

Article

Synthesis and Hydrogen Production Performance of MoP/a-TiO₂/Co-ZnIn₂S₄ Flower-like Composite Photocatalysts

Keliang Wu ¹ , Yuhang Shang ¹, Huazhen Li ², Pengcheng Wu ³ , Shuyi Li ¹, Hongyong Ye ¹, Fanqiang Jian ¹, Junfang Zhu ⁴ , Dongmei Yang ⁴, Bingke Li ^{1,*} and Xiaofei Wang ^{5,*}

¹ Henan Key Laboratory of Microbial Fermentation, School of Biology and Chemical Engineering, Nanyang Institute of Technology, Nanyang 473000, China; yehongyong2016@163.com (H.Y.)

² Anhui Yansheng New Material Co., Ltd., Hefei 230039, China

³ School of Chemistry and Chemical Engineering, Shihezi University, Shihezi 832003, China

⁴ Department of Petroleum and Chemical, Bayingoleng Vocational and Technical College, Bazhou 841000, China

⁵ College of Materials and Chemical Engineering, West Anhui University, Lu'an 237012, China

* Correspondence: libingke86@nyist.edu.cn (B.L.); smilewxf@163.com (X.W.)

Abstract: Semiconductor photocatalysis is an effective strategy for solving the problems of increasing energy demand and environmental pollution. ZnIn₂S₄-based semiconductor photocatalyst materials have attracted much attention in the field of photocatalysis due to their suitable energy band structure, stable chemical properties, and good visible light responsiveness. In this study, ZnIn₂S₄ catalysts were modified by metal ion doping, the construction of heterojunctions, and co-catalyst loading to successfully prepare composite photocatalysts. The Co-ZnIn₂S₄ catalyst synthesized by Co doping and ultrasonic exfoliation exhibited a broader absorption band edge. Next, an a-TiO₂/Co-ZnIn₂S₄ composite photocatalyst was successfully prepared by coating partly amorphous TiO₂ on the surface of Co-ZnIn₂S₄, and the effect of varying the TiO₂ loading time on photocatalytic performance was investigated. Finally, MoP was loaded as a co-catalyst to increase the hydrogen production efficiency and reaction activity of the catalyst. The absorption edge of MoP/a-TiO₂/Co-ZnIn₂S₄ was widened from 480 nm to about 518 nm, and the specific surface area increased from 41.29 m²/g to 53.25 m²/g. The hydrogen production performance of this composite catalyst was investigated using a simulated light photocatalytic hydrogen production test system, and the rate of hydrogen production by MoP/a-TiO₂/Co-ZnIn₂S₄ was found to be 2.96 mmol·h⁻¹·g⁻¹, which was three times that of the pure ZnIn₂S₄ (0.98 mmol·h⁻¹·g⁻¹). After use in three cycles, the hydrogen production only decreased by 5%, indicating that it has good cycle stability.

Keywords: ZnIn₂S₄; Co doping; TiO₂; photocatalysis; hydrogen evolution



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1. Introduction

The energy crisis is an ongoing global issue of increasing importance. Moreover, the rapid development of industrialization around the world has led to severe energy and environmental pressures [1]. Thus, there is an increased emphasis on research worldwide to successfully address the global energy crisis and to create new sustainable sources of energy [2]. The capture and conversion of solar energy by the photocatalytic splitting of water offers a promising strategy for converting inexhaustible solar energy into hydrogen (H₂) energy [3]. However, there are currently two main constraints that limit the large-scale application of hydrogen: (1) the large-scale green synthesis of hydrogen is a significant challenge; (2) the storage and transport of hydrogen is also difficult [4]. Hydrogen's shortcomings are partly explained by high infrastructure costs for production, storage, and distribution. These problems may result from their low energy density per volume, explosive characteristics, and ability to cause embrittlement in metals such as steel [5]. Many methods have been investigated for the production of hydrogen. The photocatalytic

decomposition of water for hydrogen production is one of the simplest, most environmentally friendly and low-cost methods for producing hydrogen. Therefore, this method has attracted extensive research attention [6]. In particular, the production of hydrogen via the solar photolysis of water is gaining increasing attention due to its potential for solving the global energy crisis and mitigating environmental pollution problems [7,8]. Photogenerated charge carriers can be excited from photocatalysts under sunlight, and after the photogenerated electrons migrate to the surface of semiconductors, H^+ in water receives electrons that are reduced to H_2 . The holes left behind are combined with sacrificial agents in the system and used to achieve continuous H_2 production.

