High Efficiency Electron Transfer Realized over NiS₂/MoSe₂ S-Scheme Heterojunction in Photocatalytic Hydrogen Evolution

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Abstract: S-scheme heterojunction is a major breakthrough in the field of photocatalysis. In this study, NiS₂ and MoSe₂ were prepared by a typical solvothermal method, and compounded by an *in situ* growth method to construct an S-scheme heterojunction. The obtained composite showed excellent performance in photocatalytic hydrogen evolution; the hydrogen production rate was approximately 7 mmol·h⁻¹·g⁻¹, which was 2.05 times and 2.44 times those of pure NiS₂ and MoSe₂, respectively. Through a series of characterizations, it was found that NiS₂ and MoSe₂ coupling can enhance the light absorption intensity, which is vital for the light reaction system. The efficiency of electron-hole pair separation is also among the important factors restricting photocatalytic reactions. Compared with pure NiS₂ and MoSe₂, NiS₂/MoSe₂ exhibited a higher photocurrent density, lower cathode current, and lower electrochemical impedance, which proves that the NiS₂/MoSe₂ complex can effectively promote photogenerated electron transfer. Simultaneously, the lower emission intensity of fluorescence indicated effective inhibition of electron-hole recombination in the NiS₂/MoSe₂ complex, which is favorable for the photocatalytic hydrogen evolution reaction. Further, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed that MoSe₂ is an amorphous sample surrounded by the NiS₂ nanomicrosphere, which greatly increased the contact area between the two, thus increasing the active site of the reaction. Secondly, as a photosensitizer, Eosin Y (EY) effectively enhanced the absorption of light by the catalyst in the photoreaction system. Meanwhile, during sensitization, electrons were provided to the catalyst, which effectively improved the photocatalytic reaction efficiency. The establishment of S-scheme heterojunctions contributed to improving the redox capacity of the reaction system and was the most important link in the photocatalytic hydrogen reduction of aquatic products. It was also the main reason for the improvement of the hydrogen evolution effect in this study. The locations of the conduction band and valence band of NiS₂ and MoSe₂ were determined by Mott-Schottky plots and photon energy curves, and further proved the establishment of the S-scheme heterojunction. This work provides a new reference for studying the S-scheme heterojunction to effectively improve the photocatalytic hydrogen production efficiency.

Key Words: NiS₂; MoSe₂; S-scheme heterojunction; Photocatalytic hydrogen evolution

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构建 NiS₂/MoSe₂ S 型异质结高效光催化产氢

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摘要: S型异质结的提出是光催化领域发展的一个重要新理论。本研究通过典型的溶剂热法制备了NiS₂和MoSe₂, 并通过原位生长的方法将二者复合, 构建了S型异质结。所得的复合材料在光催化析氢中显示了优异的性能, 产氢速率达7 mmol·h⁻¹·g⁻¹, 是纯NiS₂和MoSe₂的2.05倍和2.44倍。进一步研究证实, NiS₂和MoSe₂耦合可以增强对光吸收强度。与纯NiS₂和MoSe₂相比, NiS₂/MoSe₂更高的光电流密度和更低的阴极电流及更低的电化学阻抗均证明了NiS₂/MoSe₂复合物可以有效促进光生电子的转移。同时, 更低的荧光强度表明了NiS₂/MoSe₂复合物对电子-空穴再次复合的有效抑制, 这为光催化析氢反应提供了有利的条件。另一方面, 通过扫描电子显微镜和透射电子显微镜发现, MoSe₂作为一种无定型样品包围NiS₂纳米微球, 这大大增加了两者之间的接触面积, 从而增加了反应的活性位点。其次, 在该光反应体系中, 曙红(EY)作为一种光敏剂, 有效地增强了催化剂对光的吸收。同时, 在敏化过程中, 曙红提供了电子给催化剂, 这有效提高了光催化反应效率。S型异质结的建立有助于提高反应体系的氧化还原能力, 是光催化还原水产氢反应析氢效果提高的主要原因。通过模特肖特基和光子能量曲线确定NiS₂和MoSe₂的导带、价带位置, 进一步证明了S型异质结的建立。这项工作为研究S型异质结有效提高光催化制氢效率提供了新的参考。

关键词: NiS₂; MoSe₂; S型异质结; 光催化产氢

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1 Introduction

With the rapid economic development, the global energy demand has far exceeded the energy storage. At the same time, the massive use of fossil energy also brings great pressure for the global environmental governance. Therefore, sustainable clean energy research was a new field of energy development in recent years¹⁻³. Hydrogen energy (H₂) has attracted much attention due to its environmental friendliness and high energy^{4,5}. Solar energy was a sustainable energy in natural energy. Converting solar energy into chemical energy to obtain the hydrogen energy we need is the direction of many scientists' efforts after 1972⁶⁻⁹. It was a new technology with research value. Among them, the photocatalyst was the decisive substance in the photocatalytic decomposition of water to produce hydrogen. Therefore, the search for low-cost, high-efficiency photocatalysts was the main goal of researchers¹⁰.

