nanocrystal. For further purification, the obtained BiVO₄ quantum dots (20 mg) were dispersed in a solution comprising 10 mL of isopropanol

and 1 mL of KI in DMSO (0.1 M). Ultrasonic treatment was performed for 10 min to remove the ligands introduced during the synthesis process and prevent their interference in the photocatalytic N_2 fixation experiment.

2.1.3. Preparation of BiVO₄/V_S-**MoS**₂. V_S-MoS₂ nanosheets (30 mg) and BiVO₄ nanocrystals (10 mg) were dispersed in toluene (10 mL). The mixture was ultrasonicated for 10 min and stirred for 3 h in the dark. The suspension was centrifuged followed by washing 3 times with hexane. The BiVO₄/V_S-MoS₂ heterojunction can be obtained after vacuum drying at 60 °C for 12 h. In addition, a series of samples can be obtained by adjusting the mass ratio of BiVO₄ and V_S-MoS₂ as 10 mg : 10 mg, 10 mg : 20 mg, 10 mg : 40 mg, denoted as BiVO₄/V_S-MoS₂ (1/1), BiVO₄/V_S-MoS₂ (1/2) and BiVO₄/V_S-MoS₂ (1/4), respectively.

2.2. Photocatalytic N2 reduction experiment

The photocatalytic N_2 reduction reactions were carried out in a gas–solid reaction system (25 °C). 20 mg of photocatalyst was placed on the sample table of the reactor. 200 μL of water was injected into the bottom of the reactor as the proton source. Before initiating the photocatalytic reactions, the system was heated to produce water vapor. The system was meticulously degassed to remove air with N_2 (99.999%), where N_2 was bubbled through 1 M HCl as well as a mixed solution of potassium permanganate and KOH to ensure the removal of potential contaminants. A 300 W xenon lamp equipped with a UVVISCUT400 filter was employed as the light source (light intensity of 100 mW cm $^{-2}$). For detection, 2 mL of H_2O was injected into the system to dissolve the product to form the product solution.

2.3. Product detection

2.3.1. Detection of NH₄⁺. The NH₄⁺ concentration was determined with the indophenol blue method as follows: three chromogenic solutions were first prepared, divided into chromogenic agent A, chromogenic agent B, and chromogenic agent C. Chromogenic agent A was prepared by mixing NaOH (4 g), salicylic acid (5 g), and sodium citrate (5 g); chromogenic agent B was obtained by preparing a 0.05 M NaClO aqueous solution; chromogenic agent C was prepared by using 0.1 g sodium nitroferricyanide solution. The product solution (2 mL) was mixed with reagent A (2 mL), reagent B (1 mL), and reagent C (200 μ L), and then left for two hours to be detected. Finally, the absorbance at a wavelength of 655 nm was measured to quantify the NH₄⁺ content according to the established standard curve of the NH₄Cl solution.

2.3.2. Detection of NO₃⁻. The specific process is as follows: first, prepare 1.0 ppm, 0.5 ppm, 0.2 ppm, and 0.1 ppm solutions of NaNO₃ as the standard solutions to establish the standard curve. Then, the reaction solution (2 mL) was detected by using a model NEXION300 ion chromatograph.

2.3.3. Detection of NO_2^-. The colorimetric method for the detection of NO_2^- concentration is as follows: color reagent A was prepared by dissolving sulfonamide (0.5 g) in 50 mL of HCl solution (2 M); color reagent B was prepared by dissolving *N*-(1-naphthyl) ethylenediamine hydrochloride (20 mg) in 20 mL of

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a wavelength of 540 nm.

ultrapure water. The reaction solution (2 mL) was mixed with color reagent A (40 $\mu L)$ and color reagent B (40 $\mu L)$, and then left in the dark for 10 min. The absorbance was characterized by UV-vis absorption spectroscopy, and the content of NO_2^{-} was quantified according to the established standard curve at

2.3.4. Detection of N₂**H**₄. The Watt-Chrisp method was employed to determine the concentration of hydrazine hydrate as follows: the color reagent was prepared by mixing N,N-dimethyl-4-aminobenzaldehyde (2 g), concentrated HCl (10 mL), and ethanol (100 mL). The reaction solution (2 mL) was mixed with the color reagent (2 mL), and then left in the dark for 15 min. The absorbance at \sim 458 nm was obtained, and the content of N₂H₄ was quantified according to the established standard curve.