In photocatalytic systems, the mobility of photogenerated carriers is an important factor affecting photocatalytic efficiency, with a fast migration rate and high separation efficiency positively contributing to the photocatalytic reaction [9]. The electrostatic potential of $ZnIn_2S_4$ with a hexagonal laminar structure is uniformly distributed within the plane, and the small potential of this material is well conducive to carrier migration [10]. Moreover, the positive charges are densely distributed in the indium sulfide tetrahedra and octahedra within the cell, while the negative charges are concentrated in the zinc indium tetrahedral [11]. Therefore, photogenerated electrons are easily transferred to the indium sulfide polyhedra, while the photogenerated holes more easily migrate to the zinc indium tetrahedra, which improves the separation efficiency of the photogenerated carriers [12]. Furthermore, the band gap of $ZnIn_2S_4$ is 2.3~2.5 eV and the energy band of $ZnIn_2S_4$ is narrow, which is also conducive to the generation of photogenerated carriers [13]. $ZnIn_2S_4$ is therefore an ideal photocatalytic material with broad application prospects.

In 2003, Lei et al. [14] synthesized $ZnIn_2S_4$ by a hydrothermal method and used this material as an effective visible-light-driven hydrogen precipitation photocatalyst for the first time. Guo's group [15] synthesized $ZnIn_2S_4$ microspheres by a hydrothermal/solvothermal process and explored their visible-light-driven photocatalytic hydrogen production performance. Their findings showed that these microsphere catalysts had a good potential for producing photocatalytic hydrogen from water when exposed to visible light [16].

However, pure $ZnIn_2S_4$ photocatalysts still suffer from low visible light utilization and low photocatalytic activity [17]. Moreover, the photocatalytic activity of $ZnIn_2S_4$ semiconductors is affected to some extent by their limited photogenerated electron and hole separation efficiency under visible light irradiation and low photogenerated carrier mobility [18]. Therefore, Yuan Wenhui et al. [19] prepared a series of Co-doped $ZnIn_2S_4$ photocatalysts using a solvothermal synthesis method. The successful incorporation of Co into the $ZnIn_2S_4$ lattice was confirmed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). With increasing Co concentration, the absorption edge of the samples caused red-shift, but the Co also gradually disrupted the $ZnIn_2S_4$ morphology. Their photocatalytic results showed that Co^{2+} doping significantly improved the photocatalytic activity of $ZnIn_2S_4$. The optimum Co doping amount of 0.3 wt% for the $ZnIn_2S_4$ photocatalyst led to the highest photocatalytic activity [20]. Therefore, in this work, a doping amount of 0.3% was chosen to preserve the petal-like morphology and enhance the specific surface area of $ZnIn_2S_4$ while also improving its hydrogen production performance and utilization of sunlight [21,22].

TiO_2 has been widely investigated as a semiconductor photocatalyst material due to its many advantages, such as high stability and high photosensitivity. Therefore, TiO_2 -based metal oxide photocatalysts are widely used in many practical applications [23]. However, TiO_2 particles easily agglomerate, have a low adsorption capacity for organic matter, and exhibit low solar energy utilization [24]. These factors limit the photocatalytic efficiency of TiO_2 and seriously affect its application in practical production [25]. The focus of photocatalytic research has therefore shifted from the improvement of traditional TiO_2 performance to the investigation of other catalysts with better performance in the visible light range. Amorphous TiO_2 is an important category of TiO_2 materials that exhibits the common "short-range order, long-range disorder" [26] structural feature seen in amorphous materials. Amorphous semiconductors have a large number of suspended bonds. Therefore,