Semiconductor materials occupied an important position in the field of photocatalysis¹¹. Precious metals with excellent electron-transporting capabilities were not conducive to the development of industry because of the relatively large cost of testing, and semiconductor materials have become the main direction dedicated to research by researchers¹²⁻¹⁵. Nickel-based materials stand out in the continuous research of catalysts, including metals Ni, Ni(OH)₂, NiP_x, NiP₂¹⁶⁻¹⁹, etc. have excellent photocatalytic hydrogen evolution performance. Nickel sulfide (NiS₂), as a strong compound made of abundant earth elements, has a small band gap and was easily excited to generate electron-hole pairs²⁰. It has been regarded as an

efficient catalyst material in the photocatalytic hydrogen evolution reaction. However, the narrow band gap has the disadvantage of easy recombination of electrons and holes. Therefore, it was necessary to take measures for semiconductor recombination to guide electron transfer in time and reduce its recombination rate. MoS₂ has been widely studied as a non-noble metal auxiliary catalyst for modifying semiconductor photocatalysts to achieve sustainable H₂ generation²¹. The elements Se and S are elements of the same main group and usually have similar properties. Therefore, MoSe₂ also has a low Gibbs free energy ($\Delta G_H = 0.05$ eV, close to thermal neutral) and high conductivity due to its intrinsic metal properties²². The porous g-C₃N₄ phase transformation replaced the main role of the MoSe₂ nanostructure as the active catalytic site for H₂ precipitation. At the same time, the hybrid system shows high thermal catalytic stability²³.

Since the redox reaction on the semiconductor surface was so slow that the charge carriers cannot be consumed efficiently²⁴. In recent years, the concept of heterojunction has been gradually discovered and studied, including type I heterojunction, type II heterojunction, direct Z-scheme heterojunction, indirect Z-scheme heterojunction and S-scheme heterojunction. The S-scheme heterojunction has a staggered band structure, which was similar to the type II heterojunction, but the charge transfer path was completely different²⁴. In a typical type II heterojunction, photogenerated electrons and holes remain in the conduction band at a lower position and the valence band at a higher position, respectively, resulting in weak redox capacity. In the S-

scheme heterojunction, electrons and holes are retained in the higher conduction band and lower valence band, while meaningless photogenerated carriers are recombined to obtain a strong redox potential, thereby promoting redox reactions. In addition, compared to the Z-scheme heterojunction, the S-scheme heterojunction has a more stable photocatalytic reaction system²⁵.

Herein, pure NiS₂, MoSe₂ and NiS₂/MoSe₂ were prepared by a typical solvothermal method. The optical and electrical properties of NiS₂/MoSe₂ S-scheme heterojunction and the photocatalytic hydrogen production capacity were systematically studied. In addition, in the EY-sensitized photocatalytic system, EY is used as a photosensitizer to effectively enhance the light absorption efficiency, thereby promoting the progress of the photoreaction. As a result, the hydrogen production activity of NiS₂/MoSe₂ was 2.05 and 2.44 times that of NiS₂ and MoSe₂. This research provided a new strategy for constructing the S-scheme heterogeneous narrow-band gap semiconductor to be directly applied to the photocatalytic hydrogen evolution system.

2 Experimental section

2.1 Catalysts preparation

All the chemical reagents used in the experiment were analytical reagents and without further concentration. Nickel acetate (C₄H₆O₄Ni·4H₂O, Tianjin Damao Chemical Reagent Factory, China, CAS: 373-02-4, AR 98%), Sodium thiosulfate pentahydrate (Na₂S₂O₃·5H₂O, Aladdin, China, CAS: 10102-17-7, AR 99%), Polyvinylpyrrolidone ((C₆H₉NO)₃₀, Aladdin, China, CAS No: 9003-39-8, AR 98%), Selenium powder (Se, Tianjin Damao Chemical Reagent Factory, China, CAS No: 7782-49-2, AR 98%), Sodium molybdate (NaMoO₄, Xilong Chemical Co. Ltd., China, CAS: 1102-40-6, AR 98%), Sodium borohydride (NaBH₄, Sinopharm Group Chemical Reagent Co. Ltd. China, CAS: , AR 98%), Ethylene glycol (H₂NCH₂CH₂NH₂, Tianjin Damao Chemical Reagent Factory, China, CAS No: 107-24-1, AR 99%), Eosin Y (C₂₀H₆Br₄Na₂O₅, Aladdin, China, CAS: 17372-87-1, Lot# F182260, AR).