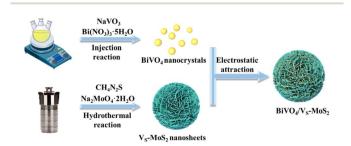
2.4. *In situ* diffuse reflectance infrared Fourier transform spectra (DRIFTS)

In situ diffuse reflectance infrared Fourier transform spectra were recorded using a Bruker IFS 66v Fourier transform spectrometer. The samples were mixed with KBr in a quartz mortar and then placed in an infrared reaction chamber. Pure N_2 (99.999%) containing water vapor was continuously introduced into the experimental chamber during in situ characterization. The IR spectrum of pure KBr was first collected as a background spectrum. The final spectra were obtained by subtracting the background spectrum from the spectrum of the sample.

Results and discussion

3.1. Preparation and structure of BiVO₄/V_S-MoS₂

The synthetic process of $BiVO_4/V_S$ -MoS $_2$ is illustrated in Scheme 1. Briefly, V_S -MoS $_2$ and $BiVO_4$ were initially prepared through the hydrothermal method and thermal injection method, respectively. The measured zeta potential (ζ) of V_S -MoS $_2$ is negative (-45 mV), opposited with that of $BiVO_4$ (33 mV) in toluene (Fig. S1†). This opposite surface charging characteristic of V_S -MoS $_2$ and $BiVO_4$ should facilitate the spontaneous assembly to form $BiVO_4/V_S$ -MoS $_2$ in solution. X-ray diffraction (XRD) patterns (Fig. 1a) show that the as-prepared V_S -MoS $_2$ and $BiVO_4$ can be indexed to the P63/mmc(194) hexagonal space group (PDF card no. 01-075-1539) and I2/a(15) monoclinic space group (PDF card no. 00-014-0688),



Scheme 1 Schematic illustration of the preparation process of $BiVO_4/V_s$ -MoS2.

respectively. The characteristic diffraction peaks at 14.39°, 32.8°, 39.65° and 58.56° of V_S -MoS₂ correspond to the (002), (100), (103), and (110) crystal planes. The diffraction peaks of BiVO₄ are located at 18.67°, 28.95°, 35.22°, 39.78°, 46.71°, 49.96°, and 59.26°, corresponding to the (110), (121), (002), (211), (240), (-202), and (123) crystal planes. Notably, the diffraction pattern of BiVO₄/V_S-MoS₂ contains the characteristic peaks of both V_S-MoS₂ and BiVO₄, indicating the successful loading of BiVO₄ nanocrystals onto V_S-MoS₂ nanosheets. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements revealed that V_S-MoS₂ exhibits a nanoflower morphology (Fig. 1b), which is formed by the gathering of nanosheets (Fig. 1c). Atomic force microscopy (AFM) analysis in Fig. S2† further confirmed that V_S-MoS₂ has a nanosheet morphology with a mean thickness of \sim 3 nm. TEM images of pure BiVO₄ and BiVO₄/V_S-MoS₂ (Fig. 1d and e) show that BiVO₄ nanocrystals are interspersed on V_S-MoS₂ nanosheets, with an average size of \sim 5 nm, which is almost identical to that of the pure BiVO₄ nanocrystal (Fig. S3†). Further highresolution TEM (HRTEM) analysis (Fig. 1f) showed clear lattice fringes of 2.72 Å and 3.08 Å, corresponding to the (100) plane of V_S-MoS₂ (ref. 35) and the (121) plane of monoclinic BiVO₄ (ref. 36) (Fig. S4†), respectively, confirming the presence of BiVO₄ nanocrystals on the surface of V_S-MoS₂ nanosheets. The corresponding energy-dispersive X-ray spectroscopy (EDS) mapping analysis (Fig. 1g) demonstrated the homogeneous distribution of Mo, S, Bi, V, and O elements on BiVO₄/V_S-MoS₂, further verifying the construction of BiVO₄/V_S-MoS₂.

