One-step hydrothermal synthesis of S-defect-controlled ZnIn$_2$S$_4$ microflowers with improved kinetics process of charge-carriers for photocatalytic H$_2$ evolution

Xuedong Jing, Na Lu, Jindou Huang, Peng Zhang, Zhenyi Zhang

PII: S2095-4956(20)30722-1
DOI: https://doi.org/10.1016/j.jechem.2020.10.032
Reference: JECHEM 1657

To appear in: Journal of Energy Chemistry

Received Date: 24 August 2020
Revised Date: 12 October 2020
Accepted Date: 13 October 2020

Please cite this article as: X. Jing, N. Lu, J. Huang, P. Zhang, Z. Zhang, One-step hydrothermal synthesis of S-defect-controlled ZnIn$_2$S$_4$ microflowers with improved kinetics process of charge-carriers for photocatalytic H$_2$ evolution, Journal of Energy Chemistry (2020), doi: https://doi.org/10.1016/j.jechem.2020.10.032

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by ELSEVIER B.V. and Science Press on behalf of Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences.
One-step hydrothermal synthesis of S-defect-controlled ZnIn$_2$S$_4$ microflowers with improved kinetics process of charge-carriers for photocatalytic H$_2$ evolution

Xuedong Jing$^a$, Na Lu$^a$, Jindou Huang$^a$*, Peng Zhang$^b$, Zhenyi Zhang$^a$*

$^a$Key Laboratory of New Energy and Rare Earth Resource Utilization of State Ethnic Affairs Commission; Key Laboratory of Photosensitive Materials and Devices of Liaoning Province, School of Physics and Materials Engineering, Dalian Minzu University, 18 Liaohe West Road, Dalian 116600, Liaoning, China.

$^b$School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, Henan, China.

* Corresponding authors. E-mail addresses: jindouhuang@dlnu.edu.cn (J. Huang); zhangzy@dlnu.edu.cn (Z. Zhang).
Abstract

Engineering lattice defects in two-dimensional (2D) sulfide semiconductors has been accepted as an effective strategy to enhance the efficiency of the solar-to-fuels conversion. Although many researches have proven the lattice defect-mediated photocatalytic activity of ZnIn$_2$S$_4$, the artificial control of S-defects for optimizing the charge-carrier kinetics process in ZnIn$_2$S$_4$ has long been a challenging task. Herein, we report a facile one-step method to modulate the lattice S-content of ZnIn$_2$S$_4$ microflowers (MFs) only through adjusting the used amount of S-precursor in the hydrothermal solution that contains the metal precursors with a fixed Zn/In stoichiometric ratio at 1:2. We also demonstrated that the S-vacancies at the In facets were the main type of lattice defects in the formed ZnIn$_2$S$_4$ MFs, which could enhance both the separation and migration processes of the photoinduced charge-carriers due to the existence of discrete defect energy-levels (DELs) and the reduced effective mass of electrons, as evidenced by the first-principles calculations and the electron spectra analyses. The ZnIn$_2$S$_4$ MFs with the optimal content of S-vacancy obtained by a hydrothermal treatment of the precursors with the Zn/In/S stoichiometric ratio of 1:2:8 possessed the long-lived photoinduced electron (~94.64 ns) for contributing to the photo-physical and -chemical processes. Thus, upon visible light irradiation, the H$_2$-evolution rate of this sample reached ~2.40 mmol h$^{-1}$ g$^{-1}$ with an apparent quantum efficiency of ~0.16% at 420 nm even though only using 5 mg of photocatalysts without any cocatalysts.

Keywords: Photocatalysis; H$_2$ evolution; Defect engineering; Charge-carrier kinetics; Hydrothermal synthesis
1. **Introduction**

Photocatalytic H$_2$ evolution from water splitting by using semiconductor-based photocatalysts has attracted extensive attention due to the potential application of H$_2$-fuel to alleviate the urgent energy problem [1–4]. Although numerous semiconductor materials have been investigated in the research field of photocatalytic H$_2$ evolution, most of them are wide-bandgap semiconductors with only UV-light photoactivity [5–8], thereby greatly restricting their utilization of solar energy in the low-energy visible/near-infrared (NIR) light region. In order to overcome this issue, a vast number of narrow-bandgap semiconductors, such as metal oxides, metal sulfides, and so forth, have been developed as visible- or NIR-light-driven photocatalysts for the purpose of the effective utilization of low photon-energy in sunlight [8–10]. As compared to narrow-bandgap metal-oxide semiconductors, the narrow-bandgap metal-sulfide semiconductors are more suitable to be applied in the photocatalytic H$_2$ evolution, because the vast majority of them possess matchable conduction band (CB) potentials with respect to the H$^+$/H$_2$ redox potential [10–13]. Thus, the design and synthesis of visible-light-active metal-sulfide semiconductor photocatalysts with various fascinating microstructures have become burning issues for extending the light absorption and utilization regions of the semiconductor photocatalysts toward highly-efficient photocatalytic H$_2$-evolution.

Owing to unique structural properties, including large specific surface area, short charge-separation channel as well as abundant surface active sites, nowadays, the two-dimensional (2D) layered metal-sulfide semiconductors have emerged as a class of
promising photocatalysts for realizing the highly-efficient photocatalytic H₂ evolution upon visible light irradiation [14–18]. Among various 2D layered metal-sulfide semiconductors, the ternary metal sulfide of hexagonal ZnIn₂S₄, which is a member of AB₂X₄ family semiconductors with a layered structure, is more popular, mainly owing to its broad visible-light absorption, strong protons reducibility as well as satisfactory chemical stability [9,11,19,20]. Nevertheless, the fast recombination process of photoinduced charge-carriers and the poor migration behavior of photoinduced electrons are still the two serious drawbacks to limit the photocatalytic activity of the 2D ZnIn₂S₄ for H₂ evolution [21,22].