2.2 Synthesis of NiS₂

NiS₂ nanospheres were synthesized by a typical solute thermal method. In detail, 30 mL ethylene glycol and 30 mL deionized water were evenly mixed under magnetic stirring. Then, 0.6 g PVP was added to the mixed solution to make it evenly distributed in the solution. After that, 2 mmol C₄H₆O₄Ni·4H₂O and 6 mmol Na₂S₂O₃·5H₂O were added to the above solution successively. After stirring for 30 min, the above solution was put into a high-pressure reaction kettle lined with polytetrafluoroethylene and heated continuously at 180 °C for 12 h. After the reactor cooled, the sediment was separated by centrifugation. The product was washed with water and ethanol and dried overnight at 60 °C. Finally, NiS₂ is ground into a solid powder²⁶.

2.3 Synthesis of MoSe₂

MoSe₂ photocatalysts were prepared by a one-pot hydrothermal method, but having a minor modification of this reported²⁷. Typically, 0.316 g (4 mmol) selenium powder was added to 50 mL deionized water and stirred evenly. Then, 0.304 g NaBH₄ was added to the above solution and stirred for 1 h. During this process, the selenium powder was gradually reduced to Se²⁻, correspondingly, the black solution became clear. Finally, after stirring, 0.484 g of NaMoO₄ was added to the clarified solution, which quickly turned black. After continuous stirring for 1 h, the uniform solution was transferred to an 80 mL reactor and heated at 180 °C for 24 h. The final product was recovered by filtration and washed several times with deionized water and finally with ethanol, followed by drying in vacuum at 60 °C for 24 h.

2.4 Synthesis of NiS₂/MoSe₂

The preparation of NiS₂/MoSe₂ is based on the preparation of NiS₂, adding the already prepared MoSe₂. As described in section 2.2, after adding the medicine required for the preparation of NiS₂ and stirring for 30 min, add the prepared MoSe₂ powder. The quality of the added MoSe₂ was different, forming different proportions of composites, which were named NiS₂/MoSe₂-5, NiS₂/MoSe₂-10, NiS₂/MoSe₂-20, NiS₂/MoSe₂-40, NiS₂/MoSe₂-60, NiS₂/MoSe₂-80. Among them, the value in the name indicates the quality of the added MoSe₂.

2.5 Characterizations

The internal structure of the synthesized sample was measured by X-ray diffraction (XRD) on Rigaku RINT-2000 (Japan) using Cu K_α radiation at a scan rate of 5 (°)·min⁻¹. The morphology of the obtained product was observed by scanning electron microscope (SEM, Carl Zeiss AG, Germany) and transmission electron microscope (TEM, FEI, USA), and its microstructure was further tested by energy dispersive X-ray spectroscopy (EDS) and high resolution transmission electron microscope (HRTEM). The UV-Vis diffuse reflectance spectrum (DRS) of the sample was tested on a UV-2550 (Shimadzu, Japan) spectrometer, which was converted to BaSO₄ using reference. X-ray photoelectron spectroscopy (XPS) of the prepared samples was performed on a fluorescence spectrometer (ESCALAB 250Xi, Thermo-fisher, USA) to test the composition of the compound and the surface state of the elements. The nitrogen adsorption-desorption isotherm was measured by Micromeritics ASAP2020M (USA) nitrogen adsorption device, and the specific surface area of the sample was calculated by BET method. The photoluminescence (PL) spectrum of the sample was measured on a Horiba Scientific (France) FluoroMax-4 fluorometer spectrometer at room temperature, and time-resolved fluorescence emission spectra were obtained on the Horiba Jobin Yvon data station.

The photocurrent response, Mott-Schottky curve, electrochemical impedance spectroscopy (EIS) measurements and linear sweep voltammetry (LSV) measurements were performed with a Princeton electrochemical workstation (USA). The working electrodes were prepared by drop-coating

homogeneous catalyst suspensions directly onto the precleaned FTO glass surfaces (1×1.5 cm). Concomitantly, platinum plate was used as the opposite electrode, saturated calomel electrode (SCE) was used as the reference electrode, and $0.2 \text{ mol} \cdot \text{L}^{-1}$ Na_2SO_4 aqueous solution was used as the electrolyte. $E^0 = 0.24$ V vs NHE (Normal Hydrogen Electrode) at 25°C for saturated calomel electrode.