To gain insights into the structural characteristics of the asprepared photocatalysts, electron paramagnetic resonance (EPR) measurements were performed initially. As depicted in Fig. 1h, a distinct EPR signal at g = 2.003 can be recognized for V_S -MoS₂, signifying the formation of the sulfur vacancies on the surface of V_S-MoS₂.³⁷ In the case of BiVO₄/V_S-MoS₂, a stronger EPR signal is detected, providing evidence for the formation of heterojunction interfaces, which can turn spin-coupled electron pairs into unpaired electron states.38 Sulfur vacancies can serve as active sites to promote carrier capture and N2 adsorption and activation.39 The X-ray photoelectron spectra (XPS) were further analyzed to investigate the potential interfacial interaction and charge transfer processes within the BiVO₄/V_S-MoS₂ heterojunction. Doublet XPS characteristic peaks can be identified at 229.3 eV and 232.4 eV in pure V_S-MoS₂, attributed to Mo 3d_{5/2} and Mo 3d_{3/2} (Fig. S5a†), which can confirm the reduction of Mo⁶⁺ to Mo⁴⁺ during the growth of V_S-MoS₂ nanosheets. 40 In addition, a comparison between pure V_S-MoS₂, BiVO₄, and BiVO₄/V_S-MoS₂ reveals noticeable shifts in binding energy for Mo 3d, S 2p, Bi 4f, and V 2p. Specifically, Mo 3d and S 2p exhibit positive shifts of 0.50 eV and 0.20 eV, while Bi 4f and V 2p display negative shifts of 0.20 eV and 0.20 eV, respectively (Fig. S5b-d \dagger). These charge redistributions within the BiVO₄/V_S-MoS₂ heterojunction reflect a strong chemical interaction at the interface of the BiVO₄/V_S-MoS₂ heterojunction. This robust interfacial electronic coupling in BiVO₄/V_S-MoS₂ is expected to facilitate the charge transfer between the V_S-MoS₂ nanosheets and BiVO₄ nanocrystals.

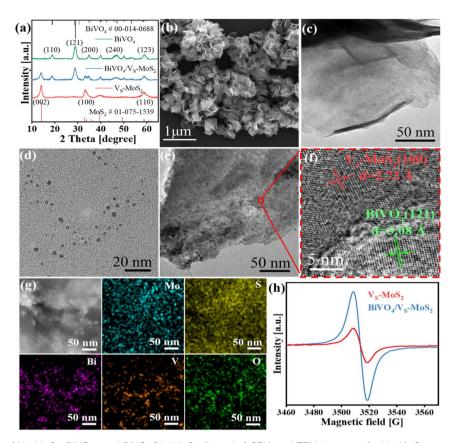


Fig. 1 (a) XRD patterns of V_S -MoS₂, BiVO₄, and BiVO₄/ V_S -MoS₂. (b and c) SEM and TEM images of a V_S -MoS₂ nanosheet. (d) TEM image of a BiVO₄ nanocrystal. (e-g) TEM, HRTEM, and corresponding EDS images of BiVO₄/ V_S -MoS₂. (h) EPR spectra of V_S -MoS₂ and BiVO₄/ V_S -MoS₂.

3.2. S-scheme mechanism of the $BiVO_4/V_s$ - MoS_2 heterojunction

The energy levels and interfacial charge transfer processes of BiVO₄/V_S-MoS₂ were explored to evaluate the photocatalytic N₂ reduction potential of the as-prepared photocatalysts. Fig. 2a and b show the UV-vis diffuse reflectance spectra (DRS), revealing a good light response for both the V_S-MoS₂ nanosheets and BiVO₄ nanocrystals. From the corresponding Tauc plots (insets of Fig. 2a and b), the band gaps (E_{g}) of V_{S} -MoS₂ and BiVO₄ can be deduced to be 1.71 eV and 2.22 eV, respectively. To ascertain the energy band structures of V_S-MoS₂ and BiVO₄, the onset edge (E_i) and the secondary electron cutoff (E_{cutoff}) were determined by carrying out ultraviolet photoelectron spectroscopy (UPS) (Fig. 2c). According to the equation $E_{VB} = 21.22 - 100$ $(E_{\text{cutoff}} - E_{\text{i}})$, the valence band edge potentials (E_{VB}) can be calculated to be 1.35 V and 2.23 V versus the standard hydrogen electrode (vs. NHE) for V_S-MoS₂ and BiVO₄, respectively. By combining the values from $E_{\rm g}$ and $E_{\rm VB}$ analysis, the corresponding conduction band edge potentials (E_{CB}) can be calculated to be -0.36 V and 0.01 V (vs. NHE) for V_S -MoS₂ and BiVO₄, respectively. The resultant energy band structures of V_S-MoS₂ and BiVO₄ are presented in Fig. 2d. The photogenerated electrons in V_S-MoS₂ possess sufficient energy to drive the photoreduction of N_2 to NH_3 (-0.13 V vs. NHE), 41 while their driving force for H₂O oxidation is relatively weak. Meanwhile, the photogenerated holes in BiVO₄ can trigger H₂O photooxidation