With the rapid development of the modification technology of nanomaterials, numerous studies have proven that the lattice defects in the 2D ZnIn₂S₄ nanosheets (NSs) is one of the important factor for influencing the kinetics process of photoinduced charge-carriers, including the charge-carriers generation, separation as well as migration. Therefore, the defect-modulation engineering on the ZnIn₂S₄ NSs-based photocatalysts has been regarded as an effective strategy to enhance their photocatalytic activity for H₂ evolution [23,36]. For instance, Wang et al. constructed the surface S-vacancy defect in the hydrothermal-produced ZnIn₂S₄ microspheres through the pressure hydrogenation method, which resulted in the improved separation process of photoinduced charge-carriers and thus the enhanced photocatalytic activity for H₂ evolution [20]. Zhang et al. reported that the S-vacancies on the Zn facets in monolayered ZnIn₂S₄ could be obtained through the ion intercalation-exfoliation treatment of the hydrothermal-produced ZnIn₂S₄ microspheres [24]. They also demonstrated that these confined S-vacancy defects built an important link between the electronic manipulation and photocatalytic activities of ZnIn₂S₄. However, to date, most of the used
strategies to dig the lattice defects of ZnIn$_2$S$_4$ are mainly based on the secondary treatment of hydrothermal-produced ZnIn$_2$S$_4$ micro/nanostructures by using the complex physical or/and chemical processes [20,23,24], which inevitably increase the producing cost and time. What’s more, an inappropriate secondary treatment of the ZnIn$_2$S$_4$ micro/nanostructures may also induce their crystal-structure destroy rather than the surface S-vacancy defects. Therefore, it is an urgent need to seek a convenient and effective strategy for the one-step controllable synthesis of S-defective ZnIn$_2$S$_4$ micro/nanostructures, and thus optimizing the kinetics process of photoinduced charge-carriers for photocatalytic H$_2$ evolution.

In the viewpoint of wet-chemical synthesis process of metal-sulfides, the S-containing organic precursor used to construct the lattice units of ZnIn$_2$S$_4$ micro/nanostructures should be competitive with that reacted with the aqueous solution for releasing H$_2$S during the hydrothermal synthesis process (Scheme 1). Thus, in theory, the stoichiometric introduction of the S and metal precursors into the hydrothermal solution could not guarantee the formation of a defect-free ZnIn$_2$S$_4$ micro/nanocrystal due to the above competition process. Moreover, in the viewpoint of thermodynamics, the lattice S-vacancy defects of ZnIn$_2$S$_4$ micro/nanocrystals are more easy to form as compared to their metal-vacancy defects, because the formation energies of S-vacancy defects in both surface and body of ZnIn$_2$S$_4$ are much lower than those of either the metal Zn- or In-vacancy defects, as shown in Fig. 1 and S1. The above analyses suggest that when the stoichiometric ratio of the used Zn to In precursors was fixed at 1:2 in the hydrothermal reaction solution, only adjusting the amount of the used S-precursor would lead to a controllable content of the lattice S in the formed ZnIn$_2$S$_4$ micro/nanocrystals, but without any secondary treatment. This facile one-step
hydrothermal modulation process of S-vacancy defects is conducive to the optimization of kinetics process of photoinduced charge-carriers in the ZnIn$_2$S$_4$ micro/nanocrystals for highly-efficient photocatalytic H$_2$ evolution. Nevertheless, to date, no relevant study has been reported in this research field.

In this work, we present a facile one-step hydrothermal method to modulate the lattice S content in ZnIn$_2$S$_4$ nanosheets (NSs)-aggregated microflowers (MFs) through simply changing the used amount of S precursor during the hydrothermal process. By combining first-principles calculations with the electron spectra analyses, we demonstrate that an appropriate amount of S-vacancy defects in the ZnIn$_2$S$_4$ MFs could not only construct discrete defect energy-levels (DELs) in their interband, but also decrease the effective mass of electrons, thereby enhancing the separation and migration processes of the photoinduced charge-carriers in the ZnIn$_2$S$_4$ MFs. Further investigations by using the transient absorption and surface photovoltage spectroscopy indicate that the S-defective ZnIn$_2$S$_4$ MFs made by the precursors with the Zn/In/S stoichiometric ratio of 1:2:8 possessed the optimal separation behavior of photoinduced charge-carriers accompanied with a long lifetime of photoinduced electrons (94.64 ns). As such, upon visible light irradiation, the photocatalytic activity of this sample for H$_2$ evolution reached to ~2.40 mmol h$^{-1}$ g$^{-1}$ in the absence of cocatalysts, and its apparent quantum efficiency was ~0.16% at 420 nm by using only 5 mg of photocatalysts. Our work offers a new simple strategy to the controllable synthesis of S-defective ZnIn$_2$S$_4$ MFs for highly-efficient photocatalytic H$_2$ evolution.

2. Experimental

2.1. Chemicals and Materials
Zn(CH$_3$COO)$_2$·2H$_2$O (99%) was purchased from Kermel chemical reagent Co. Ltd. L-Cysteine (98.5%), triethanolamine (TEOA, 78%), lactic acid (85%), Na$_3$S·9H$_2$O (98%), and Na$_2$SO$_4$ (99%) were obtained from Sinopharm Chemical Reagent Co. Ltd. In(NO$_3$)$_3$·xH$_2$O (99.99%) was purchased from Aladdin Industrial Corporation and ethyl alcohol was obtained from Damao Chemical Reagent Factory. All the materials were used without further purification. The deionized water used throughout the experiments was from local sources.

2.2. Synthesis of S-defect-controlled ZnIn$_2$S$_4$ MFs

ZnIn$_2$S$_4$ MFs with controllable content of lattice S-content were synthesized through a facile one-step hydrothermal method. Typically, the fixed amounts of metal precursors, consisting of 0.5 mmol of Zn(CH$_3$COO)$_2$·2H$_2$O and 1 mmol of In(NO$_3$)$_3$·xH$_2$O, and different amounts of L-Cysteine as the S precursor were dissolved in 40 mL of deionized water. After stirring for 30 min, the mixed solution was sealed into a 25 mL Teflon-lined autoclave. And the autoclave was then transferred into an electric oven for maintaining the temperature at 180 °C for 24 h. After being cooled to room temperature, the precipitate was collected, washed with ethanol and deionized water 3 times, and finally dispersed into the deionized water. In order to change the lattice S-content of ZnIn$_2$S$_4$ MFs, the stoichiometric ratio of the used S to Zn precursors was adjusted from 4:1, 6:1, 8:1, to 16:1, respectively. The obtained samples were denoted as ZnIn$_2$S$_4$ MFs-1, ZnIn$_2$S$_4$ MFs-2, ZnIn$_2$S$_4$ MFs-3, and ZnIn$_2$S$_4$ MFs-4, respectively.