2.6 Photocatalytic hydrogen production

In the H_2 production experiments, 10 mg catalyst and 20 mg Eosin Y (EY) were added to a 62 mL quartz bottle and then 30 mL of 15% v/v triethanolamine (TEOA) solution was added to seal the reaction bottle with a rubber pad. The catalyst was suspended in solution and N_2 was used to replace the air in the bottle. Finally, place the bottle in a nine-channel reaction system with a white light source of 5 W, $\lambda \geq 420$ nm. During the photocatalytic process, 0.5 mL of gas was extracted with a syringe every 0.5 h, and H_2 was analyzed by phase chromatography (using Tianmei GC7900, TCD and N_2 as carriers).

3 Results and discussion

3.1 Structure and morphology analysis

3.1.1 X-ray diffraction analysis

In order to determine the crystalline phase structure of the material, we gave the X-ray diffraction patterns of the NiS_2 , MoSe_2 and $\text{NiS}_2/\text{MoSe}_2$ composites, as shown in Fig. 1. First, we identify the phase and crystallinity of pure NiS_2 and MoSe_2 , as shown in Fig. 1A. The diffraction peaks at 27.03° , 31.5° ,

35.25° , 38.7° , 47.95° , 53.45° , 45.05° , 56.05° , and 58.53° in the XRD spectrum of NiS_2 correspond to (111), (200), (210), (211), (220), (221), (311), (222), (230) crystal planes confirm the successful synthesis of NiS_2 ²⁶. In the meantime, the clear diffraction peak indicates that NiS_2 has good crystallinity^{27–29}. In contrast, MoSe_2 has poor crystallinity. The peak envelopes at 32.77° and 55.81° correspond to the MoSe_2 standard card (PDF#72-1420). Fig. 1B shows the diffraction spectra of the composite catalyst NiS_2 and pure NiS_2 and bare MoSe_2 . By comparison, it was found that there was no obvious MoSe_2 diffraction peak in the composite catalyst, which was attributed to the poor crystallinity of MoSe_2 itself. The above results can confirm the successful preparation of the catalyst.

3.1.2 Transmission electron microscopy characterization

Fig. 2A,B show the scanning electron microscope (SEM) images of pure NiS_2 and bare MoSe_2 , respectively. It can be found that the microscopic appearance of NiS_2 was a uniform nanosphere with a size of about 100 nm and a uniform distribution. However, pure MoSe_2 does not show obvious morphological structure. This was consistent with XRD results.

Fig. 3 was a transmission electron microscope (TEM) image of the composite catalyst. Combining literature reports²⁶ and Fig. 2, it can be determined that the nanospheres in Fig. 3A are NiS_2 , and the surrounding amorphous material should belong to MoSe_2 . Fig. 3B was a high magnification view of Fig. 3A, which further proved the spherical structure of NiS_2 . A high-resolution transmission electron microscopy (HRTEM) test was performed on the catalyst. As shown in Fig. 3C, the 0.235 nm lattice fringe

Fig. 1 XRD patterns of (A) pure NiS_2 and bare MoSe_2 samples and (B) $\text{NiS}_2/\text{MoSe}_2$ - x ($x = 5\text{--}80$) samples.

Fig. 2 SEM images of (A) bare NiS_2 and (B) pure MoSe_2 .

Fig. 3 TEM images (A, B), HRTEM image (C) and EDX patterns (D) taken from NiS₂/MoSe₂-40.

Fig. 4 (A) N₂ adsorption-desorption isotherms and (B) pore size distribution curves of the NiS₂, MoSe₂ and NiS₂/MoSe₂-40 samples.

corresponds to the (211) crystal plane of NiS₂, which further confirmed the existence of NiS₂. At the same time, the lattice spacing of 0.27 nm can also coincide with the (012) crystal plane of MoSe₂²³. The energy dispersive X-ray pattern (Fig. 3D) shows the presence of Ni, S, Mo, and Se elements, which determines the successful preparation of NiS₂/MoSe₂.

3.2 Brunauer-Emmett-Teller analysis

Nitrogen adsorption-desorption isotherms and pore size distribution curves were used to verify the pore structure of pure NiS₂ and MoSe₂ and NiS₂/MoSe₂ composite catalysts. As shown in Fig. 4A, the isotherm curves are all typical type IV isotherms with H3 type hysteresis loop³⁰. The sample showed high adsorption in the range of 0.8–1.0, indicating the mesoporous structure of the material³¹. The pore size distribution curve further proves this point, as shown in Fig. 4B. At the same time, it can be seen that NiS₂ has a larger pore size, which corresponds to the results in Table 1. Besides, pure NiS₂ also shows the smallest specific surface area (16.18 m²·g⁻¹), while the specific

surface area of the composite material lies between the two. The above results were related to the appearance of the catalyst. Combining Figs. 2 and 3, NiS₂ is a uniformly distributed nanosphere, so it must have the smallest specific surface area and the largest pore size. However, MoSe₂ is an amorphous substance with a smaller size, which surrounds the NiS₂ nanospheres, thereby reducing the pore diameter of the catalyst and increasing the specific surface area of the catalyst (28.18 m²·g⁻¹).

