available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

MoS₂/Zn₃In₂S₆ composite photocatalysts for enhancement of visible light-driven hydrogen production from formic acid

Sujuan Zhang, Shixiang Duan, Gaoli Chen, Sugang Meng, Xiuzhen Zheng, You Fan, Xianliang Fu, Shifu Chen *

Key Laboratory of Clean Energy and Green Circulation, Huaibei Normal University, Huaibei 235000, Anhui, China

ARTICLE INFO

Article history:

Received 23 February 2020

Accepted 13 April 2020

Published 5 January 2021

Keywords:

Hydrogen production

Zn₃In₂S₆

Formic acid

MoS₂

Photocatalysis

ABSTRACT

Enhancing the separation efficiency of photogenerated carriers is propitious for the promotion of photocatalytic hydrogen production from formic acid decomposition. Herein, MoS₂/Zn₃In₂S₆ (MoS₂/ZIS6) composite photocatalysts containing varying mass percentages of MoS₂ were obtained by a straightforward synthetic method. The results confirmed that MoS₂, as a cocatalyst, markedly promoted the photogenerated charge separation efficiency and visible light-driven hydrogen production activity of ZIS6 ($\lambda > 400$ nm). Specifically, the as-prepared 0.5% MoS₂/ZIS6 photocatalyst exhibited the highest photocatalytic hydrogen production rate (74.25 $\mu\text{mol}\cdot\text{h}^{-1}$), which was approximately 4.3 times higher than that of ZIS6 (17.47 $\mu\text{mol}\cdot\text{h}^{-1}$). The excellent performance of the 0.5% MoS₂/ZIS6 photocatalyst may be due to the fact that MoS₂ has a low Fermi energy level and can thus enrich photogenerated electrons from ZIS6, and furthermore reduce H⁺ derived from formic acid, to form hydrogen. The structure and morphology of the MoS₂/ZIS6 photocatalysts and the reactive species were determined by X-ray diffraction, transmission electron microscopy, and field emission scanning electron microscopy, among others; a plausible mechanistic rationale is discussed based on the results.

© 2021, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Formic acid (FA) is rapidly becoming a potential hydrogen storage material due to its non-toxic, low cost, non-flammable characteristics, and high hydrogen content [1,2]. As visible light accounts for approximately 43% of the solar spectrum, utilizing clean energy-visible light to drive hydrogen production from formic acid would be an effective approach for ameliorating the energy crisis [3,4]. Therein, the development of efficient visible light catalysts is of crucial importance. Hitherto, numerous

active photocatalysts, such as phosphides, nitrides, sulfides, metal oxides and so on [5–12], have been developed and applied in the field of visible light photocatalysis for hydrogen production and other areas. However, the majority of these catalysts suffer from shortcomings such as poor light absorption, light corrosion, deactivation, or poor stability [13–18]. In addition, the development of semiconductor photocatalysts faces significant challenges regarding optical absorption capacity, stability, low toxicity, and other factors [19]. Therefore, research into the development of efficient visible light-related

* Corresponding author. Tel: +86-561-3802061; Fax: +86-561-3090518; E-mail: chshifu@chnu.edu.cn

This work was supported by the National Natural Science Foundation of China (51972134, 51472005, 51772118), the Natural Science Foundation of Anhui Province for Distinguished Young Scholars (1808085J24), the Project of Anhui Province for Excellent Young Talents in Universities (gxyq2019029), and the Natural Science Foundation of Educational Committee of Anhui Province (KJ2019A0602, KJ2018A0387).

DOI: 10.1016/S1872-2067(20)63584-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 42, No. 1, January 2021

semiconductor photocatalysts for FA photocatalytic hydrogen production is prolific and ongoing [20–22].

The key to achieving the above-mentioned objective is efficient photogenerated charge separation and transfer during the process of photocatalysis, which leads to an improvement in the catalyst's photocatalytic performance. In recent years, ZIS6 has rapidly become a "photocatalyst semiconductor star", due to characteristics such as strong visible light absorption, chemical stability, and low environmental impact [23–26]. More importantly, the nanosheet structure of ZIS6 facilitates the formation of a heterojunction between it and other catalysts that can promote the separation of photo-generated carriers, thereby increasing its photocatalytic activity [27]. It is currently accepted that noble metals (such as Pt [28,29], Au [30,31], Rh [32], and Pd [33,34]) can generally be applied as cocatalysts to enhance the separation efficiency of photoelectron-hole pairs. However, the limitation of noble metals is their high cost. Thus, the development of noble metal-free cocatalysts remains a considerable challenge for photocatalytic hydrogen production.

MoS₂ has attracted considerable attention due to its excellent ability to promote photocatalytic hydrogen production, as well as its accessibility and high chemical stability. Numerous previous reports confirm that coupling MoS₂ with a second semiconductor is an effective approach for enhancing the performance of semiconductor photocatalysts [35–38]. For example, MoS₂/ZnIn₂S₄ composite photocatalysts, synthesized by Li and co-workers, exhibited remarkable photocatalytic activity as a result of MoS₂ loading. However, the synthesis of MoS₂ involved numerous unfavorable procedures, such as the necessity for elevated temperatures, lengthy solvothermal treatment, and the use of toxic H₂S gas, all of which limit the applicability of MoS₂ [39].

In this study, the preparation of MoS₂/ZIS6 samples was achieved by a straightforward hydrothermal method, and their photocatalytic activity was investigated under visible light irradiation. The MoS₂/ZIS6 (0.5%) catalyst exhibited outstanding photocatalytic performance in the FA hydrogen production system. In addition, morphology effects and MoS₂/ZIS6 photocatalyst properties were systematically studied, revealing key structural features of MoS₂/ZIS6. On the basis of the obtained data, a reaction mechanism of the promoted photocatalytic hydrogen production is proposed. It is noteworthy that the MoS₂ introduced into the ZIS6 photocatalyst can serve as an efficient electronic enrichment center, enhancing the separation efficiency of photogenerated charges, thereby promoting the photocatalytic performance of ZIS6 photocatalysts.

2. Experimental

2.1. Sample preparation

The synthesis of MoS₂/ZIS6 was performed according to a literature procedure [40], and adjusted accordingly. Typically, InCl₃·4H₂O (2 mmol), ZnSO₄·7H₂O (3 mmol), appropriate amounts of C₂H₅NS and (NH₄)₆Mo₇O₂₄·4H₂O were placed into a 100 mL Teflon-lined autoclave filled with 70 mL deionized wa-

ter as the solvent and stirred for 60 min. The autoclave was sealed and maintained at 160 °C for 12 h, and then allowed to cool to room temperature. The resultant precipitate was alternately and thoroughly washed with deionized water and absolute ethanol several times. Finally, the products were collected and dried in vacuum at 60 °C for 10 h. The various mass percentages of MoS₂ in the MoS₂/ZIS6 photocatalysts were achieved by simply adjusting the amounts of (NH₄)₆Mo₇O₂₄·4H₂O and C₂H₅NS, and labeled accordingly as follows: 0.25% MoS₂/ZIS6, 0.5% MoS₂/ZIS6, 1% MoS₂/ZIS6, 3% MoS₂/ZIS6, 5% MoS₂/ZIS6 and 10% MoS₂/ZIS6. The synthesis of pure MoS₂ followed the same procedure, without the addition of ZIS6.