the energy band structures of amorphous materials exhibit a gap band between the valence band and the conduction band [27]. Amorphous TiO_2 with a lower band gap width can be obtained by modifying its electronic structure. This reduces the energy intensity required for electrons to transfer from the valence band to the conduction band [28]. Therefore, visible light irradiation can be used to activate these materials, improving their photocatalytic activity [29]. Zywitzki et al. reported amorphous titania-based photocatalysts synthesized using a facile, UV-light mediated method and evaluated as photocatalysts for hydrogen evolution from water/methanol mixtures. The resulting amorphous materials exhibited an overall higher hydrogen evolution rate ($1.09 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) compared to a crystalline TiO_2 reference (P25 $0.80 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) on a molar basis of the photocatalyst due to their highly porous structure and high surface area [30].

The photocatalytic activity of a photocatalyst is determined by its light absorption capacity as well as its electron–hole transfer and separation efficiency [31]. These factors are related to the catalyst surface properties, which play an important role in photocatalytic processes. For instance, the loading of co-catalysts on a photocatalyst surface to provide hydrogen production sites has been commonly reported in the literature [32]. Some common co-catalysts include alumina and potassium oxide. MoP is commonly used as an efficient catalyst for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions [33]. Depending on the reversibility of hydrogen bonding to the catalyst, some catalysts used for HDS reactions are also useful for HER reactions because of the similar pathways and mechanisms of hydrogen production and hydrogenation as well as their low Tafel slope and low over potential. For example, Chen et al. [34] impregnated precursors on sponges to obtain MoP with a large specific surface area and enhanced photocatalytic activity. MoP cannot be directly used as a photocatalyst, but it can be used as an efficient hydrogen precipitation co-catalyst. Du et al. used MoP as a highly active co-catalyst on CdS nanorods for the first time, which significantly improved the photocatalytic activity of their CdS catalyst [35]. Thus, MoP is an efficient co-catalyst for hydrogen precipitation.

At present, the utilization of solar energy by metal oxide photocatalysts for hydrogen production has mainly focused on the UV wavelength range. Furthermore, most research is based on TiO_2 semiconductor photocatalytic materials. The majority of the wavelengths that make up solar energy, though, do not fall inside the visible spectrum. ZnIn_2S_4 shows promise as a visible-light-responsible ternary metal–sulfur compound photocatalyst, but its performance still needs to be improved. Therefore, in this work, ZnIn_2S_4 materials were prepared and modified (as shown in Figure 1): (1) Petal-shaped ZnIn_2S_4 catalysts were produced, their morphology was studied, and their photocatalytic performance was investigated. (2) Co- ZnIn_2S_4 was prepared by Co doping and ultrasonic exfoliation to broaden the absorption band edge and retain the petal-shaped morphology of the catalyst. (3) An a- TiO_2 /Co- ZnIn_2S_4 composite photocatalyst was successfully prepared by coating amorphous TiO_2 on the Co- ZnIn_2S_4 surface, and the effect of loading different amounts of TiO_2 on the photocatalytic performance was investigated. At the same time, a TiO_2 and Co- ZnIn_2S_4 heterojunction was constructed, which led to the red-shift of the absorption band, enhanced light absorption properties, and a reduction in photogenerated electron–hole recombination. (4) Finally, MoP was loaded on the a- TiO_2 /Co- ZnIn_2S_4 catalyst as a co-catalyst, which enhanced the light absorption intensity and provided reaction sites to promote the overall efficiency of catalytic hydrogen production. Therefore, MoP/a- TiO_2 /Co- ZnIn_2S_4 flower-like composite photocatalysts with good photocatalytic hydrogen production activity and stability were prepared. This catalyst uses Co- ZnIn_2S_4 as the main body for photo generated electron excitation, and amorphous a- TiO_2 is combined with it to improve the efficiency of electron hole separation. Finally, MoP is used as a co-catalyst to provide hydrogen production sites, thus achieving efficient hydrogen production.