to O_2 (0.82 V vs. NHE, pH = 7), while they are insufficient for the photoreduction of N2. In addition, the Fermi levels were also estimated according to the UPS spectra, to be -4.62 eV and -5.27 eV (vs. vacuum) for V_S -MoS₂ and BiVO₄, respectively. These results reveal that both V_S-MoS₂ and BiVO₄ are n-type semiconductors, consistent with the results from the Mott-Schottky tests, where the slopes of Mott-Schottky curves for both BiVO₄ and V_S-MoS₂ are positive (Fig. S6†). From the above results and analysis, we can preliminarily deduce that, given the higher Fermi level of V_S-MoS₂ compared to that of BiVO₄, the free electrons in V_S-MoS₂ would spontaneously flow to BiVO₄ to establish a Fermi level equilibrium upon contact (Fig. S7(I-II)†). A built-in electric field and band bending of the interface in BiVO₄/V_S-MoS₂ would be formed. Driven by the interfacial builtin electric field, photogenerated electrons in BiVO4 would recombine with the photogenerated holes in V_S-MoS₂ (Fig. S7(III)†), facilitating the formation of the S-scheme charge transfer pathway.

To scrutinize the S-scheme charge transfer pathway in the $BiVO_4/V_S$ -MoS₂ heterojunction, *in situ* irradiated XPS (ISI-XPS) spectra were first measured to detect photoinduced changes in the electron cloud density around the nuclei of elements. As depicted in Fig. S8a and b,† the binding energies of Mo 3d and V 2p in $BiVO_4/V_S$ -MoS₂ demonstrate a negative displacement (\sim 0.40 eV) and positive movement (\sim 0.30 eV) under illumination, respectively, compared with those in the dark. These

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(a) (b) V_c-MoS BiVO -Mos [a.u.] Intensity [a.u.] Intensity [a.u.] 6.60 eV BiVO. Intensity BiVO. BiVO. 15.95 eV 1 46 eV hv [eV] hv [eV] 17 490 560 16 600 650 420 630 3 Wavelength [nm] Wavelength [nm] Binding energy [eV] $(d)_{-1}$ DMPO-OH DMPO-O2 -0.36 VPotential [V vs. NHE] ntensity [a.u.] ntensity [a.u.] BiVO₄/V_S-MoS BiVO₄/V_S-MoS BiVO ·H₂O/O₂ BiVO 1.35 V 3400 3450 3500 3550 3600 3400 3450 3500 3550 3600

Fig. 2 (a and b) UV-vis DRS spectra of V_S -MoS₂ and BiVO₄. The insets show the corresponding Tauc plots. (c) UPS spectra of V_S -MoS₂ and BiVO₄. (d) Energy band structures of V_S -MoS₂ and BiVO₄ (pH = 7). EPR signals of (e) DMPO $-\cdot$ O₂ and (f) DMPO $-\cdot$ OH over V_S -MoS₂, BiVO₄, and BiVO₄/ V_S -MoS₂ under illumination.