2.2. Experimental materials

Zinc sulfate heptahydrate (ZnSO₄·7H₂O, ≥99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, ≥99.0%), Formic acid (AR, 88%), thioacetamide (C₂H₅NS, TAA, ≥98%), indium chloride tetrahydrate (InCl₃·4H₂O, 99.9%), potassium ferricyanide (K₃Fe(CN)₆, ≥99.5%), potassium ferrocyanide trihydrate (K₄Fe(CN)₆·3H₂O, 99.0%), potassium chloride (KCl, 99.5%) and sodium sulfate anhydrous (Na₂SO₄, 99.0%) were all supplied by Aladdin Reagent (Shanghai, China) and used as received.

2.3. Materials characterization

X-ray diffraction (XRD) patterns of the prepared photocatalysts were detected by a Bruker D8 X-ray powder diffractometer using Cu K_α radiation at room temperature. UV-visible diffuse reflection spectra (UV-Vis DRS) were conducted on a TU-1950 Vis-NIR spectrophotometer (TU-1950, Persee) with BaSO₄ as a reference. Field emission scanning electron microscopy (FESEM) images were studied on a FEI Quanta 650 scanning electron microscope. The morphologies and microstructures of the photocatalysts were determined by transmission electron microscopy (TEM, FEI Tecnai G2 F20) and high-resolution transmission electron microscopy (HRTEM) at an accelerating voltage of 200 kV, elemental mappings were performed using an energy-dispersive X-ray spectrometer (EDS) attached to the TEM instrument. X-ray photoelectron spectroscopy (XPS) analysis was obtained on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) equipped with an Al K_α X-ray beam (1486.6 eV). The binding energies were corrected with reference to the C 1s peak of the surface adventitious carbon at 284.6 eV. The Brunauer-Emmett-Teller (BET) data of the samples was obtained by N₂ adsorption-desorption at 77.3 K using a Micromeritics ASAP 2460 instrument.

Photoluminescence (PL) emission spectra were recorded on a JASCO FP-6500 type fluorescence spectrophotometer and time-resolved photoluminescence spectroscopy (TR-PL) was recorded on an Edinburgh FS5 fluorescence spectrophotometer. Average lifetime model for calculating the total lifetime of time-resolved fluorescence spectroscopy:

$$\tau = \sum A_n \tau_n^2 / A_n \tau_n \quad (n = 1, 2, 3, \dots) \quad (1)$$

The fitting model of time-resolved fluorescence spectrum is E-exponential model:

$$Y = A + B_1 \exp(-i/T_1) + \dots + B_n \exp(-i/T_n) \quad (n=1, 2, 3, \dots) \quad (2)$$

	B1	T1/ns	B2	T2/ns	T/ns
1	4.389175	0.01489459	3.815503E-04	6.761111	0.2709953377
2	0.7557613	0.04515458	5.743187E-04	5.486072	0.5050377595

The electrochemical characteristics of the prepared samples were recorded on a CHI 660E electrochemical workstation (Chenhua, Shanghai) at a bias of 0.1 V (vs. SCE) in a standard three-electrode cell with the samples, Pt wire and Ag/AgCl electrode as the working electrode, counter electrode and reference electrode, respectively. The catalyst powder was deposited on the fluoride tin oxide (FTO) substrate to serve as working electrode. A quartz electrolysis cell filled with 0.2 M Na₂SO₄ or 0.1 M KCl electrolyte containing 0.1 M K₃[Fe(CN)₆]/K₄[Fe(CN)₆] was used as the reaction system of photocurrent and EIS experiments, respectively. The same light source as that for the photocatalytic reaction was applied as a visible light source. The Mott-Schottky (MS) analysis of MoS₂ and ZIS6 were also completed on the above electrochemical workstation to estimate the flat band position (*V*_{fb}). The potential range is from −1.0 V to 0.5 V (vs. Ag/AgCl) and the frequencies are at 500, 1000 and 1500 Hz, respectively. 0.2 M Na₂SO₄ aqueous solution was used as electrolyte (pH = 0). Before the measurement, N₂ purification should be carried out.

2.4. Evaluation of the photocatalytic activity

The photocatalytic hydrogen production reactions were performed using a Lab Solar 6A commercial reaction system. The Pyrex top-irradiation reaction cell is connected as a reaction vessel to a glass-enclosed gas circulation system. For convenience of comparison, the amount of all the photocatalyst added to a mixture of 100 ml 6.0 M formic acid solution (without plus sacrificial reagent) were selected to be 0.1 g. Before irradiation, the reaction suspension was degassed using a mechanical pump, and stirred for 30 min to attain an adsorption-desorption equilibrium. Visible light was provided by a 300 W Xe lamp equipped with a 400 nm cutoff filter ($\lambda = 420$ nm). The temperature of reaction solution was remained at 4 °C by a water cool system. The generated H₂ was measured using an online gas chromatograph (GC7806, Tian Mei, Shanghai) with N₂ as the carrier gas.

The apparent quantum efficiency (AQE) for hydrogen generation was calculated according to the following equation, where *N*_e, *N*_p and *N*_H represent the numbers of reacted electrons, incident photons and evolved H₂ molecules, respectively.

$$AQE = N_e / N_p \times 100\% = (2 \times N_H / N_p) \times 100\%$$

2.5. Photogenerated charge behavior

Transient photovoltage (TPV) and transient photocurrent (TPC) measurements were applied to study the kinetic features of the photogenerated charges with a 355 nm laser pulse and power of 50 μJ/pulse from a third-harmonic Nd:YAG laser (Po-

laris II, New Wave Research, Inc.) [41,42]. These kinetic features are helpful for us to understand the mechanism of semiconductor photocatalytic reaction and has certain guiding significance for the design of outstanding photocatalysts.

Practically speaking, the time-resolved-based transient surface photovoltage system (TSPVS) is composed of a laser (Q-smart450, New Wave Research, Inc.), a preamplifier with a light chopper, a photovoltaic sample cell and a 500 MHz digital phosphor oscilloscope (MC-TPV355, Tektronix). The structure of the transient-photovoltage-spectra sample cell is ordered ITO-mica-sample (Figure 13a, inset). TPC measurement system not only contains a laser (Q-smart450, New Wave Research, Inc.), a preamplifier with a light chopper, a photovoltaic sample cell and a 500 MHz digital phosphor oscilloscope, but also contains a voltage/current converter. Both TPV and TPC measurements were carried out at room temperature in air atmosphere. The samples were excited with a laser radiation pulse with the wavelength of 355 nm laser pulse and power of 50 μJ/pulse from a third-harmonic Nd:YAG laser (Polaris II, New Wave Research, Inc.). Moreover, the structure of the transient-photocurrent-spectra sample cell is ordered ITO-sample (Fig. 13(b), inset). It should be pointed out that during the TPC test, the conductive layer of ITO (the part that will be in contact with the sample) is pre-divided by laser nick into two parts that are not conductive to each other.