3.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to detect the chemical state of chemical elements in the material³². As shown in Fig. 5, the fine spectra of elements of pure substances and complexes are shown in the figure. Fig. 5A shows the typical binding state of Ni in NiS₂. The binding energies at 853.28 eV and 871.16 eV are attributable to the Ni 2p_{3/2} and Ni 2p_{1/2} electron orbitals, respectively, which proved the existence of Ni²⁺ in the catalyst, and the results were consistent with XRD.

Fig. 5 XPS spectra of (A) Ni 2p; (B) S 2p; (C) Mo 3d and (D) Se 3d of pure NiS₂, bare MoSe₂ (up) and NiS₂/MoSe₂ composite (down).

Table 1 Textural properties of different samples.

Samples	BET specific surface area (m ² ·g ⁻¹)	Pore size (nm)	Pore volume (cm ³ ·g ⁻¹)
NiS ₂	16.18	33.333	0.1316
MoSe ₂	43.64	18.900	0.2040
NiS ₂ /MoSe ₂ -40	28.18	19.787	0.1352

Moreover, 876.78 eV are the binding energies of Ni³⁺, and the binding energies at 854.97 eV and 859.74 eV are attributable to the electron orbitals of Ni in (Ni(OH)₂), which may come from the slight oxidation of NiS₂ surface^{33,34}. The electron binding energy spectrum of S 2p orbital was shown in Fig. 5B. The binding energies of S 2p_{3/2} and S 2p_{1/2} electron orbitals are at 162.11 eV and 163.30 eV, respectively. According to literature reports, the binding energy is attributed to S₂²⁻³⁵. Meanwhile, we also detected a peak at 164.58 eV, which was assigned to the spin orbital at S₈ 2p_{1/2}, indicating that S remains during the vulcanization, while the peaks at 167.92 eV may be caused by the S—O bond³⁶. In addition, in the NiS₂/MoSe₂ composite, we found two more peaks than pure NiS₂, at 160.47 eV and 169.27 eV, respectively. Where, the binding energy at 169.27 eV was derived from SO₄²⁻³⁷, while the binding energy at 160.47 eV corresponds to the S 2p_{1/2} orbital of S²⁻, which may be due to the formation of Mo—S bond³⁸.

Fig. 5C, D show the photoelectron spectra of the elements Mo and Se, respectively. In Fig. 5C, the peaks at 228.56 and 231.63 eV come from the 3d_{5/2} and 3d_{3/2} spin orbitals of Mo⁴⁺. The peak at 229.66 eV and 232.76 eV is the splitting peak of 3d_{5/2} and 3d_{3/2}, which was attributed to the 2H phase polymorph of MoSe₂.

Moreover, the binding energy of 235.83 eV was ascribed to Mo⁶⁺^{39,40}. In addition, according to the literature⁴¹, 226.32 eV was the binding energy of S 2s. Fig. 5D shows the electronic energy spectrum of Se²⁻, with 54.33 eV and 55.33 eV belong to the Se 3d_{5/2} and Se 3d_{3/2} electronic orbitals⁴².

Charge transfer in photocatalytic reaction mechanism was further explored by comparing the migration of binding energy of each element in pure NiS₂, bare MoSe₂ and complex⁴³. The upper electron spectrum corresponds to the elements in pure matter in Fig. 5, while the under electron spectrum corresponds to the same elements in the complex. It can be observed from the figure that both Ni and S elements in the composite have shifted to the higher energy direction, while the shifting directions of Mo and Se elements are opposite. This result indicates that there was an interfacial electric field in the composite, and electrons migrate from NiS₂ to MoSe₂⁴⁴.