Magnetic field [G]

binding energy changes indicate the accumulation of photogenerated electrons on V_S-MoS₂ and photogenerated holes on BiVO₄, revealing the occurrence of S-scheme interfacial charge transfer within the BiVO₄/V_S-MoS₂ heterojunction. To further confirm this S-scheme interfacial charge transfer mechanism in the BiVO₄/V_S-MoS₂ heterojunction, the EPR spectra were recorded using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the trapping agent. 42 In the case of pure V_S-MoS₂, only the DMPO-· O_2 characteristic signal can be identified (Fig. 2e), as its E_{VB} potential is insufficient to drive the oxidation of H₂O to ·OH. Conversely, in pure BiVO₄, only the DMPO-·OH characteristic signal can be recognized (Fig. 2f), due to the insufficient driving force of photogenerated electrons in $E_{\rm CB}$ to trigger the reduction of O_2 to $\cdot O_2^-$ (-0.33 V vs. NHE). For the BiVO₄/V_S-MoS₂ heterojunction, more obvious DMPO-·O2⁻ and DMPO-·OH signals can be simultaneously identified, providing compelling evidence for the establishment of an interfacial S-scheme charge transport channel. That is to say, the photogenerated electrons in BiVO₄ and the photogenerated holes in V_S-MoS₂ initially recombine through the interfacial S-scheme channel, leading to the accumulation of photogenerated holes on BiVO₄ and photogenerated electrons on V_S-MoS₂. This spatial separation of charge carriers in the BiVO₄/V_S-MoS₂ heterojunction would more effectively promote their participation in the redox reaction.

3.3. Photogenerated carrier evolution

In general, the evolution of photogenerated charges within photocatalysts plays a pivotal role in determining their photocatalytic activity. ^{43,44} To evaluate the behavior of photogenerated carriers in BiVO₄/V_S-MoS₂, steady-state photoluminescence (PL) spectrum measurements were first performed. As presented in Fig. 3a, the PL spectrum of BiVO₄ displays an intrinsic emission

band at ~490 nm under 365 nm excitation, which is related to photogenerated electron-hole recombination. Upon the construction of the BiVO₄/V_S-MoS₂ heterojunction, the PL spectrum exhibits significant quenching, indicating the effective transfer of photogenerated carriers between the BiVO₄ nanocrystals and V_S-MoS₂ nanosheets. In addition, the photoelectrochemical properties of the samples were characterized to assess the potential positive influence of the construction of a heterostructure on charge evolution behavior. Notably, under light irradiation, BiVO₄/V_S-MoS₂ exhibits a smaller chargetransport resistance compared with both pure BiVO₄ and V_S-MoS₂ (Fig. 3b and Table S1†), indicating that the construction of the electric field in the heterojunction improves the charge transport characteristics. From the transient photocurrent (I-t)measurements (Fig. 3c), it is evident that BiVO₄/V_S-MoS₂ has a higher current density than both BiVO₄ and V₅-MoS₂, providing further evidence of expedited charge separation kinetics within the BiVO₄/V_S-MoS₂ heterojunction. Moreover, to more intuitively reveal the space charge separation, Kelvin probe force microscopy (KPFM) was utilized to measure the surface photovoltage (SPV) response of photocatalysts under light. Atomic force microscope (AFM) images (Fig. 3d and f) present the morphology outline of V_S-MoS₂ and BiVO₄/V_S-MoS₂ nanosheet clusters, which are basically consistent with the SEM results (Fig. 1b). Under illumination, the SPV response zone (Fig. 3e and g) emerges, aligning with the morphology outlines of the samples. These observations also indicate the spatial charge separation and redistribution after light irradiation. 45 As shown in Fig. 3h, pure V_S-MoS₂ presents a feeble SPV signal under light irradiation, primarily due to rapid photogenerated carrier recombination. Benefiting from the construction of heterojunctions, BiVO₄/V_S-MoS₂ displays a noticeable enhancement of the SPV response, of ~100 mV, far surpassing

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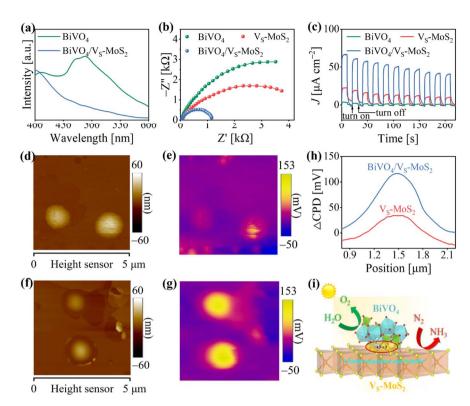