3. Results and discussion

3.1. X-ray diffraction studies

XRD was applied to investigate the effect of MoS₂ on the crystallographic structure and crystallinity of the as-prepared photocatalysts. The comparison results of pure MoS₂, ZIS6, and a series of MoS₂/ZIS6 composite photocatalysts are shown in Fig. 1. The diffraction patterns of all the composite photocatalysts were analogous, and indexed to a peak of ZIS6 (JCPDS card No. 65-4003). Although the MoS₂/ZIS6 composite photocatalysts contain varying amounts of MoS₂, no peak of MoS₂ can be seen, which may be due to the small size of ZIS6 [43] and the relatively low diffraction intensity of MoS₂. Figure 1 further indicated that the peak position of ZIS6 combined with MoS₂ had no apparent shift compared to that of pure ZIS6. The hex-

Fig. 1. XRD patterns of ZIS6, MoS₂ and MoS₂/ZIS6 samples and standard patterns of ZIS6 and MoS₂.

agonal phase ZIS6 sample exhibits five representative crystal planes (005), (100), (102), (110) and (200), corresponding to the peaks located at five 2θ values, 20.3° , 27.6° , 28.8° , 47.1° and 56.5° , respectively [44]. This suggests that the effect of the MoS_2 load on the crystal structure of ZIS6 can be ignored. In addition, the XRD pattern of pure MoS_2 contained four weak and wide peaks at 14.3° , 32.6° , 44.1° and 58.2° , corresponding to (002), (100), (006), (110) (JCPDS card No. 65-0160), respectively. This result indicates that the MoS_2 synthesized by the hydrothermal method exhibits low crystallinity [37,45,46].

3.2. Morphology and structure characterization

Common morphology and structure characterization techniques (TEM, FESEM, high-resolution transmission electron microscopy (HRTEM), and energy-dispersive X-ray spectrometer (EDS)) were employed for the investigation of the pre-prepared photocatalysts. Figure 2 displays the typical SEM and TEM images of pre-prepared pure ZIS6, and 0.5% MoS_2 /ZIS6 composite. Evidently, pure ZIS6 (Fig. 2(a), (b), (e)) is self-assembled into micro-scale particles (1–3 μm) with a lamellar surface structure [43]. Comparing Fig. 2(c), (d), and (f), it is clear that with the introduction of MoS_2 , the change in the apparent structure of ZIS6 was marginal, indicating that the formation of MoS_2 has no effect on the growth of ZIS6 during the preparation of composite photocatalysts [23]. To examine the structural information of the composite photocatalysts, pure MoS_2 and 0.5% MoS_2 /ZIS6 samples were further analyzed by HRTEM. As shown in Fig. 2(g), (h), and (i), the crystal lattice fringes of 0.32 nm can all be attributed to the (102) crystal plane of ZIS6, while the crystal lattice fringes of 0.27 nm (Fig. 2(h)) and 0.62 nm (Fig. 2(i)) correspond to the (100) and (002) inter-planar spacings of MoS_2 [47–49], respectively, which is consistent with the XRD result (Fig. 1). In addition, the element distribution information of the 0.5% MoS_2 /ZIS6 sample was investigated by means of EDX technology, and the corresponding results are shown in Fig. 2(k). Evidently, the distribution of Mo corresponds to the distribution of Zn, In and S elements in the 0.5% MoS_2 /ZIS6 sample, indicating a very uniform distribution of MoS_2 on pure ZIS6. The distribution of Zn, In and S elements in pure ZIS6 was additionally studied and the results are shown in Fig. 2(j), being exactly the same as those in 0.5% MoS_2 /ZIS6. Note that the presence of C and O elements may be due to the conductive graphite adhesive used in the testing process, and the O_2 molecules adsorbed by the tested samples, respectively. The results confirmed that MoS_2 /ZIS6 samples were successfully obtained by the hydrothermal method, and that MoS_2 was evenly distributed and in close contact with the ZIS6 microspheres, factors favoring efficient photocatalytic hydrogen production from formic acid.

3.3. UV-visible diffuse reflectance spectroscopy analysis

UV-visible diffuse reflectance spectroscopy (UV-Vis DRS) was adopted to examine the light absorption properties of MoS_2 , ZIS6 and MoS_2 /ZIS6 samples, and the spectra and images are shown in Fig. 3. Compared to pure ZIS6, the DRS spectrum

Fig. 2. SEM (a, b), TEM (e), HRTEM (g), elemental mapping images and EDX analysis graph (j) of ZIS6; SEM (c, d), TEM (f), HRTEM (h, i), elemental mapping images and EDX analysis graph (k) of 0.5% MoS_2 /ZIS6.

of the 0.5% MoS_2 /ZIS6 sample displays a discernable red shift. This may indicate that the absorption performance of 0.5% MoS_2 /ZIS6 is superior to that of ZIS6, when the wavelength range is 420–750 nm. Furthermore, pure MoS_2 and pure ZIS6 samples exhibited strong absorption band edges, and the corresponding band gaps (E_g) (Fig. 3 right inset) were calculated to be approximately 1.31 and 2.84 eV, respectively, according to the formula [23]:

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

where, α , h , ν , A and E_g represent absorption coefficient, Planck's constant, frequency of the incident light, a constant, band gap energy, respectively, and $n = 2$ for direct band gap semiconductors. In addition, the minimal shift in light absorp-

Fig. 3. UV-Vis DRS spectra and photos (left inset) of ZIS6, 0.5% MoS₂/ZIS6 and MoS₂ photocatalysts and band gap energy (right inset) of ZIS6 and MoS₂ samples.

tion indicates that MoS₂ with its narrow band gap is densely anchored in the surface phase, rather than the body phase of ZIS6 [50]. In conclusion, these results imply that the MoS₂/ZIS6 composite photocatalyst can utilize the full visible light spectrum for photocatalytic hydrogen production, based on the appropriate band gap.

3.4. XPS analysis

To better understand the surface composition and chemical valence of the elements, XPS analysis of ZIS6, 0.5% MoS₂/ZIS6 and MoS₂ was performed. In Fig. 4(a), XPS pattern of pure ZIS6 indicates that it is predominantly composed of Zn, In and S elements. These results are in agreement with the chemical composition of the as-synthesized samples. However, in the 0.5% MoS₂/ZIS6 samples, Zn, In and S elements are evident, however the presence of the Mo element was not detected,