3.4 Optical properties

UV-Vis diffuse reflectance spectroscopy was used to study the light absorption properties of the prepared samples. According to Fig. 6A, the NiS₂, MoSe₂ and NiS₂/MoSe₂ composite catalysts all showed good absorption performance. Moreover, due to the inherent narrow band gap characteristics of the material, it cannot show obvious absorption band edge. In addition, the color of the catalyst was black, which plays an important role in the test of light absorption performance⁴⁵. Obviously, the light absorption intensity of composite photocatalyst NiS₂/MoSe₂ was higher than that of pure NiS₂ and bare MoSe₂. Stronger light absorption was more favorable for photocatalytic activity⁴⁶. Through the Tauc equation ($ah\nu = A(h\nu - E_g)^{1/2}$), the direct band

Fig. 6 (A) UV-Vis diffuse reflectance spectra of as-prepared samples and (B) the corresponding $(ah\nu)^2$ vs photon energy curves of NiS_2 and MoSe_2 samples.

gap of two narrow band gap semiconductor materials was obtained based on the tangent line of $(ah\nu)^2$ to $h\nu$ curve (where α was the absorption coefficient and $h\nu$ was the photon energy)^{43,47}. As shown in Fig. 6B, the band gaps of NiS_2 and MoSe_2 are 1.32 eV and 1.41 eV, respectively.

Photoluminescence (PL) spectroscopy was used to study the transfer of interface electrons. As shown in Fig. 7A, all samples are in the EY system, so all samples exhibit an emission peak of 534 nm when excited at 480 nm. Here, the emission peak of fluorescence was caused by electron-hole recombination in the excited semiconductor⁴⁸. More importantly, compared with EY NiS_2 and MoSe_2 , the emission intensity of the $\text{NiS}_2/\text{MoSe}_2$ composite was the lowest, indicating that the electron-recombination in the composite was effectively suppressed, which is beneficial to the improvement of photocatalytic activity⁴⁹.

The time resolution characterization of PL was performed to further explore the electron transfer dynamics within the material⁵⁰. As shown in Fig. 7B, the attenuation curve shows observable differences. Time-resolved photoluminescence

(TRPL) was fitted using a two-exponential decay model, and the formula was as follows:

$$I(t) = \sum_{i=1,2,3} B_i \exp(-t/\tau_i) \quad (1)$$

I is the normalised emission intensity; t is the time after the pulsed laser excitation; τ_i are the respective decay lifetimes; B_i are the amplitude (pre-exponential factor);

$$\langle \tau \rangle = \sum_{i=1,2,3} B_i \tau_i^2 / \sum_{i=1,2,3} B_i \tau_i \quad (2)$$

$\langle \tau_{av} \rangle$ is the average lifetime; τ_i is the respective decay times; B_i is the amplitude (pre-exponential factor);

The fitting results are shown in Table 2, short lifetime τ_1 carrier radiation combination, namely the electron relaxation from the excited state to the ground state, which was caused by the carrier combination. The reduction of recombination indicates that the utilization rate of photoexcited electrons or holes was higher^{51,52}. Long lifetime τ_2 reveals the non-radiation combination of carriers⁵². Obviously, compared with pure NiS_2 and MoSe_2 , the τ_1 , τ_2 , and τ_{av} of $\text{NiS}_2/\text{MoSe}_2$ compounds are the

Fig. 7 (A) Photoluminescence spectra and (B) time-resolved fluorescence spectra of as-prepared samples.

Table 2 Kinetic analysis of emission decay for as-prepared samples.

Samples	τ_1 (ns)	τ_2 (ns)	Average lifetime $\langle \tau_{av} \rangle$ (ns)	χ^2
EY	0.40 (90.61%)	7.14 (9.39%)	0.44	1.40
NiS_2	0.32 (93.54%)	6.53 (6.46%)	0.34	1.39
MoSe_2	0.36 (91.67%)	7.27 (8.33%)	0.39	1.36
$\text{NiS}_2/\text{MoSe}_2\text{-40}$	0.12 (98.46%)	2.63 (1.54%)	0.12	1.59

minimum values, which indicated that the formation of the heterojunction accelerated electron transfer and promoted photocatalytic reduction.

3.5 Photocatalytic performance

The catalytic activity of EY sensitized catalysts was evaluated in triethanolamine (TEOA) solution. As shown in Fig. 8A, the hydrogen production activity of the composite photocatalyst was significantly higher than that of the two pure substances under the same conditions. This was owing to the strong light absorption in the composite photocatalyst and the formation of the S-scheme heterojunction promoted photocatalytic reaction. However, the proportion of MoSe₂ in the corresponding amount of composite catalyst was different, and the final hydrogen evolution effect was also different. As shown in Fig. 8B, in the original preparation process of the composite catalyst, when the addition amount of MoSe₂ was 40 mg, the catalytic activity of the catalyst was the highest, about 7 mmol·h⁻¹·g⁻¹. At this time, the hydrogen production rate of the composite catalyst (NiS₂/MoSe₂-40) was 2.05 and 2.44 times that of NiS₂ (3.417 mmol·h⁻¹·g⁻¹) and MoSe₂ (2.877 mmol·h⁻¹·g⁻¹), respectively. After the amount of MoSe₂ exceeded 40 mg, there was a slight drop in hydrogen production, which may be because of the “shading effect”⁵³. When there was too much MoSe₂ on the surface of NiS₂ nanospheres, it affected the light absorption of NiS₂ and direct contact with the aqueous solution. From the perspective of catalytic activity, it was necessary to find the optimal ratio of photocatalyst.