Fig. 3 (a) Steady-state photoluminescence spectra of BiVO₄ and BiVO₄/V₅-MoS₂. (b and c) EIS plots and I-t curves of BiVO₄, V₅-MoS₂, and BiVO₄/V₅-MoS₂ plotted at a bias potential of -0.4 V vs. Ag/AgCl. AFM height images of (d) V₅-MoS₂ and (f) BiVO₄/V₅-MoS₂. SPV images of (e) V₅-MoS₂ and (g) BiVO₄/V₅-MoS₂ under illumination. (h) Potential difference changes (Δ CPD) of V₅-MoS₂ and BiVO₄/V₅-MoS₂ by subtracting the potential under dark conditions from that under illumination. (i) Schematic illustration of the photogenerated carrier separation.

that of pure V_S -MoS₂. Ultimately, these characterization studies underscore that the construction of heterojunctions can promote charge separation, and enhance the accumulation of electrons/holes on V_S -MoS₂ and BiVO₄, respectively, which is beneficial for these carriers to participate in the subsequent multi-electron transfer processes during the photoreduction N_2 reaction (Fig. 3i).

3.4. Photocatalytic N2 reduction activity

The photocatalytic N2 reduction reactions were conducted in a gas-solid reaction apparatus (Fig. S9†) containing N₂ and H₂O vapor under simulated sunlight irradiation (100 mW cm⁻²). To ensure the accuracy of our experiments, the samples were pretreated with a DMSO solution of KI. This step is crucial to remove any residual ligands introduced during the synthesis process, preventing any interference with the experimental results (Fig. S10,† details are described in the Experimental section). The photocatalytic activities were evaluated by evaluating the NH₄⁺ production using the indophenol blue method (Fig. S11,† details are described in the Experimental section).⁴⁶ As illustrated in Fig. S12,† a prominent absorption signal at \sim 655 nm can be observed, indicating that N₂ is effectively photoreduced to NH3 in the presence of light for BiVO4/Vs-MoS₂. The NH₃ generation performances for the as-prepared photocatalysts are presented in Fig. 4a and S13.† For pure BiVO₄, there is virtually no NH₃ synthesis activity due to the

insufficient driving force of electron energy in its conduction band (Fig. 2d). Meanwhile, V_S-MoS₂ exhibits a weak N₂ photoreduction to NH₃ activity, with a rate of $20.0 \pm 1.1 \,\mu\text{mol g}^{-1} \,\text{h}^{-1}$, resulting from its insufficient thermodynamic driving force for H₂O oxidation and serious charge recombination. Upon combining the V_S-MoS₂ nanosheets with the BiVO₄ nanocrystals, the corresponding photocatalytic N2 reduction activity improves significantly, reaching 132.8 \pm 4.2 μ mol g⁻¹ h⁻¹ within 4 hours, which is nearly 7-fold that of pure V_S-MoS₂. The apparent quantum efficiency at 575 nm can reach 0.3% (Fig. S14†). Certainly, we also analyzed the NH₄⁺ production by ion chromatography (Fig. S15†), and the results are in agreement with those obtained by the indophenol blue method. Obviously, this improvement of NH3 evolution activity can be attributed to the increased driving force for water oxidation and the enhanced separation of photogenerated carriers in the BiVO₄/V_S-MoS₂ heterojunction, compared with pure V_S-MoS₂ nanosheets. By adjusting the mass ratio of BiVO₄ and V_S-MoS₂ (Fig. S16†), the NH₃ evolution activities of the samples were screened, in which BiVO₄/V_S-MoS₂ with a mass ratio (BiVO₄: V_S- MoS_2) of 1:3 exhibits the best performance (Fig. 4a).

Moreover, the O_2 evolution activity of BiVO₄/V_S-MoS₂ was also measured through a gas chromatograph, to be 110.0 \pm 4.5 μ mol g⁻¹ h⁻¹ (Fig. S17†). This result suggests that the rate of consumed electrons ($R_{\rm electron}$) for N₂ reduction to NH₃ is nearly equal to the rate of consumed holes ($R_{\rm hole}$) for water oxidation to O₂, in accordance with the formulae of $R_{\rm electron} = 3 \times R_{\rm NH_3}$ and