because the loading amount of low-crystallinity MoS₂ was merely 0.5%. Therefore, to confirm the successful preparation of the composite photocatalyst, high resolution XPS analyses of Zn, In, S, and Mo elements in ZIS6, 0.5% MoS₂/ZIS6 and MoS₂ were additionally performed, and the results are shown in Figs. 4(b)–(e), respectively. In Fig. 4(b), the binding energy values of the Zn 2p peak at 1022.3 and 1045.3 eV correspond to Zn 2p_{3/2} and Zn 2p_{1/2} of Zn²⁺ in ZIS6, respectively, and the spin-orbit splitting energy was approximately 23.0 eV [23]. Compared to the two peaks in pure ZIS6, the two peaks located at approximately 1022.5 and 1045.5 eV in 0.5% MoS₂/ZIS6 had increased by 0.2 eV. The two peaks at approximately 445.3 and 452.9 eV in Fig. 4(c) correspond to the In 3d_{5/2} and In 3d_{3/2} states of In³⁺ in 0.5% MoS₂/ZIS6 [51], respectively, which exhibit a shift of 0.1 eV compared to the two corresponding peaks (445.2 and 452.8 eV) in ZIS6. In Fig. 4(d), the representative peaks of S 2p in pure ZIS6 that appear at 161.1 and 162.2 eV were attributed to S 2p_{3/2} and S 2p_{1/2} of S²⁻ [52], respectively, and the spin-orbit splitting energy between them was approximately 1.1 eV. Evidently, the shifts in Zn²⁺, In³⁺ and S²⁻ bonding energies provide the possibility for the existence of the Mo element, and further confirm the charge transfer between ZIS and MoS₂ interfaces. As a verification of this result, the high resolution XPS spectrum of MoS₂ was further explored and compared with that of 0.5% MoS₂/ZIS6, as shown in Fig. 4(e). In pure MoS₂, the representative peaks of Mo 3d are located at 229.2, 232.5 and 235.7 eV, and correspond to Mo 3d_{5/2} and Mo 3d_{3/2} of Mo⁴⁺, and Mo 3d_{3/2} of Mo⁶⁺ [35,37,53], respectively. The peak at approximately 226.2 eV is consistent with the binding energy of S 2s, corresponding to characteristics of S²⁻ [35,37]. These shifts in the binding energies of S and Mo verified the distinct interaction between MoS₂ and ZIS6, and further confirmed the charge transfer between MoS₂ and ZIS6 interfaces.

Fig. 4. (a) Full XPS spectra of ZIS6, 0.5% MoS₂/ZIS6 and MoS₂; high resolution XPS spectra of Zn 2p (b), In 3d (c), S 2p (d), Mo 3d (e) in pure ZIS6, 0.5% MoS₂/ZIS6 and MoS₂.

Fig. 5. Steady-state (a), and time-resolved PL spectra (b) of ZIS6 and 0.5% MoS₂/ZIS6.

3.5. Photoluminescence analysis

It is well known that the recombination rate of photogenerated electrons and holes can be demonstrated by the intensity of fluorescence emission [54,55]. For an in-depth investigation of the photogenerated carrier separation efficiency, the steady-state and the time-resolved photoluminescence (TR-PL) emission spectra of ZIS6 and 0.5% MoS₂/ZIS6 samples were analyzed, and the results are shown in Fig. 5. As seen in Fig. 5(a), pure ZIS6 displayed a significantly higher steady-state PL intensity compared to 0.5% MoS₂/ZIS6, implying a more drastic charge recombination. Figure 5(b) displays the average lifetimes of the photogenerated charges generated from ZIS6 and 0.5% MoS₂/ZIS6 samples, calculated as 0.27 and 0.51 ns, respectively, according to the fitting equation in S2. According to the literature [56], the longer transient fluorescence lifetime represents a lower photogenerated electron-hole pair recombination, and translates to enhanced photocatalytic activity. Overall, the results indicate that the ability of 0.5% MoS₂/ZIS6 to restrict photogenerated electron-hole pair recombination, and thus improve photocatalytic activity, is superior to that of pure ZIS6.

3.6. Brunauer-Emmett-Teller BET analysis

At 77 K, BET surface area and pore structure of pure ZIS6, MoS₂ and 0.5% MoS₂/ZIS6 samples were characterized by ad-

sorption-desorption experiments, and the results are shown in Fig. 6. According to the IUPAC classification, the three samples display representative type IV isotherms with a representative H3 hysteresis loop characteristic, which implies that they are all mesoporous materials. Agreeably, the TEM and SEM results in Fig. 2 indicate the existence of mesoporous structures derived from crosslinked nanosheets [57]. Figure 6(a) illustrates the N₂ adsorption-desorption isotherms of as-prepared ZIS6, MoS₂ and 0.5% MoS₂/ZIS6 samples, where it can be seen that the specific surface area of 0.5% MoS₂/ZIS6 (158.39 m²·g⁻¹) is larger than that of the pure ZIS6 (97.22 m²·g⁻¹) and MoS₂ (9.68 m²·g⁻¹). The increase in the BET surface area of 0.5% MoS₂/ZIS6 compared to that of pure ZIS6, resulted from hindered formation and stacking, brought about by the introduction of MoS₂, which results in 0.5% MoS₂/ZIS6 exhibiting a looser state compared to pure ZIS6. The pore size distribution depicted in Fig. 6(b) clearly shows that ZIS6, MoS₂ and 0.5% MoS₂/ZIS6 possess varied pore diameters in a range of approximately 2–135 nm, indicating the formation of mesoporous and macropore structures in the as-prepared samples. The markedly higher pore volume of 0.5% MoS₂/ZIS6 compared to that of the other two samples will be beneficial for the mass transfer process of reactants, and thus increase the efficiency of photocatalytic hydrogen production [35].

3.7. Evaluation of photocatalytic activity

Under visible light irradiation ($\lambda > 400$ nm), the photoca-

Fig. 6. N₂ adsorption-desorption isotherms and the pore size distribution of as-prepared ZIS6, MoS₂ and 0.5% MoS₂/ZIS6 samples.

Fig. 7. Comparison of H₂ production rates of 0.1 g MoS₂/ZIS6 composite photocatalysts containing different amounts of MoS₂ from formic acid under visible light irradiation ($\lambda > 400$ nm).

lytic properties of the samples were evaluated in 6.0 M aqueous formic acid. From the control experiment, it was found that in the absence of light, the photocatalyst does not generate H₂ and other products, which indicates that the release of H₂ is attributed to the photocatalytic process. As can be seen from Fig. 7, when the mass percentage of MoS₂ is in the range of 0 to 10%, the hydrogen production rates of the MoS₂/ZIS6 photocatalysts initially increase, and then decrease; the 0.5% MoS₂/ZIS6 sample exhibited the highest photocatalytic activity, reaching a maximum value of 74.25 μmol·h⁻¹, which was approximately 4.3 times higher than that of ZIS6 (17.47 μmol·h⁻¹). The results of hydrogen production activity substantiate the expectation of PL and BET experiments discussed in sections 3.5 and 3.6, respectively. When the amount of MoS₂ increases above 0.5%, the possible reasons for the observed decrease in hydrogen production rate are as follows: excessive MoS₂ may partially reflect visible light, thus shielding the surface of ZIS6 and resulting in a decrease in visible light utilization ratio, and additionally serve as a recombination center of photogenerated charges, which may lead to diminished photocatalytic hydrogen production performance, from formic acid [58].

The photocatalytic performances of MoS₂/ZIS6 samples were influenced by the dosage of MoS₂, as well as by their inherent stabilities. The stability of a representative 0.5% MoS₂/ZIS6 sample was tested by employing visible irradiation in the formic acid dehydrogenation system, coupled with GC analysis, for a period of 10 h (Fig. 8). Evidently, the hydrogen production rate improved rapidly with time during the continuous hydrogen production reaction, which indicated that the 0.5% MoS₂/ZIS6 catalyst maintained a favorable photocatalytic performance in the process of hydrogen production from formic acid.