2.3. Characterization

X-ray diffractometer detector (Shimadzu XRD-600, Japan) with Cu-k$_{a1}$ radiation ($\lambda=0.15406$nm) was used to measure the crystallographic structures of the as-synthesized
samples. The morphologies and structures of the as-synthesized samples were obtained from scanning electron microscope (SEM; XL-30 ESEM FEG, Micro FEI Philips) and transmission electron microscope (TEM; JEOL JEM-2100). The compositions of the as-synthesized samples were measured by Energy dispersive X-ray (EDX) spectroscopy being attracted to scanning electron microscopy (SEM). The steady-state photoluminescence (PL) spectra were measured by using a Hitachi F-4600 fluorescence spectrophotometer equipped with a Xe lamp as the excitation source. X-ray photoelectron spectroscopy (XPS VG-ESCALAB LKII) with a Mg kₐ ADES (hυ=1253.6 eV) source at a residual gas pressure below 10⁻⁸ Pa was used to acquire the binding energy of Zn, In, S. A Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer, USA) was used to measure the UV-vis diffuse reflectance spectra (DRS). The specific surface areas of the samples were taken with a Micromeritics ASAP-2020 instrument and analyzed by the Brunauer-Emmett-Teller (BET) method. Transient absorption spectrum (TAS) was recorded on an LFP1000 spectrometer (nanosecond transient absorption spectroscopy, NTAS) in air at room temperature. A Xe lamp and a picosecond pulsed diode laser (355 nm) were used as the excitation source. The surface photovoltage spectroscopy (SPV) was analyzed by PL-SPS1000 instrument (Beijing Perfectlight Technology Co., Ltd). The samples were put on the indium tin oxide (ITO) glass and stainless steel electrodes to form a sandwich structured photovoltage cell during the process.

2.4. Photocatalytic H₂ evolution

The photocatalytic H₂ evolution activities were performed in a 35 mL quartz reactor at room temperature and atmospheric pressure. Typically, 5 mg of the as-synthesized samples
were suspended in 10 mL of 15 vol% TEOA aqueous solution. Then the reactor was sealed by a rubber plug and degassed by argon for 30 min to drive away the residual air. Subsequently, the reactor loaded with the suspension was exposed under a 300-W Xe lamp (PLS-SXE300UV) equipped with a cut-off filter (\( \lambda > 420 \text{ nm} \)). The composition of the gas product generated in the space above the liquid in the quartz reactor was periodically detected by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) (SP-3420A, Beifen-Ruili Analytical Instrument) after the photocatalyst was irradiated every 30 min. To further investigate the influence of the used sacrifice agent on the photocatalytic activity of the sample, the photocatalytic H\(_2\)-evolution tests were also performed by using the lactic acid (10 vol%) and Na\(_2\)S (0.35 M) as sacrificial agents, respectively. The monochromatic light irradiation was monitored by using the Xe lamp coupled with different bandpass filters such as 365±15, 380±15, 420±15, 435±15, 475±15, 500±15, 520±15, 550±15, and 600±15 nm. The apparent quantum efficiency (AQE) was calculated by the following formula (1).

\[
\text{AQE} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% = 2 \times \frac{\text{number of evolved hydrogen molecules}}{\text{number of incident photons}} \times 100\% \quad (1)
\]

The number of incident photons \( (N) \) was calculated according to equation (2):

\[
N = \frac{Pt}{hv} = \frac{ESt}{hc} \quad (2)
\]

Where \( P \) is the light power; \( E \) is the light density; \( S \) is the irradiation area; \( t \) is the irradiation time; \( \lambda \) is the wavelength of incident light; \( h \) is Planck constant; \( \nu \) is the incident light frequency; \( c \) is the speed of light. In our work, the measured \( E \) values are 19.43, 71.97, 86.62, 85.03, 93.63, 79.94, 92.99, 81.85 and 81.21 mW/cm\(^2\) for the incident light with
wavelengths at 365, 380, 420, 435, 475, 500, 520, 550, and 600 nm, respectively. S is ca. 6 cm², and t is 3600 s.

2.5. Photoelectrochemical measurements

The photocurrent responses and Mott-Schottky plots were measured by an electrochemical analyzer (CHI 600D, CH Instruments Inc.) that contains three-electrode system. A Na₂SO₄ (0.2 M) aqueous solution was used as the electrolyte, and Pt wire and Ag/AgCl were acted as the counter and reference electrodes, respectively. For preparing the working electrode, the as-synthesized samples to be tested were coated onto an In-doped SnO₂ (ITO) glass with an effective area of 1cm × 1cm, and then Nafion (10 µL, 1wt%) was dripped evenly onto the working electrodes followed by drying 12 h at the temperature of 60 °C.

2.6. Computational methods

Our first-principles calculations were performed within the framework of density-functional theory (DFT) using the plane-wave pseudo potential approach as implemented in the VASP code [25]. The electron–core interactions are described with the frozen-core projected augmented wave pseudo potentials. We use the generalized gradient approximation (GGA) formulated by Perdew, Burke, and Ernzerhof (PBE) as the exchange-correlation functional [26]. The equilibrium structural parameters of bulk ZnIn₂S₄, ZnIn₂S₄ surface, as well as the ones with different atomic defects are obtained by total energy minimization via the conjugate-gradient algorithm. The cutoff energy for the plane-wave basis set is 500 eV and the force on each atom is converged to 0.01 eV Å⁻¹. A set of 4×4×4 Monkhorst–Pack special k-points [27] has been used for structural relaxations and the total
3. Results and discussion

ZnIn$_2$S$_4$ MFs with controllable contents of lattice S were synthesized via a facile one-step hydrothermal method, where the stoichiometric ratio of Zn/In metal precursors was fixed at 1:2, while the used ratios of S to Zn precursors was changed at 4, 6, 8, and 16, respectively. The crystal structures and parameters of the as-synthesized samples were identified by the X-ray diffraction (XRD) patterns. As shown in Fig. 2(a), all samples present seven pronounced diffraction peaks. The peaks located at 21.6°, 27.7°, 30.4°, 39.8°, 47.2°, 52.4°, and 55.6° are well consistent with the (006), (102), (104), (108), (110), (116), and (202) planes of hexagonal ZnIn$_2$S$_4$ (JCPDS NO. 65-2023), respectively [20,24,28–32]. No diffraction peaks originated from the impurities, such as binary sulfides, oxide, or organic compound, were detected, indicating good phase purities of the as-synthesized ZnIn$_2$S$_4$ even though the used amount of S precursor was different during the hydrothermal synthesis processes. However, further comparison of the above XRD patterns found that when the used amount of S precursor with the molar ratio to Zn exceeded 8, the diffraction peak intensities of the obtained ZnIn$_2$S$_4$ were slightly decreased as compared to the other samples. This may be attributed to the residual organic S intermediates coated onto the ZnIn$_2$S$_4$ surface, resulting in the signal noises on the XRD patterns.