Fig. 8C shown the hydrogen-producing activity of the composite photocatalyst in sacrificial reagents with different pH values, aiming to explore the influence of pH value on the hydrogen-producing activity of photocatalyst. As can be seen from the figure, when pH value was 11, the photocatalytic activity of the sample was the highest, about 7.59 mmol·h⁻¹·g⁻¹. On the one hand, when pH value was too small, triethanolamine (TEOA) will undergo protonation, which weakens its ability to provide electrons⁵⁴. On the other hand, the amount of H⁺ decreases sharply under overalkaline conditions, thus reducing the hydrogen-producing activity. Stability was an important index to evaluate the quality of photocatalysts. We tested the stability of the best proportional photocatalyst within 20 h⁵⁵, as shown in Fig. 8D. Since the dye EY was easily degraded under light, the less EY will participate in the photocatalytic reaction through the increase of light time⁴³. However, when EY was added again in the third cycle experiment, the catalytic activity of the photocatalyst increased again. The results shown that the photocatalyst has good stability.

In order to explore the influence of the photoreaction process on the photocatalyst, XRD and SEM of the used hydrogen catalyst were tested, as shown in Fig. 9. Fig. 9A showed the XRD pattern of the catalyst before and after the photocatalytic reaction. Through comparative study, it was found that the intensity of diffraction peak of used catalyst decreases, which was related to the amount of sample used in the test. The pure NiS₂ sample after reaction has several more diffraction peaks in

Fig. 8 (A) Time dependent photocatalytic H₂ production and (B) average hydrogen production rates of EY sensitized pure NiS₂, bare MoSe₂ and NiS₂/MoSe₂-x (x = 5, 10, 20, 40, 60); (C) effect of the pH value on the hydrogen production of the NiS₂/MoSe₂-40 photocatalyst; (D) stability test for H₂ evolution over the NiS₂/MoSe₂-40 photocatalyst in cycle runs under visible light irradiation (λ ≥ 420 nm).

Fig. 9 (A) XRD results before (used) and after (fresh) hydrogen production tests and SEM images of used pure NiS₂ (B), MoSe₂ (C) and NiS₂/MoSe₂-40 (D).

Fig. 10 (A) Transient photocurrent response; (B) LSV curve and (C) the electrochemical impedance spectroscopy for EY-sensitized NiS₂, MoSe₂ and NiS₂/MoSe₂-40 samples in 0.5 mol·L⁻¹ Na₂SO₄.

the range of 15°–17° than the fresh sample. This was owing to the photoetching effect in the reaction process leading to the production of S elemental substance⁵⁶. In addition, the XRD results of other samples remain unchanged. Fig. 9B–D were SEM images of pure NiS₂, MoSe₂ and NiS₂/MoSe₂ composite catalysts after use, respectively. In combination with Fig. 2, it can be found that there was no change in the morphology and structure of the catalyst after use, which further proved that the catalyst has good stability.

3.6 Photoelectrochemical properties

Here, we further explore the electron-hole separation efficiency of the photocatalyst by testing the photoelectrochemical performance of the sample. The transient photocurrent density-time curve of NiS₂, MoSe₂ and the composite catalyst were shown in Fig. 10A. In the four cycles of on-off, the photocurrent showed obvious changes. According to previous reports⁵⁷, the photocurrent density has a positive correlation with the charge separation efficiency. It can be seen from Fig. 10A that the photocurrent density of the composite

photocatalyst is higher than that of NiS₂ and MoSe₂, which indicates that the composite photocatalyst has a higher electron-hole separation efficiency. In order to further confirm the above results, we used linear voltammetry to test the samples, as shown in Fig. 10B. It can be observed that the composite photocatalyst has a lower cathode current than NiS₂ and MoSe₂, which was attributed to the S-scheme heterojunction between the composite catalysts, which promoted the electron mobility of the photocatalyst⁵⁸.