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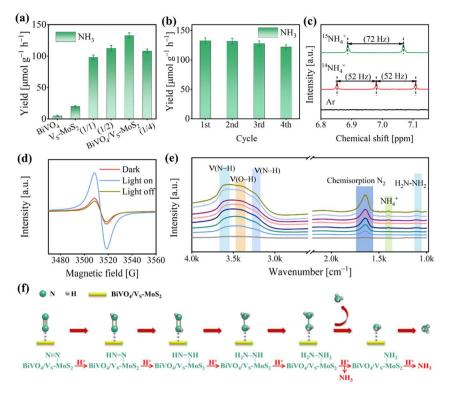


Fig. 4 (a) Photocatalytic NH $_3$ production rates for BiVO $_4$, V $_5$ -MoS $_2$, BiVO $_4$ /V $_5$ -MoS $_2$, BiVO $_4$ /V $_5$ -MoS $_2$ (1/1), BiVO $_4$ /V $_5$ -MoS $_2$ (1/2), and BiVO $_4$ /V $_5$ -MoS $_2$ (1/4) under 4 h light irradiation. (b) NH $_3$ synthesis for four cyclic tests of BiVO $_4$ /V $_5$ -MoS $_2$. (c) The 1 H NMR spectra of products with 14 N $_2$ or 15 N $_2$ as the reaction atmosphere. (d) In situ EPR spectra of BiVO $_4$ /V $_5$ -MoS $_2$ in the dark or under light irradiation in a N $_2$ atmosphere or light off in a N $_2$ atmosphere. (e) In situ DRIFTS spectra of the photoreduction N $_2$ reaction. (f) The proposed reaction pathway of the photoreduction N $_2$ reaction.

 $R_{\rm hole}=4\times R_{\rm O_2}.$ This balance signifies the effective utilization of the photogenerated electrons and holes. Based on the above analysis, the whole photocatalytic reaction including N₂ reduction and H₂O oxidation by BiVO₄/V_S-MoS₂ can be described as 2N₂ + 6H₂O \rightarrow 4NH₃ + 3O₂. Additionally, the robustness of BiVO₄/V_S-MoS₂ was evaluated by reemploying the photocatalyst in four cycles of tests (Fig. 4b), which reveals little decrement in activity. In addition, the XRD patterns (Fig. S18†) and TEM images (Fig. S19†) of BiVO₄/V_S-MoS₂ after the photocatalytic reaction exhibit no obvious changes, confirming the good stability of the photocatalyst in this gas–solid photocatalytic system. The Mo 3d and Bi 4f XPS spectra of BiVO₄/V_S-MoS₂ after catalysis show almost no significant changes, further suggesting the maintenance of the local coordination environment of the Bi and Mo sites.

To elucidate the origin of NH $_3$ and O $_2$ during the photocatalytic reaction, several controlled experiments were carried out using BiVO $_4$ /V $_8$ -MoS $_2$ as the photocatalyst (Fig. S21 \dagger). In the absence of a photocatalyst (BiVO $_4$ /V $_8$ -MoS $_2$), N $_2$, light, or H $_2$ O, there is nearly no NH $_3$ evolution, unequivocally demonstrating that the N $_2$ reduction reaction is indeed a photocatalytic reaction using BiVO $_4$ /V $_8$ -MoS $_2$ as the photocatalyst with H $_2$ O as the proton source. According to the characterization by the colorimetric method and ion chromatography (the details are described in the Experimental section), nearly no NO $_2$ ⁻ and NO $_3$ ⁻ signals in the product system can be detected before and

after the photocatalytic reaction (Fig. S22 and S23†). In addition, we have further measured the N content in the obtained photocatalyst by EDS analysis (Fig. S24 and Table S2†), and no N atoms are present. These results confirm that NH3 remained unoxidized, and substantiate that NH₃ originated solely from N₂ reduction, excluding impurity conversion as a source. To further verify the origin of NH₃ in the product system, isotope labeling experiments were performed using BiVO₄/V_S-MoS₂ as the photocatalyst in atmospheres containing ¹⁵N₂, ¹⁴N₂, or Ar, respectively (Fig. S25†). More specifically, no NH₄⁺ signal is detected under a Ar atmosphere in the nuclear magnetic resonance (NMR) spectra, while distinct signals belonging to ¹⁵NH₄ or ¹⁴NH₄ can be observed in a ¹⁵N₂ or ¹⁴N₂ atmosphere, respectively (Fig. 4c). These results directly confirm that NH₄⁺ is indeed generated from the N2 in the system. In addition, the mass spectrometry analysis of the product (Fig. S26†) was also performed, revealing an $^{18}O_2$ signal at m/z = 36, which confirms that O_2 is produced from H_2O oxidation.