The morphologies and structures of the as-synthesized ZnIn$_2$S$_4$ samples were further characterized by the scanning electron microscope (SEM). As shown in Fig. 2(b-e), all the ZnIn$_2$S$_4$ samples possess flower-like microstructures with sizes of 2–6 μm. Furthermore, these ZnIn$_2$S$_4$ microflowers (MFs) are made up of a large number of petaloid nanosheet (NS)
units. These observations suggest that the morphological structure of ZnIn$_2$S$_4$ MFs was not influenced by the used amount of S precursors during the hydrothermal process. To further clarify this viewpoint, the specific surface areas of these MFs were tested through the nitrogen sorption isotherm technique by using the Brunauer-Emmett-Teller (BET) method (Fig. S2). The results show that all the samples presented the type IV isotherms with type H$_3$-hysteresis loops at the relative pressure $P/P_0$ of 0.5-1. Meanwhile, the BET analyses indicated that the specific surface areas of ZnIn$_2$S$_4$ MFs-1, ZnIn$_2$S$_4$ MFs-2, ZnIn$_2$S$_4$ MFs-3, and ZnIn$_2$S$_4$ MFs-4 were 99.2 m$^2$/g, 95.6 m$^2$/g, 79.5 m$^2$/g, and 103.2 m$^2$/g, respectively. The slight change of BET values for these ZnIn$_2$S$_4$ MFs could be attributed to the existence of different amount of S defects or residual organic S intermediates on their surface for influencing their surface activities. Moreover, the SEM elemental-mapping images and energy dispersive X-ray (EDX) spectra of the single MF reveal that Zn, In, and S elements are homogenously dispersed in the MF, while the content of S element was increased with the used amount of S precursor (Fig. 2f and S3). These results imply the controllable content of lattice S in the ZnIn$_2$S$_4$ MFs due to the introduction of different amount of S precursor during the hydrothermal process.

The detailed structural information of the as-synthesized ZnIn$_2$S$_4$ MFs was further investigated via the transmission electron microscopy (TEM) combined with the high resolution (HR) TEM. As observed in Fig. 3(a and b) and S4, all the ZnIn$_2$S$_4$ MFs are assembled by large numbers of ultra-thin NSs in spite of introducing different amounts of S-precursors. The thicknesses of these NSs are 3–8 nm, indicating that the 2D layered structure of hexagonal ZnIn$_2$S$_4$ is stacked along the [001] direction based on van der Waals
interactions. Further observations by using the HRTEM images reveal that the exposed surface (perpendicular to the [001] direction) of all these ZnIn$_2$S$_4$ NSs displayed uniform fringe-distances of ~0.32 nm, which could be corresponded to the (102) planes of the hexagonal ZnIn$_2$S$_4$. It further confirms that the content change of the used S-precursor during the hydrothermal process did not influence the crystal structures of the synthesized ZnIn$_2$S$_4$ NSs in the MFs. Nevertheless, there are still many discontinuous lattice fringes, leading to the formation of lattice defects and even micropores on the surface of these ZnIn$_2$S$_4$ NSs. Furthermore, the formed lattice defects or micropores decreased with increasing the used amount of S-precursor during the hydrothermal method, which indicates that the defects or micropores were related to the content of lattice S in the ZnIn$_2$S$_4$ MFs.

To further illustrate the presence of lattice S-related defects in the as-synthesized ZnIn$_2$S$_4$ MFs, the X-ray photoelectron spectroscopy (XPS) measurements were performed to detect their chemical composition, and the corresponding results were shown in Fig. 4(a-c). It could be found two pronounced peaks on the In 3$d$ core-level spectrum of each sample (Fig. 4a). The binding energy peak around 444.7 and 452.2 eV were ascribed to the In 3$d_{5/2}$ and In 3$d_{3/2}$ of In$^{3+}$, respectively [20,31,33,34]. Interestingly, after the XPS curve-fitting treatment, the In 3$d$ core-level spectra of ZnIn$_2$S$_4$ MFs-1, ZnIn$_2$S$_4$ MFs-2, and ZnIn$_2$S$_4$ MFs-3 could be further fitted into four symmetric peaks. The binding energy peaks at 444.7 and 452.2 eV could be derived from the In$^{3+}$ ions positioned at the defect-free areas of the ZnIn$_2$S$_4$, while the other two weaker peaks were attributed to the existence of lattice S defects for changing the local environment of the In$^{3+}$ ions in the ZnIn$_2$S$_4$. However, when the used amount of S precursor was further increased to hydrothermally synthesize the sample of ZnIn$_2$S$_4$ MFs-4,
the S defect-induced XPS peaks on the In 3d core-level spectra disappeared, suggesting the decreased content of lattice S defects in the ZnIn$_2$S$_4$ MFs-4. As observed in Fig. 4(b), there are two characteristic peaks on the Zn 2p core-level spectrum of each sample. The peak positioned around 1021.7 eV is in accordance with the Zn 2p$_{3/2}$, and another peak positioned around 1044.8 eV corresponded to the Zn 2p$_{1/2}$ [20,31,33–35]. Meanwhile, the observed spin-orbit splitting between the Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ is about 23 eV, indicating a normal state of Zn$^{2+}$ ions in all the as-synthesized ZnIn$_2$S$_4$ samples. In the case of ZnIn$_2$S$_4$ MFs-1, the Zn 2p core-level spectrum could be fitted into four peaks. The two intense fitted peaks (1021.7 eV for Zn 2p$_{3/2}$ and 1044.8 eV for Zn 2p$_{1/2}$) were assigned to the Zn$^{2+}$ ions in the normal ZnIn$_2$S$_4$ lattices, while the other two fitted peaks with very weak intensities (1023.7 eV for Zn 2p$_{3/2}$ and 1046.6 eV for Zn 2p$_{1/2}$) could be originated from the Zn$^{2+}$ ions in the lattices of S defect areas due to the changed local environment of Zn$^{2+}$ ions in the S-vacancy regions.