Moreover, the utilization of visible light can additionally be demonstrated by the hydrogen production quantum efficiency. For this experiment, 0.1 g of the 0.5% MoS₂/ZIS6 sample was irradiated at various incident light wavelengths (300 W Xe lamp equipped with specific band-pass filters) for 2 h, as shown

Fig. 8. Photocatalytic H₂ production activity of the 0.5% MoS₂/ZIS6 sample under extended irradiation time.

in Fig. 9. It can be seen that when all other conditions are constant, varying the wavelength led to differences in hydrogen production. Of these, 0.5% MoS₂/ZIS6 exhibited the highest hydrogen production, and at a wavelength of 400 ± 10 nm it exhibited a hydrogen production of 117.86 and quantum efficiency of up to 2.9%. It can be seen that the hydrogen production rates and visible light absorption trends are correlated, suggesting that the reaction is indeed governed by visible light absorption by the photocatalyst.

3.8. Electrochemical characteristics of the photocatalysts

It is widely accepted that the behavior of a photocatalyst during the excitation and transfer of photogenerated carriers is an important embodiment of its photocatalytic performance. Specifically, photogenerated electron-hole pairs are generated by visible light irradiation onto the photocatalyst; h⁺, found on the surface of the photocatalyst, is harvested by the h⁺ acceptors present in the electrolyte solution, and the photogenerated e⁻ is collected to generate a photocurrent. Therefore, under identical experimental conditions, photoelectrochemical methods were employed to qualitatively study the performance of the ZIS6, MoS₂ and 0.5% MoS₂/ZIS6 photocatalysts in the excitation and transfer of photogenerated carriers. Fig. 10 displays transient photocurrent diagrams of the ZIS6, MoS₂ and 0.5% MoS₂/ZIS6 samples. Among them, MoS₂ presents a mini-

Fig. 9. Comparison of quantum efficiencies based on hydrogen production amounts under a distinct wavelength illumination for 2 h with the 0.5% MoS₂/ZIS6 photocatalyst.

Range (nm)	QE (%)
550 ± 10	0.008
500 ± 10	0.09
450 ± 10	1.0
420 ± 10	1.2
400 ± 10	2.9

Fig. 10. Comparison of transient photocurrent diagrams of pure ZIS6 and 0.5% MoS₂/ZIS6 samples.

mal photocurrent response, and pure ZIS6 exhibits relatively low photocurrent intensity, which may be due to a rapid photogenerated electron-hole pair recombination rate. Furthermore, the weaker photocurrent response of ZIS6 may be partially attributed to the wide band gap of pure ZIS6 [58,59]. However, 0.5% MoS₂/ZIS6 displays significantly a higher photocurrent intensity than that of pure ZIS6, resulting from the heterojunction interfaces formed between MoS₂ and ZIS6. It is understood that the photocurrent intensity is positively correlated with the photocatalytic activity [23,60]. The photocurrent response intensity trend is in agreement with previously discussed photocatalytic performance results, indicating that the introduction of MoS₂ is beneficial to the charge transfer process from ZIS6 to MoS₂ at the heterojunction interfaces, and in turn to the enhancement of photocatalytic hydrogen production activity.

As a further investigation into the aspects of photogenerated carrier transfer, electrochemical impedance spectroscopy (EIS) was conducted for ZIS6, MoS₂ and 0.5% MoS₂/ZIS6, and the results are as shown in Fig. 11. It is well known that a smaller arc radius indicates that the working electrode has a lower resistance in the EIS experiment, which translates to a higher separation and transfer rate of photogenerated electron-hole pairs. Although MoS₂, a common cocatalyst, exhibits a marginal photocurrent response, it has outstanding charge transfer capability, as confirmed by the smallest resistance radius of MoS₂ among the tested samples. As expected, the 0.5% MoS₂/ZIS6 photocatalyst exhibited a smaller resistance radius compared to pure ZIS6, indicating a higher charge transfer rate than that of pure ZIS6, which is in agreement with the results of photocatalytic performance experiments discussed in Section 3.7.

On the basis of thermodynamics, additional important factors that can affect photocatalytic performance are the conduction band (CB) and valence band (VB) positions of the photocatalyst. Specifically, the more negative the CB, the easier it is to produce H₂. Fortunately, the Mott-Schottky determination method is a reliable means of determining the type and position of the catalyst's CB and VB. For n-type semiconductor photocatalysts, the CB edge potential (E_{cb}) is approximately equal to the flat band potential (E_{fb}), and the value of E_{fb} is the tangent intercept of the Mott-Schottky curve on the X-axis. As

Fig. 11. Electrochemical impedance spectroscopy of ZIS6, MoS₂ and 0.5% MoS₂/ZIS6.

shown in Fig. 12, the slopes of the Mott-Schottky curves of ZIS6 and MoS₂ samples at three distinct fixed frequencies (500, 1000 and 1500 Hz) are all positive, which confirms that they are all n-type semiconductors [23,60]. Thus, the corresponding E_{cb} values for ZIS6 and MoS₂ were -1.0 V and -0.58 V, respectively. In addition, because the conversion potential of the normal hydrogen electrode (NHE) vs. Ag/AgCl is approximately 0.2 V, the E_{cb} values of ZIS6 and MoS₂ samples were -0.8 and -0.38 V (vs. NHE, pH = 0), respectively. Considering the UV-vis DRS results, the valence band potential (E_{vb}) values of ZIS6 and MoS₂ were calculated as 2.04 and 0.93 V, respectively, according to the following equation:

$$E_{vb} = E_{cb} + E_g$$

3.9. Photoinduced charge-transfer properties of photocatalysts

It is generally accepted that in semiconductors containing analogous components, there is a positive correlation between the transient photovoltage intensity and the separation efficiency of photogenerated charges, namely, a more intense photovoltage signal translates to higher separation efficiency [61]. To compare the separation efficiencies of photogenerated charges between samples, transient photovoltage (TPV) measurements of pure ZIS6 (red) and 0.5% MoS₂/ZIS6 (blue) were conducted under a 355 nm laser pulse and a power of 50 μ J/pulse, and the results are shown in Fig. 13(a). Two interesting characteristics can be observed: (1) the 0.5% MoS₂/ZIS6 sample displays a significantly stronger and wider delay peak than the pure ZIS6 sample, suggesting its superior photogenerated charge transfer and separation efficiency; (2) all tested photocatalysts exhibited negative TPV photovoltaic signals, indicating that photogenerated electrons move towards the surface of the sample's top electrode, which is being irradiated [62,63]. Thus, the introduction of MoS₂ with its low Fermi energy level enables the enrichment of photogenerated electrons from the surface of ZIS6. Specifically, when the laser irradiates the sample, the photogenerated charges are separated because of the action of the electric field in the space charge region, presenting the TPV photovoltaic signal in the range of 0–10⁻⁶ s, and the diffused photovoltage signals are observed in a range

Fig. 12. Mott-Schottky plots of ZIS6 (a) and MoS₂ (b) in 0.2 M Na₂SO₄.

exceeding 10^{-4} s [64]. Because MoS₂ can capture photogenerated electrons from the surface of ZIS6, photogenerated charges are separated rapidly in MoS₂/ZIS6, and the separation rate is inherently higher than that of ZIS6. Overall, MoS₂ loading on ZIS6 can effectively enhance the separation efficiency of photoinduced charges, suppress their recombination, and prolong their lifetime [65–67]. Undoubtedly, the photocatalytic hydrogen production efficiency, from formic acid decomposition, will likewise be enhanced. To further investigate the role of MoS₂ in enriching photogenerated electrons derived from ZIS6, the transient photocurrent (TPC) spectra of pure ZIS6 and 0.5% MoS₂/ZIS6 samples were compared, as shown in Fig. 13(b). It is evident that the TPC of 0.5% MoS₂/ZIS6 is significantly higher than that of ZIS6 under equivalent conditions, which indicates that MoS₂ plays a significant role in enriching the photoelectrons [65]. Once again, the TPV and TPC results supported the experimental results of photocatalytic performance.