To gain insight into the photocatalytic N_2 reduction process of the $BiVO_4/V_S$ - MoS_2 heterojunction, we conducted further characterization to explore the active sites and monitor the evolution of intermediates during the photocatalytic reaction, by using *in situ* EPR spectra and *in situ* diffuse reflectance infrared Fourier transform spectra (DRIFTS), respectively. As presented in Fig. 4d, the intensity of the sulfur vacancy signal for $BiVO_4/V_S$ - MoS_2 exhibits an increment when exposed to light

irradiation for 15 min, and decreases once the light was turned off for 10 min, suggesting that the sulfur vacancies facilitate the trapping of photogenerated electrons from the conduction band.47,48 The exposed Mo site at the sulfur vacancy is in a coordination unsaturated state, and can act as the photocatalytic active site bonding with N2. The trapped photogenerated electrons at sulfur vacancies can transfer to N2 molecules to achieve N₂ reduction and transformation. As the photocatalytic N2 reduction reaction proceeded, a series of absorption signals were detected belonging to intermediates adsorbed on BiVO₄/V_S-MoS₂ (Fig. 4e). Specifically, an obvious peak at 1648 cm⁻¹ belonging to the chemisorbed N₂ (-N≡N) appeared,49 which can be attributed to the efficient adsorption and activation of N2 by the Mo sites at the vacancies of the nanosheets. The peak at 3432 cm⁻¹ is attributed to ν (O-H) of H₂O, which serves as the proton source for N₂ activation. The overlapped signal bands at 3230 cm⁻¹ and 3555 cm⁻¹ can be attributed to $\nu(N-H)$ stretching modes of NH₃, and the peak at 1403 cm⁻¹ can be attributed to NH₄⁺ adsorption. The enhancement of these characteristic signals implies the progression of N2 activation and conversion to NH3 via a multistep proton-coupled electron transfer (PCET) process over BiVO₄/V_S-MoS₂. In addition, a peak at 1102 cm⁻¹ can be identified, originating from the H2N-NH2 characteristic signal.51 Given that there is no hydrazine formation in the product (Fig. S27†), we thus speculate that the photocatalytic N₂ fixation process on BiVO₄/V_S-MoS₂ follows an associative alternating pathway (Fig. 4f). In this pathway, hydrogenation occurs alternatively on two N atoms, with the final step involving the cleavage of the N-N bond to generate the first NH3 molecule, followed by the last hydrogenation and another NH3 desorption.

4. Conclusions

In summary, we have successfully prepared an S-scheme heterojunction of BiVO₄/V_S-MoS₂ by coupling the N₂-activated component (V_S-MoS₂) and the water-oxidized module (BiVO₄) to facilitate the process of photocatalytic N2 reduction. BiVO4/VS-MoS₂ exhibits efficient NH₃ synthesis activity using H₂O as a proton source under illumination (100 mW cm⁻²), with an NH₃ yield of 132.8 μ mol g⁻¹ h⁻¹, nearly 7 times higher than that of pure V_S-MoS₂. Our experimental findings underscore the pivotal roles played by the V_S-MoS₂ nanosheet with sulfur-rich vacancies in enhancing N2 adsorption and activation. Furthermore, the construction of the S-scheme heterojunction substantially elevates the driving force for H2O oxidation and significantly improves charge separation within the system. Moreover, an alternate association pathway for N2 photoreduction reaction is proposed according to the in situ DRIFTS characterization. This study presents an efficient example for achieving the N₂ conversion process under mild conditions.

Author contributions

Han-Ying Luo: data curation, formal analysis, validation. Zhao-Lei Liu: data curation, formal analysis, validation. Meng-Ran Zhang: formal analysis, supervision. Yan-Fei Mu: validation, writing – original draft preparation, funding acquisition. Min Zhang: conceptualization, funding acquisition, supervision, validation, writing – reviewing and editing.

Conflicts of interest

There are no conflicts of interest to declare.

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