Notably, the two XPS peaks related to the lattice S defects of ZnIn$_2$S$_4$ were vanished on the Zn 2p spectra of the ZnIn$_2$S$_4$ MFs-2, ZnIn$_2$S$_4$ MFs-3, and ZnIn$_2$S$_4$ MFs-4 due to the increased amount of the used S precursor during the hydrothermal process. The S 2p core-level spectra of the as-synthesized ZnIn$_2$S$_4$ MFs were given in Fig. 4(c) and all the XPS curves could be fitted into two symmetric peaks. The peaks positioned around 161.3 and 162.5 eV were consistent with the S 2p$_{3/2}$ and S 2p$_{1/2}$ peaks of the reported metal sulfides, respectively [20,24,31,33]. Besides, the corresponding element content analyses suggested that the S content in the as-synthesized ZnIn$_2$S$_4$ MFs was gradually increased with the used amount of S precursor during the hydrothermal synthesis process (Fig. 4d). The above results prove that when the molar ratio of the used S to Zn precursor was 4:1 during the hydrothermal process,
the competitive reaction between the lattice-S formation and the H$_2$S formation would result in the lattice S-vacancy defects on both the In and Zn facets ($V_{S-In}$ and $V_{S-Zn}$) at the hexagonal ZnIn$_2$S$_4$ (Fig. 4e and f). However, with further increasing the used amount of S precursor with the molar ratio to Zn from 6 to 16, the lattice S-vacancy defects were mainly formed on the In facet at the ZnIn$_2$S$_4$ (Fig. 4e). These observations are consistent with our first-principles calculation results, further confirming that the $V_{S-In}$ defects were more easily generated in the hydrothermally-produced ZnIn$_2$S$_4$ MFs because of its lower formation energy as compared to that of the $V_{S-Zn}$ defects.

To further investigate the influence of the different S-vacancy defects on the kinetics process of photoinduced charge-carriers in the hexagonal ZnIn$_2$S$_4$, the electronic properties of the ZnIn$_2$S$_4$ containing surface S-vacancy defects were calculated in comparison with that of defect-free ZnIn$_2$S$_4$. As shown in Fig. 5(a), the calculated bandgap of defect-free ZnIn$_2$S$_4$ is about 0.80 eV, much smaller than the experimental bandgap of ~2.6 eV due to the well-known GGA error. However, in this study we focus on the change of the bandgap after the introduction of different S-vacancy defects, so we expect the GGA bandgap error is largely canceled between different systems. As shown in Fig. 5(b), the S-vacancy defects at the In facets lead to the formation of defect energy-levels (DELs) in the interband, which would extend the light absorption range of ZnIn$_2$S$_4$ to the visible light region. More importantly, for the ZnIn$_2$S$_4$ surfaces with S-vacancy defects at the In facets, the estimated carrier effective masse of the electrons localized on the conduction band minimum (CBM) are significantly smaller than those localized on the CBM of ZnIn$_2$S$_4$ surface, and the carrier effective masse of the holes localized on the DELs is one order of magnitude smaller than
those localized on the valence band maximum (VBM) of perfect ZnIn$_2$S$_4$ surfaces (see Table S1), which indicates that the photoinduced electron-hole pairs formed between the electron in the CBM and the hole located in DEL could migrate to reaction sites rapidly and decrease the recombination probability. Therefore, adjusting the S-vacancy defects at the In facets is an effective approach to tune the bandgaps and carrier effective masses in a large range, and further improve photocatalytic activity. Compared with S-vacancy defects at the In facets, the DELs induced by S-vacancy defects at the Zn facets hybridize with the CB edge and result in strikingly extended bandgap, which is unfavorable to the absorption of visible light of the solar spectrum. However, as compared to ZnIn$_2$S$_4$ surface, S-vacancy defects at the Zn facets could lead to a smaller effective mass of hole localized on VB edge, and thus the efficiency of charge separation and migration could increase to some extent. These results demonstrate that the formation of V$_{S-In}$ defects in the hexagonal ZnIn$_2$S$_4$ can not only create the DELs to improve the separation process of photoinduced charge-carriers, but also boost the migration process of electron carriers through reducing their effective mass. However, the V$_{S-Zn}$ defects in the hexagonal ZnIn$_2$S$_4$ contribute to the enlargement of bandgap width, leading to the blue-shift of their intrinsic absorption edge.

The optical properties of the as-synthesized ZnIn$_2$S$_4$ MFs were then studied by the UV-vis absorption spectra. As shown in Fig. 6, all the ZnIn$_2$S$_4$ samples possess the similar visible-light response behavior. And, their intrinsic absorption edges are located around 480 nm, corresponding to the intrinsic bandgap of ~2.58 eV. This result reveals that the intrinsic light absorption properties of the as-synthesized ZnIn$_2$S$_4$ MFs were not affected by the used amount of S precursor in our work. Besides these intrinsic absorption bands, the weak
absorption bands at 500–600 nm also appeared on the absorption spectra of these ZnIn$_2$S$_4$ MFs. These absorption bands could be attributed to the formation of the DELs in the interband of ZnIn$_2$S$_4$ due to the existence of V$_{S-In}$ defects, which is in agreement with the conclusions obtained by the above simulation calculations. Further investigations found that the light absorption intensity originated from the V$_{S-In}$ defects of ZnIn$_2$S$_4$ MFs was basically decreased with increasing the used amount of S precursor during the hydrothermal process. It implies that the amount of DELs in the interband of ZnIn$_2$S$_4$ could be controlled by adjusting the used amount of S precursor during the hydrothermal process. However, the blue-shift phenomenon of light absorption was not observed on the absorption spectra of these as-synthesized ZnIn$_2$S$_4$ MFs, suggesting the negligible amount of V$_{S-Zn}$ defects in the hexagonal ZnIn$_2$S$_4$ [24,36]. Apparently, the V$_{S-In}$ defect is the main type of lattice defects for the hydrothermally-produced ZnIn$_2$S$_4$ MFs in our work, which would affect the kinetics process of the photoinduced charge-carriers through creating the DELs and reducing the effective mass of electron-carriers.