3.10. Proposed mechanism

Combining all of the above-discussed analyses, a mechanistic rationale for hydrogen production from FA, facilitated by the MoS₂/ZIS6 photocatalyst (Fig. 14), is proposed as follows. When the MoS₂/ZIS6 composite photocatalyst is exposed to visible light, the photogenerated e^- and h^+ are generated in ZIS6. The photogenerated electrons derived therein are transferred from the CB of ZIS6 to MoS₂, due to their matching energy band potentials, while h^+ remains in the VB of ZIS6

[68,69], which enhances the separation efficiency of photogenerated charges. Meanwhile, FA is firstly dissociated into H^+ and $HCOO^-$ under the action of water molecules. Two reactions then occur on the MoS₂/ZIS6 photocatalyst: on the VB of ZIS6, h^+ promotes the decomposition of $HCOO^-$ into CO_2 and H^+ ; simultaneously, H^+ ions dissociated from FA, and generated by the decomposition of $HCOO^-$ are reduced to H_2 by the photogenerated electrons from the MoS₂ promoter, which provides electron enrichment and serves as an active center. Overall, these processes accomplish effective separation of photogenerated carriers, as well as the transfer and enrichment of photogenerated charges, thereby enhancing hydrogen production from FA.

4. Conclusions

A straightforward one-pot hydrothermal method was successfully implemented for the preparation of a MoS₂/ZIS6 composite photocatalyst, which was then applied to hydrogen production from FA, exhibiting excellent efficiency; the related charge transfer mechanism of this process was additionally discussed. Under visible light irradiation, the majority of synthesized MoS₂/ZIS6 composite photocatalysts exhibited superior photocatalytic performance compared to pure ZIS6 and MoS₂. The 0.5% MoS₂/ZIS6 composite photocatalyst exhibited the highest photocatalytic hydrogen production activity ($74.25 \mu\text{mol}\cdot\text{h}^{-1}$) from formic acid and a 2.9% hydrogen production quantum efficiency at approximately 400 nm. Integrated MoS₂ captures photogenerated electrons from ZIS6 and is the active

Fig. 13. TPV (a) and TPC (b) spectra of ZIS6 and 0.5% MoS₂/ZIS6 samples under a 355 nm laser pulse and power of 50 μJ /pulse. Insets show the schematic setup of TPV (a) and TPC (b) measurements, respectively.

Fig. 14. Possible charge transfer mechanism of hydrogen production from FA on the MoS₂/ZnIn₂S₆ photocatalyst.

center for the reduction reaction of H⁺ to H₂, thus successfully realizing effective separation of photogenerated charges and enhancing hydrogen production from formic acid. This study will likely provide a valuable reference for the design and fabrication of high-performance hydrogen production photocatalysts.

References

- [1] T. C. Johnson, D. J. Morris, M. Wills, *Chem. Soc. Rev.*, **2010**, 39, 81–88.
- [2] M. Grasmann, G. Laurenczy, *Energy Environ. Sci.*, **2012**, 5, 8171–8181.
- [3] H. L. Wang, Y. Chi, D. W. Gao, Z. L. Wang, C. Wang, L. Y. Wang, M. G. Wang, D. W. Cheng, J. J. Zhang, C. Wu, Z. K. Zhao, *Appl. Catal. B*, **2019**, 255, 117776.
- [4] F. Pellegrino, F. Sordello, L. Mino, C. Minero, V. D. Hodoroaba, G. Martra, V. Maurino, *ACS Catal.*, **2019**, 9, 6692–6697.
- [5] Y. J. Wang, Y. Li, S. W. Cao, J. G. Yu, *Chin. J. Catal.*, **2019**, 40, 867–874.
- [6] J. W. Fu, J. G. Yu, C. J. Jiang, B. Cheng, *Adv. Energy Mater.*, **2018**, 8, 1701503.
- [7] T. M. Di, Q. L. Xu, W. K. Ho, H. Tang, Q. J. Xiang, J. G. Yu, *ChemCatChem*, **2019**, 11, 1394–1411.
- [8] Q. H. Li, X. Q. Qiao, Y. L. Jia, D. F. Hou, D. S. Li, *Appl. Surf. Sci.*, **2019**, 498, 143863.
- [9] M. S. Akplea, J. X. Low, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, J. Zhang, *Appl. Surf. Sci.*, **2015**, 358, 196–203.
- [10] X. Q. Qiao, Z. W. Zhang, Q. H. Li, D. F. Hou, Q. C. Zhang, J. Zhang, D. S. Li, P. Y. Feng, X. H. Bu, *J. Mater. Chem. A*, **2018**, 6, 22580–22589.
- [11] F. He, A. Y. Meng, B. Cheng, W. K. Ho, J. G. Yu, *Chin. J. Catal.*, **2020**, 41, 9–20.
- [12] D. D. Ren, R. C. Shen, Z. M. Jiang, X. Y. Lu, X. Li, *Chin. J. Catal.*, **2020**, 41, 31–40.
- [13] N. Qin, J. H. Xiong, R. W. Liang, Y. H. Liu, S. Y. Zhang, Y. H. Li, Z. H. Li, L. Wu, *Appl. Catal. B: Environ.*, **2017**, 202, 374–380.
- [14] L. L. Li, B. Cheng, Y. X. Wang, J. G. Yu, *J. Colloid Interf. Sci.*, **2015**, 449, 115–121.
- [15] Y. Li, B. Wang, S. Liu, X. Duan, Z. Hu, *Appl. Surf. Sci.*, **2015**, 324, 736–744.
- [16] C. Yang, P. D. Tran, P. P. Boix, P. S. Bassi, N. Yantara, L. H. Wong, J. Barber, *Nanoscale*, **2014**, 6, 6506–6510.
- [17] D. Lang, F. Y. Cheng, Q. J. Xiang, *Catal. Sci. Technol.*, **2016**, 6, 6207–6216.
- [18] T. M. Di, B. C. Zhu, J. Zhang, B. Cheng, J. G. Yu, *Appl. Surf. Sci.*, **2016**, 389, 775–782.
- [19] Z. Kong, Y. J. Yuan, D. Q. Chen, G. L. Fang, Y. Yang, S. H. Yang, D. P. Cao, *Dalton Trans.*, **2017**, 46, 2072–2076.
- [20] Y. Amao, S. Takahara, Y. Sakai, *Int. J. Hydrogen Energy*, **2014**, 39, 20771–20776.
- [21] M. A. Deyab, *J. Power Sources*, **2013**, 242, 86–90.
- [22] P. Y. M. Liu, Z. J. Cai, Y. You, H. Huang, S. M. Chen, C. Gao, Z. M. Qi, R. Long, J. F. Zhu, L. Song, Y. J. Xiong, *Chem. Eur. J.*, **2018**, 24, 18398–18402.
- [23] X. J. Ye, Y. H. Chen, Y. H. Wu, X. M. Zhang, X. C. Wang, S. F. Chen, *Appl. Catal. B*, **2019**, 242, 302–311.
- [24] Q. Li, Y. Xia, C. Yang, K. L. Lv, M. Li, *Chem. Eng. J.*, **2018**, 349, 287–296.
- [25] C. Yang, Q. Li, Y. Xia, K. L. Lv, M. Li, *Appl. Surf. Sci.*, **2019**, 464, 388–395.
- [26] Y. Xia, Q. Li, K. L. Lv, D. G. Tang, M. Li, *Appl. Catal. B*, **2017**, 206, 344–352.
- [27] Y. Wu, H. Wang, W. G. Tu, Y. Liu, S. Y. Wu, Y. Z. Tan, J. W. Chew, *Appl. Catal. B*, **2018**, 233, 58–69.
- [28] R. Z. Zhang, J. Wang, P. D. Han, *J. Alloys Compd.*, **2015**, 637, 483–488.
- [29] L. C. Pop, V. Dracopoulos, P. Lianos, *Appl. Surf. Sci.*, **2015**, 333, 147–151.
- [30] J. Y. Zhang, Y. H. Wang, J. Zhang, Z. Lin, F. Huang, J. G. Yu, *ACS Appl.*