Furthermore, electrochemical impedance spectroscopy (EIS) Nyquist plots of NiS₂, MoSe₂ and NiS₂/MoSe₂ composite samples were obtained through testing, as shown in Fig. 10C. The arc radius is positively correlated with the charge transfer resistance of the sample⁵⁹. Therefore, the NiS₂/MoSe₂ composite sample has a small charge transfer resistance. In other words, compared with pure NiS₂ and MoSe₂, NiS₂/MoSe₂ composite catalyst has the strongest charge transfer efficiency. The above results are consistent, which further emphasizes the excellent charge transfer efficiency of NiS₂/MoSe₂ composite

Fig. 11 (A) Mott-Schottky plots for EY-sensitized NiS₂ and MoSe₂ samples in 0.5 mol·L⁻¹ Na₂SO₄; (B) Schematic illustration of band structures for NiS₂ and MoSe₂.

catalyst.

In order to explain the reaction mechanism of the composite photocatalyst, Mott-Schottky (M-S) test was performed on NiS₂ and MoSe₂ samples, as shown in Fig. 11A. The C^{-2} - E curves of the samples show a positive slope, indicating that NiS₂ and MoSe₂ were n -type semiconductors^{60,61}. Besides, we obtain the flat band potentials of NiS₂ and MoSe₂ through formula (3), which were -0.42 eV and -0.26 eV respectively. For n -type semiconductors, the conduction band (E_{CB}) position was negative 0.1 V or 0.2 V compared with the measured flat band potential⁶². Further, formula (4) was used to convert the guide band position corresponding to the normal hydrogen electrode (NHE), which were -0.38 eV and -0.22 eV respectively. Meanwhile, combining the band gap values of NiS₂ and MoSe₂ (Fig. 6B), their valence band (E_{VB}) positions were obtained through formula (5), as shown in Fig. 11B. It can be determined that the band arrangement between NiS₂ and MoSe₂ conforms to the photocatalytic mechanism of S-scheme.

$$1/C^2 = 2(N_D e \epsilon \epsilon_0)^{-1} \cdot (E - E_{fb} - kT/e) \quad (3)$$

C is the capacitance of the space charge region; N_D is charge carrier concentration; e is electron charge; ϵ is dielectric constant; ϵ_0 is vacuum permittivity; E is electrode applied potential; E_{fb} is flat band potentials; k is Boltzmann constant; T is absolute temperature;

$$E_{NHE} = E_{SCE} + 0.24V \quad (4)$$

According to the UV-Vis band gap (E_g) data, the valence band (E_{VB}) position of NiS₂ and MoSe₂ was calculated by Eq. (5):

$$E_{CB} = E_{VB} - E_g \quad (5)$$

3.7 Proposed photocatalytic hydrogen evolution mechanism

Based on the above conclusions, the charge transfer mechanism of NiS₂/MoSe₂ composite material under illumination was shown in Scheme 1. EY molecules adsorb on the surface of the catalyst and form a singly excited state EY^{1*}, which absorbs photons and then forms EY^{3*} through an interphase transition (ISC). EY^{3*} was reduced and quenched by TEOA to produce oxidized TEOA⁺ and EY^{•-}. EY^{•-} instability will transfer electrons to the conduction band of NiS₂ and MoSe₂, and the reducing dye molecule will return to the ground state. At the same time, after NiS₂ and MoSe₂ contact, the internal electric field and band bending are generated. Under light, the electrons of NiS₂ and MoSe₂ were excited to transition from the valence band to the conduction band. Owing to the effect of the internal electric field, the electrons in MoSe₂ conduction band were more inclined to combine with the holes in NiS₂ valence band⁶³⁻⁶⁵. Thus, NiS₂ with greater potential difference generates H₂ by combining with H⁺, while holes were consumed by TEOA. This process not only speeded up the separation efficiency of electron and hole, but also effectively inhibited the recombination of electron and hole, thus forming efficient hydrogen evolution mechanism.

4 Conclusions

In a nutshell, this study constructed a new type S-scheme heterojunction of NiS₂/MoSe₂ for photocatalytic decomposition of water and hydrogen production system. As a result, the hydrogen production rate of the composite was 2.05 and 2.44 times that of pure NiS₂ and MoSe₂, respectively. This was because the S-scheme heterojunction causes a larger potential difference in the redox reaction, which was beneficial to the effective separation of electrons and holes and the redox reactions. Meanwhile, in the EY-sensitized photocatalytic reaction system, EY not only acts as a photosensitizer to enhance light absorption, but also transfers electrons to NiS₂ and MoSe₂.

to promote the reduction of H^+ to produce H_2 . This work provided a new reference for the study of S-scheme heterojunction to effectively improve the efficiency of photocatalytic hydrogen production.

Author contributions: Yang Liu and Xuqiang Hao conceived and designed the experiments; Yang Liu and Haiqiang Hu performed the experiments; Zhiliang Jin contributed reagents/materials and analysis tools; Yang Liu wrote the paper.

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