In order to verify the above assumption, the transient absorption (TA) spectroscopy spectra of the representative ZnIn$_2$S$_4$ MFs (MFs-1 and MFs-3) were measured, during which a pump laser with 355 nm was employed for promoting the excitons from VB to CB of the ZnIn$_2$S$_4$ MFs. As shown in Fig. 7(a and b), both two samples behave obvious light absorption properties in UV-vis light region. Interestingly, the fluorescence signal around ~530 nm can be also observed on the TA spectrum of both ZnIn$_2$S$_4$ MFs-1 and ZnIn$_2$S$_4$ MFs-3. This signal is ascribed to the exciton recombination process from the V$_{S-In}$ defects-induced DELs to the VB of ZnIn$_2$S$_4$ MFs. Meanwhile, the fluorescence signal of the ZnIn$_2$S$_4$ MFs-3 is stronger
than that of the ZnIn$_2$S$_4$ MFs-1, which implies different amounts of V$_{S-In}$ defects between ZnIn$_2$S$_4$ MFs-1 and ZnIn$_2$S$_4$ MFs-3. To further investigate the influence of the V$_{S-In}$ defects-induced DELs on the kinetics processes of the photoinduced charge-carriers in the above ZnIn$_2$S$_4$ MFs, we fitted the TA curves of the ZnIn$_2$S$_4$ MFs at 550 nm by using the exponential decay functions. As illustrated in Fig. 7(c and d), the TA decay curves of both two samples obey the monoexponential function. The decay lifetime of the photoinduced electrons for the ZnIn$_2$S$_4$ MFs-3 was 94.64 ns, which is much longer than that for the ZnIn$_2$S$_4$ MFs-1 (47.67 ns). The long-lived photoinduced electrons for the ZnIn$_2$S$_4$ MFs-3 suggest the strong suppression of recombination process of the photoinduced charge-carriers due to the existence of appropriate amount of DELs induced by the V$_{S-In}$ defects. That is to say, the creation of appropriate amount of V$_{S-In}$ defects in the ZnIn$_2$S$_4$ MFs through controlling the hydrothermal process can effectively boost the separation process of the photoinduced charge-carriers.

Furthermore, the surface photovoltage spectroscopy (SPV) measurement was performed on the as-synthesized ZnIn$_2$S$_4$ MFs in order to further reveal the separation and migration abilities of the photoinduced charge-carriers affected by the V$_{S-In}$ defects [23,37]. As shown in Fig. 8(a), all the ZnIn$_2$S$_4$ samples display distinct photovoltage signals at 300–600 nm, suggesting the effective separation and migration of charge-carriers due to light absorption of the samples. Among these samples, the ZnIn$_2$S$_4$ MFs-3 exhibited the highest intensity of the photovoltage signal at both UV and visible light regions. Moreover, with increasing the used amount of S precursor to reduce the amount of V$_{S-In}$ defects in the hydrothermally-produced ZnIn$_2$S$_4$ MFs, the intensity of photovoltage signal was increased gradually from ZnIn$_2$S$_4$.
MFs-1 to ZnIn$_2$S$_4$ MFs-3. This phenomenon implies that the excess amount of V$_{S-In}$ defects in the ZnIn$_2$S$_4$ MFs could result in the formation of the combination center of the photoinduced charge-carriers at the DELs of ZnIn$_2$S$_4$ MFs, which accelerates on the recombination of photoinduced charge-carriers in the ZnIn$_2$S$_4$ MFs. However, when the used amount of S precursor was further increased to synthesize the low-defect sample of such ZnIn$_2$S$_4$ MFs-4, the obtained photovoltage signal-intensity was abruptly decreased. This decreased signal intensity can be attributed to the limited amount of V$_{S-In}$ defects to slightly improve the migration process of photoinduced charge-carriers in the ZnIn$_2$S$_4$ MFs-4. Additionally, when a large amount of the S precursor was used in the hydrothermal reaction, the residual organic S intermediates may cover on the surface of the synthesized ZnIn$_2$S$_4$ MFs, which is also not conducive to the charge separation/migration process.

To investigate the contribution of the V$_{S-In}$ defects-improved kinetics process of charge-carriers on the photocatalytic activity of the ZnIn$_2$S$_4$ MFs, the photocatalytic H$_2$ evolution tests were performed in deionized water with TEOA (15 vol%) as a sacrificial agent, but without adding the cocatalyst. As shown in Fig. 8(b), the H$_2$ evolution amounts of all the as-synthesized ZnIn$_2$S$_4$ MFs are linearly increase with irradiation time. Among these MFs, the ZnIn$_2$S$_4$ MFs-3 exhibited the highest photocatalytic activity for H$_2$ evolution. This observation can be attributed to the fact that the appropriate amount of the V$_{S-In}$ defects in the ZnIn$_2$S$_4$ MFs is beneficial to the separation and migration processes of the photoinduced charge-carriers toward photocatalytic protons reduction. In order to further examine the photocatalytic activity, the H$_2$ production rates were calculated and shown in Fig. 8(c). The ZnIn$_2$S$_4$ MFs-3 containing the appropriate amount of the V$_{S-In}$ defects possesses the H$_2$
evolution rate of \(~2.40\ \text{mmol h}^{-1}\ \text{g}^{-1}\), which is more than three times higher than that of the ZnIn\(_2\)S\(_4\) MFS-1 (0.73 mmol h\(^{-1}\) g\(^{-1}\)) that has the excess amount of V\(_{S-In}\) defect. However, when we changed the used sacrificial agent as lactic acid and Na\(_2\)S, respectively, the optimal sample of ZnIn\(_2\)S\(_4\) MFS-3 displayed a decreased photocatalytic activity for H\(_2\) evolution (Fig. S6b). This may be ascribed to the different of electron-donating abilities for the different sacrificial agents [38]. Furthermore, the apparent quantum efficiency (AQE) of the ZnIn\(_2\)S\(_4\) MFS-3 could achieve \(~0.16\%\) at 420 nm by using only 5 mg of the photocatalyst without any cocatalysts (Fig. S5). Besides, after three cycling tests, the photocatalytic H\(_2\)-evolution amount of the ZnIn\(_2\)S\(_4\) MFS-3 could also maintain >90\% of its initial amount of H\(_2\) evolution in the first cycling test (Fig. S6), revealing a satisfactory stability of the photocatalyst.