Graphical Abstract

Chin. J. Catal., 2021, 42: 193–204 doi: 10.1016/S1872-2067(20)63584-7

MoS₂/Zn₃In₂S₆ composite photocatalysts for enhancement of visible light-driven hydrogen production from formic acid

Sujuan Zhang, Shixiang Duan, Gaoli Chen, Sugang Meng, Xiuzhen Zheng, You Fan, Xianliang Fu, Shifu Chen *
Huaibei Normal University

A novel MoS₂/Zn₃In₂S₆ (MoS₂/ZIS6) heterojunction photocatalyst was constructed with matching energy band potentials; it exhibited excellent performance in the excitation and transfer of photogenerated carriers and consequently, in visible-light-driven hydrogen production from formic acid.

- Mater. Interfaces*, **2013**, 5, 1031–1037.
- [31] S. Y. Wang, B. Zeng, C. Li, *Chin. J. Catal.*, **2018**, 39, 1219–1227.
- [32] Y. J. Cho, G. H. Moon, T. Kanazawa, K. Maeda, W. Choi, *Chem. Commun.*, **2016**, 52, 9636–9639.
- [33] B. Weng, Q. Quan, Y. J. Xu, *J. Mater. Chem. A*, **2016**, 4, 18366–18377.
- [34] F. Chen, X. Z. Jiang, L. L. Zhang, R. Lang, B. T. Qiao, *Chin. J. Catal.*, **2018**, 39, 893–898.
- [35] Z. W. Zhang, Q. H. Li, X. Q. Qiao, D. F. Hou, D. S. Li, *Chin. J. Catal.*, **2019**, 40, 371–379.
- [36] Z. D. Wei, M. Q. Xu, J. Y. Liu, W. Q. Guo, Z. Jiang, W. F. Shangguan, *Chin. J. Catal.*, **2020**, 41, 103–113.
- [37] Y. Y. Qin, H. Li, J. Lu, Y. S. Yan, Z. Y. Lu, X. L. Liu, *Chin. J. Catal.*, **2018**, 39, 1470–1483.
- [38] D. Lang, T. T. Shen, Q. J. Xiang, *ChemCatChem*, **2015**, 7, 943–951.
- [39] L. Wei, Y. J. Chen, Y. P. Lin, H. S. Wu, R. S. Yuan, Z. H. Li, *Appl. Catal. B*, **2014**, 144, 521–527.
- [40] S. H. Shen, L. Zhao, L. J. Guo, *Inter. J. Hydrogen Energy*, **2010**, 35, 10148–10154.
- [41] X. Wei, T. F. Xie, D. Xu, Q. D. Zhao, S. Pang, D. J. Wang, *Nanotechnology*, **2008**, 19, 275707.
- [42] T. F. Jiang, T. F. Xie, L. P. Chen, Z. W. Fu, D. J. Wang, *Nanoscale*, **2013**, 5, 2938–2944.
- [43] S. G. Meng, X. J. Ye, J. H. Zhang, X. L. Fu, S. F. Chen, *J. Catal.*, **2018**, 367, 159–170.
- [44] Q. Zhang, S. Z. Kang, D. Wang, X. Q. Li, L. X. Qin, J. Mu, *Catal. Commun.*, **2016**, 82, 7–10.
- [45] M. Khaili, N. Fazouan, H. Abou El Makarim, G. ElHalani, E. H. Atmani, *J. Alloys Compd.*, **2016**, 688, 368–375.
- [46] J. Wan, X. Du, E. Z. Liu, Y. Hu, J. Fan, X. Y. Hu, *J. Catal.*, **2017**, 345, 281–294.
- [47] A. Lamouchi, I. Ben Assaker, R. Chtourou, *Appl. Surf. Sci.*, **2019**, 478, 937–945.
- [48] A. P. Wu, C. G. Tian, Y. Q. Jiao, Q. Yan, G. Y. Yang, H. G. Fu, *Appl. Catal. B*, **2017**, 203, 955–963.
- [49] F. J. Zhang, X. Li, X. Y. Sun, C. Kong, W. J. Xie, Z. Li, J. Liu, *Appl. Surf. Sci.*, **2019**, 487, 734–742.
- [50] C. Liu, B. Chai, C. L. Wang, J. T. Yan, Z. D. Ren, *Int. J. Hydrogen Energy*, **2018**, 43, 6977–6986.
- [51] Z. Z. Zhang, L. Huang, J. J. Zhang, F. J. Wang, Y. Y. Xie, X. T. Shang, Y. Y. Gu, H. B. Zhao, X. X. Wang, *Appl. Catal. B*, **2018**, 233, 112–119.
- [52] G. P. Zhang, D. Y. Chen, N. J. Li, Q. F. Xu, H. Li, J. H. He, J. M. Lu, *Appl. Catal. B*, **2018**, 232, 164–174.
- [53] B. Han, S. Q. Liu, N. Zhang, Y. J. Xu, Z. R. Tang, *Appl. Catal. B*, **2017**, 202, 298–304.
- [54] X. C. Jiao, Z. W. Chen, X. D. Li, Y. F. Sun, S. Gao, W. S. Yan, C. G. Wang, Q. Zhang, Y. Lin, Y. Luo, Y. Xie, *J. Am. Chem. Soc.*, **2017**, 139, 7586–7594.
- [55] P. X. Qiu, J. H. Yao, H. Chen, F. Jiang, X. C. Xie, *J. Hazard. Mater.*, **2016**, 317, 158–168.
- [56] Y. J. Yuan, D. Q. Chen, M. Xiong, J. S. Zhong, Z. Y. Wan, Y. Zhou, S. Liu, Z. T. Yu, L. X. Yang, Z. G. Zou, *Appl. Catal. B*, **2017**, 204, 58–66.
- [57] Y. H. Wu, X. J. Ye, S. J. Zhang, S. G. Meng, X. L. Fu, X. C. Wang, X. M. Zhang, S. F. Chen, *J. Catal.*, **2018**, 359, 151–160.
- [58] T. T. Zhu, X. J. Ye, Q. Q. Zhang, Z. Z. Hui, X. C. Wang, S. F. Chen, *J. Hazard. Mater.*, **2019**, 367, 277–285.
- [59] S. X. Duan, S. J. Zhang, S. S. Chang, S. G. Meng, Y. Fan, X. Z. Zheng, S. F. Chen, *Int. J. Hydrogen Energy*, **2019**, 44, 21803–21820.
- [60] L. Zhang, X. L. Fu, S. G. Meng, X. L. Jiang, J. H. Wang, S. F. Chen, *J. Mater. Chem. A*, **2015**, 3, 23732–23742.
- [61] Z. Y. Liu, D. D. Sun, P. Guo, J. O. Leckie, *Nano Lett.*, **2007**, 7, 1081–1085.
- [62] Q. L. Zhang, D. J. Wang, X. Wei, T. F. Xie, Z. H. Li, Y. H. Lin, M. Yang, *Thin Solid Films*, **2005**, 491, 242–248.
- [63] B. Mahrov, G. Boschloo, A. Hagfeldt, L. Dloczik, T. Dittrich, *Appl. Phys. Lett.*, **2004**, 84, 5455–5457.
- [64] V. Y. Timoshenko, V. Duzhko, T. Dittrich, *Phys. Status Solidi A*, **2000**, 182, 227–232.
- [65] F. Raziq, L. Q. Sun, Y. Y. Wang, X. L. Zhang, M. Humayun, S. Ali, L. L. Bai, Y. Qu, H. T. Yu, L. Q. Jing, *Adv. Energy Mater.*, **2018**, 8, 1701580.
- [66] J. Bian, Y. Qu, X. L. Zhang, N. Sun, D. Y. Tang, L. Q. Jing, *J. Mater. Chem.*, **2018**, 6, 11838–11845.
- [67] P. Wang, T. F. Xie, H. Y. Li, L. Peng, Y. Zhang, T. S. Wu, S. Pang, Y. F. Zhao, D. J. Wang, *Chem. Eur. J.*, **2009**, 15, 4366–4372.
- [68] D. Z. Lu, Q. P. Wang, K. K. Kondamareddy, A. X. Wang, H. J. Hao, Q. Wu, *J. Alloys Compd.*, **2018**, 761, 31–40.
- [69] X. M. Zhou, M. Lickleder, P. Schmuki, *Electrochem. Commun.*, **2016**, 73, 33–37.