To further consolidate the result of V\(_{S-In}\) defects-enhanced kinetics process of charge-carriers in the ZnIn\(_2\)S\(_4\) MFs, the transient photocurrent response tests under several on-off cycles of irradiation were executed. As observed in Fig. 8(d), all the samples present the stable photon-to-electricity conversion curves in intermittent visible light. More importantly, the photocurrent intensity of ZnIn\(_2\)S\(_4\)-3 was much higher than other samples (0.831 \(\mu\)A/cm\(^2\)), further confirming the more efficient separation and migration processes of the photoinduced charge-carriers in the ZnIn\(_2\)S\(_4\) with appropriate amount of the V\(_{S-In}\) defects. Interestingly, there are the regular shoulders on the photocurrent curve of ZnIn\(_2\)S\(_4\) MFS-4, which could be ascribed to the residual organic S intermediates covered on the surface of ZnIn\(_2\)S\(_4\) MFS-4 for forming the reaction photocurrent rather than the real photocurrent. This result is consistent with the results analyzed by XRD, BET, and SPV results.

In order to clarify the photocatalytic mechanism of the V\(_{S-In}\) defects-enhanced
photocatalytic H\textsubscript{2} evolution of these hydrothermally-produced ZnIn\textsubscript{2}S\textsubscript{4} MFs, the Mott-Schottky measurements were carried out to calculate the electrochemical flat-band potential (\(E_{fb}\)) of ZnIn\textsubscript{2}S\textsubscript{4} MFs based on the following equation [39–42]

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 N_D} \left( E - E_{fb} - \frac{k_B T}{q} \right)
\]

(2)

where C signifies the space charge capacitance, \(N_D\), \(\varepsilon\) and \(\varepsilon_0\) denote the donor density, dielectric constant of semiconductor film electrode, and permittivity in vacuum, respectively; \(E\) is the applied potential; and \(k_B\), \(T\) and \(q\) are the Boltzmann’s constant, absolute temperature and the electronic charge. As shown in Fig. S7, the intercepts of the tangent to the plot give \(E_{fb}\) values of -0.95, -0.94, -0.94 and -0.95 V (vs. Ag/AgCl) for the ZnIn\textsubscript{2}S\textsubscript{4} MFs-1, ZnIn\textsubscript{2}S\textsubscript{4} MFs-2, ZnIn\textsubscript{2}S\textsubscript{4} MFs-3, and ZnIn\textsubscript{2}S\textsubscript{4} MFs-4, respectively. The potentials obtained under the Ag/AgCl reference electrode can be further converted into the normal hydrogen electrode (NHE) potentials through the following equation [39–42,]

\[
E_{fb(vs \ NHE)} = E_{fb(pH = 0, vs \ Ag/AgCl)} + E_{AgCl} + 0.059 \times pH
\]

(3)

where \(E_{AgCl}=0.197\) V; the pH value of the electrolyte in our work is 6.8. Thus, the \(E_{fb}\) values for the ZnIn\textsubscript{2}S\textsubscript{4} MFs-1, ZnIn\textsubscript{2}S\textsubscript{4} MFs-2, ZnIn\textsubscript{2}S\textsubscript{4} MFs-3, and ZnIn\textsubscript{2}S\textsubscript{4} MFs-4 are calculated to be -0.35, -0.34, -0.34, and -0.35 V versus NHE (pH=0), respectively. As such, the CB positions of these hydrothermally-produced ZnIn\textsubscript{2}S\textsubscript{4} MFs are located at similar potentials with the values of -0.65 ~ -0.64 V (vs. NHE).

Combining with the bandgap values of the as-synthesized ZnIn\textsubscript{2}S\textsubscript{4} MFs calculated from the UV-vis absorption spectra (inset in Fig. 6), the VB positions of these MFs should be situated at 1.93~1.94 V (vs. NHE). According to the above calculations and analyses, the energy band structures of these ZnIn\textsubscript{2}S\textsubscript{4} MFs were illustrated in Fig. 9. Upon visible light
irradiation, the photoinduced electrons on the VB of ZnIn$_2$S$_4$ MFs could be excited to their CB, thereby leaving the same amount of photoinduced holes on the CB of the ZnIn$_2$S$_4$ MFs. When the lattice S vacancies of V$_{S-In}$ and V$_{S-Zn}$ were created in the ZnIn$_2$S$_4$ MFs, the effective mass of the photoinduced electrons and holes could be reduced, which led to the improved migration process of the charge-carriers during the photocatalytic H$_2$ evolution. Furthermore, the created V$_{S-In}$ defects in the ZnIn$_2$S$_4$ MFs could result in the formation of DELs in the interband of ZnIn$_2$S$_4$ MFs (Fig. S8), which are beneficial to the separation process of photoinduced charge-carriers. With increasing the content of V$_{S-In}$ defects, the formed DELs in the interband of the ZnIn$_2$S$_4$ MFs would be changed from discrete to continuous levels. However, the continuous DELs could act as the combination centers of charge-carriers to hinder the separation process of photoinduced charge-carriers in the ZnIn$_2$S$_4$ MFs (Fig. 9a and b) [43,44]. This process was confirmed indirectly through the comparing study of steady-state PL spectra of the as-synthesized samples (Fig. S9). Thus, the excess amount of V$_{S-In}$ defects in the ZnIn$_2$S$_4$ MFs leads to the low photocatalytic activity for H$_2$ evolution (Fig. 9a). Meanwhile, when the content of V$_{S-In}$ defects was too low in the ZnIn$_2$S$_4$ MFs, the photocatalytic H$_2$-evolution activity of the ZnIn$_2$S$_4$ MFs was also unsatisfactory due to the limited amount of discrete DELs to boost the separation process of photoinduced charge-carriers. As a result, the creation of the appropriate amount of V$_{S-In}$ defects in the ZnIn$_2$S$_4$ MFs is important to enhance the separation process of photoinduced charge-carriers for highly-efficient photocatalytic H$_2$ evolution. Overall, controlling the used amount of S precursor during the hydrothermal process is a simple and effective strategy to adjust the lattice S defects of ZnIn$_2$S$_4$ MFs for optimizing the charge-carrier kinetics toward
photocatalytic H₂ evolution.

4. Conclusions

In summary, we have presented a facile and effective one-step strategy to modulate the S-vacancy content of ZnIn₂S₄ MFs only through adjusting the used amount of S-prefcursor during the hydrothermal process. By combining the first-principles calculations with the electron spectra analyses, we demonstrated that the main type of S defects controlled by this hydrothermal modulation method was the S-vacancies at the In facets (V₅₆-In) of the ZnIn₂S₄ MFs. The formed V₅₆-In defects could enhance both the separation and migration processes of the photoinduced charge-carriers through introducing the discrete defect energy-levels (DELs) and reducing the effective mass of electrons. Thus, the optimal S-defective ZnIn₂S₄ MFs obtained by a hydrothermal treatment of the precursors with the Zn/In/S stoichiometric ratio of 1:2:8 exhibited the photocatalytic H₂-evolution rate of ~2.40 mmol h⁻¹ g⁻¹ with an apparent quantum efficiency of ~0.16% at 420 nm. It is believed that our work offers a new idea to modulate the lattice defects of 2D sulfide semiconductors toward highly-efficient photocatalytic solar-to-fuels conversion.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Grant No. 51772041, 12074055, 62005036), the LiaoNing Revitalization Talents Program (XLYC1807176), the Natural Science Foundation of Liaoning Province (Grant No. 2020-MZLH-15), and the Dalian Science Foundation for Distinguished Young Scholars (2018RJ05). Prof. Zhenyi Zhang acknowledges the support from the Liaoning BaiQianWan Talents Program.
Reference


Scheme 1. Schematic representation of the competitive reaction process during the hydrothermal synthesis of ZnIn$_2$S$_4$ MFs.
Fig. 1. Crystallographic structures and formation energies of ZnIn$_2$S$_4$ with different kinds of lattice vacancy defects: (a) S-vacancies at the In facets; (b) S-vacancies at the Zn facets; (c) In-vacancies; (d) Zn-vacancies.
Fig. 2. (a) XRD patterns of the as-synthesized ZnIn$_2$S$_4$ MFs: (1) ZnIn$_2$S$_4$ MFs-1; (2) ZnIn$_2$S$_4$ MFs-2; (3) ZnIn$_2$S$_4$ MFs-3, and (4) ZnIn$_2$S$_4$ MFs-4; SEM images of (b) ZnIn$_2$S$_4$ MFs-1; (c) ZnIn$_2$S$_4$ MFs-2; (d) ZnIn$_2$S$_4$ MFs-3, and (e) ZnIn$_2$S$_4$ MFs-4; (f) the representative elemental mapping images of Zn, In, and S in a single MF of the ZnIn$_2$S$_4$ MFs-3.
**Fig. 3.** TEM images of the as-synthesized ZnIn$_2$S$_4$ MFs: (a) ZnIn$_2$S$_4$ MFs-1, and (b) ZnIn$_2$S$_4$ MFs-3; HRTEM images of (c) ZnIn$_2$S$_4$ MFs-1; (d) ZnIn$_2$S$_4$ MFs-2; (e) ZnIn$_2$S$_4$ MFs-3, and (f) ZnIn$_2$S$_4$ MFs-4.
Fig. 4. XPS spectra of the as-synthesized ZnIn$_2$S$_4$ MFs: (a) In 3$d$ core-level spectra; (b) Zn 2$p$ core-level spectra; (c) S 2$p$ core-level spectra; (d) the molar ratios of S to Zn in the as-synthesized ZnIn$_2$S$_4$ MFs: (1) ZnIn$_2$S$_4$ MFs-1; (2) ZnIn$_2$S$_4$ MFs-2; (3) ZnIn$_2$S$_4$ MFs-3, and (4) ZnIn$_2$S$_4$ MFs-4; crystallographic structures of ZnIn$_2$S$_4$ with (e) the lattice S defects at the In facets and (f) the lattice S defects at the Zn facets.
Fig. 5. The simulated band structures and geometric structures of (a) defect-free ZnIn$_2$S$_4$, (b) the ZnIn$_2$S$_4$ surface with S-vacancy defects at the In facets and (c) the S-vacancy defects at the Zn facets.
Fig. 6. UV-Vis absorption spectra of the as-synthesized samples: (1) ZnIn$_2$S$_4$ MFs-1; (2) ZnIn$_2$S$_4$ MFs-2; (3) ZnIn$_2$S$_4$ MFs-3, and (4) ZnIn$_2$S$_4$ MFs-4; insets showing the plots of the $(\alpha h\nu)^2$ vs photon energy $(h\nu)$ for the corresponding samples.
Fig. 7. TA spectra of the as-synthesized ZnIn$_2$S$_4$ MFs excited by a 355-nm nanosecond laser pulse: (a) ZnIn$_2$S$_4$ MFs-1; (b) ZnIn$_2$S$_4$ MFs-3; TA decay curves of the as-synthesized samples at 550 nm: (c) ZnIn$_2$S$_4$ MFs-1; (d) ZnIn$_2$S$_4$ MFs-3.
Fig. 8. (a) SPV spectra of the as-synthesized ZnIn$_2$S$_4$ MFs; (b) time-dependent H$_2$ evolution of the ZnIn$_2$S$_4$ MFs under visible light irradiation ($\lambda > 420$ nm); (c) photocatalytic H$_2$ evolution rates of different ZnIn$_2$S$_4$ MFs under visible light irradiation ($\lambda > 420$ nm); (d) photocurrent tests of as-synthesized samples: (1) ZnIn$_2$S$_4$ MFs-1; (2) ZnIn$_2$S$_4$ MFs-2; (3) ZnIn$_2$S$_4$ MFs-3, and (4) ZnIn$_2$S$_4$ MFs-4.
**Fig. 9.** Schematic diagram of kinetics process of photoinduced charge-carriers in the as-synthesized ZnIn$_2$S$_4$ MFs for photocatalytic H$_2$ evolution: (a) ZnIn$_2$S$_4$ MFs-1; (b) ZnIn$_2$S$_4$ MFs-2; (c) ZnIn$_2$S$_4$ MFs-3, and (d) ZnIn$_2$S$_4$ MFs-4.
A facile one-step hydrothermal method was developed to modulate the lattice S-content of ZnIn$_2$S$_4$ microflowers (MFs). The S-vacancies at the In facets were the main type of lattice defects in ZnIn$_2$S$_4$ MFs, which could enhance both the separation and migration processes of the photoinduced charge-carriers, thereby leading to the enhanced photocatalytic activity for H$_2$ evolution.

Highlights
- A facile one-step hydrothermal method is used to modulate the lattice S-content in ZnIn$_2$S$_4$ MFs.
- S-vacancies at the In facets are the main type of lattice defects in the formed ZnIn$_2$S$_4$ MFs.
- The S-defects of ZnIn$_2$S$_4$ MFs induce discrete defect energy-levels and low electron-effective-mass.
- The proper S-defects of ZnIn$_2$S$_4$ MFs improve the separation and migration of photoinduced charge-carriers.
- The photocatalytic activity of the ZnIn$_2$S$_4$ MFs for H$_2$ evolution is enhanced by adjusting the amount of S-defects.