MoS₂/Zn₃In₂S₆复合光催化剂构建：高效提升可见光驱动甲酸制氢

张素娟, 段世祥, 陈高礼, 孟苏刚, 郑秀珍, 樊佑, 付先亮, 陈士夫*

淮北师范大学清洁能源及绿色循环重点实验室, 安徽淮北235000

摘要: 虽然传统的化石燃料依然能够满足当今快速工业化发展对能源的巨大需求, 但其固有的不可再生性及其燃烧产物对环境的污染, 严重阻碍了其在生产和生活中的广泛使用. 因此, 可持续清洁能源开发的研究已快速成为人类研究的热点. 氢是一种具备高热值、可持续等优点的清洁能源, 也兼备成本及污染低等优势. 甲酸(FA)以其无毒、低成本、氢含量高优点, 是一种潜在的热门储氢材料, 而可见光占太阳光谱的43%左右. 因此, 开发高效可见光催化剂驱动FA制氢将是一种应对能源危机的有效途径.

许多传统光催化剂已被用于可见光催化FA制氢, 但制备成本高、过程复杂、条件苛刻及可见光响应差、稳定性和选择性差、有毒气体释放等缺点严重限制了其光催化性能. 光催化研究关键之一是实现光生电荷的高效率分离和转移, 从而光催化剂光催化性能的提高. Zn₃In₂S₆(ZIS6)因具有强可见光吸收、稳定性好及环保等特点正迅速成为光催化剂半导体的“明星”, 常与助催化剂(如贵金属Pt、Au、Pd等)复合形成异质结以促进光生载流子分离和提高其光催化活性, 但制备成本高等因素却严重限制其发展. 将成本低、化学稳定性好的MoS₂与其它半导体耦合也是提高半导体光催化剂性能的有效手段之一, 但高温、热处理时间长及有毒气体释放等却成了制约因素.

本文选用价格低廉的反应前驱体, 采用简单的一锅法水将MoS₂紧密地结合到ZIS6的表面, 热制备了一系列含有不同

质量百分比 MoS_2 的 $\text{MoS}_2/\text{Zn}_3\text{In}_2\text{S}_6$ ($\text{MoS}_2/\text{ZIS6}$)复合光催化剂,有效降低了制备成本和有毒气体(H_2S)的释放.结果表明,可见光照射下($\lambda > 400 \text{ nm}$), MoS_2 的引入可大大提高ZIS6光生电荷分离效率及制氢活性,尤其以0.5% $\text{MoS}_2/\text{ZIS6}$ 性能最优,光催化制氢速率高达 $74.25 \mu\text{mol}\cdot\text{h}^{-1}$ (量子效率约2.9%),约ZIS6的4.3倍($17.47 \mu\text{mol}\cdot\text{h}^{-1}$). XRD结果表明, $\text{MoS}_2/\text{ZIS6}$ 样品中含有无定型 MoS_2 紧密固定在晶型ZIS6片状结构表面,未影响ZIS6晶型,SEM表征也证实了此结果.随后的TEM、HRTEM及EDX结果也进一步确认了各组成元素的存在和分布.采用XPS对元素化学环境进行了分析,通过S和Mo元素的成键能变化证实了 MoS_2 和ZIS6间的紧密接触. UV-Vis DRS测试表明, $\text{MoS}_2/\text{ZIS6}$ 可以利用可见光在适当带隙的基础上进行光催化制氢.通过BET、PL和电化学技术研究了比表面积、光生电荷分离和传递速率等对光催化性能的影响.最终,结合上述表征结果成功阐述了可见光驱动FA制氢的反应机理.

关键词: 产氢; $\text{Zn}_3\text{In}_2\text{S}_6$; 甲酸; MoS_2 ; 光催化

收稿日期: 2020-02-23. 接受日期: 2020-04-13. 出版日期: 2021-01-05.

*通讯联系人. 电话: (0561)3802061; 传真: (0561)3090518; 电子信箱: chshifu@chnu.edu.cn

基金来源: 国家自然科学基金(51972134, 51472005, 51772118); 安徽省杰出青年科学基金(1808085J24); 安徽省高校优秀青年人才基金(gxyq2019029); 安徽省高校自然科学研究项目基金(KJ2019A0602, KJ2018A0387).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).