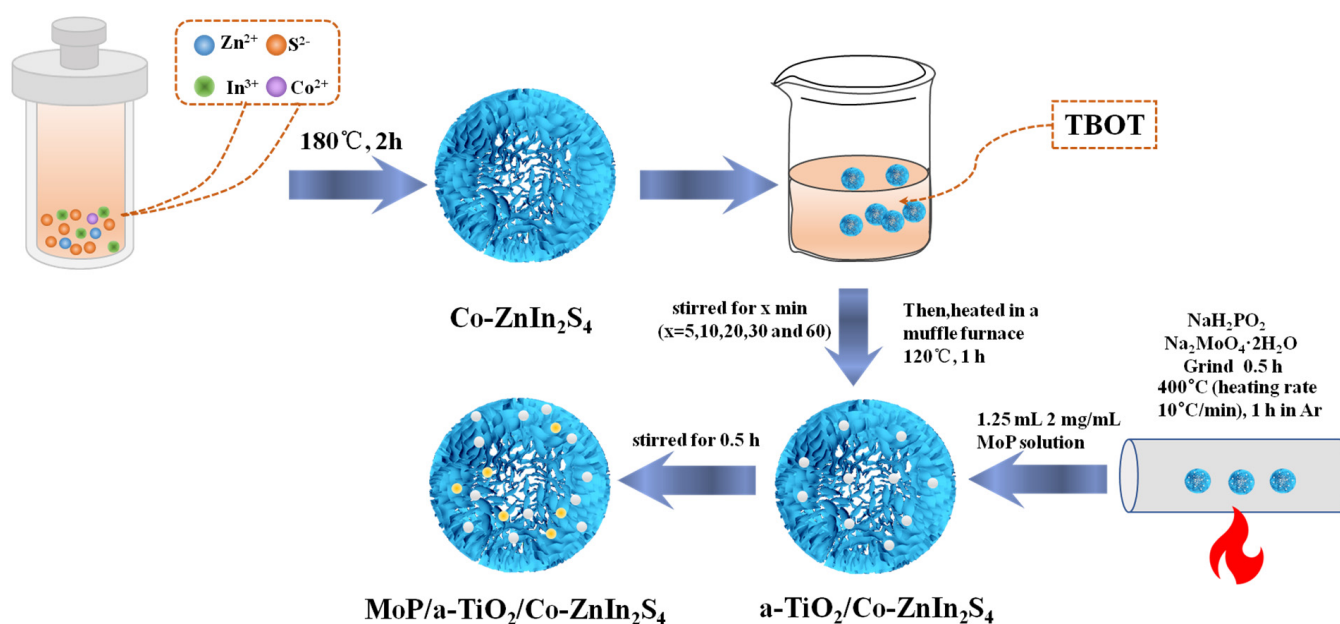


Figure 1. Steps for preparation of MoP/a-TiO₂/Co-ZnIn₂S₄ flower-like composite photocatalysts.

2. Results and Discussions

2.1. Structure, Morphology and Composition of Composite Photocatalysts

The synthesized ZnIn₂S₄ and loaded catalyst samples were characterized to investigate their morphology and microstructures, as shown by the SEM images in Figure 2. Figure 2a shows that the synthesized ZnIn₂S₄ was a petal-like microsphere consisting of a large number of nanoflakes, which are all made of ZnIn₂S₄ nanosheets. These nanoflakes were cross-linked to each other and formed many uniform slit-type pore structures between the petal layers. Figure 2b shows that Co doping did not change the flower-like structure of ZnIn₂S₄. No particles of Co aggregation were observed on the surface of the petals, so this demonstrated that Co was potentially doped into the lattice structure of ZnIn₂S₄. Figure 2c shows that the petals were loaded with a granular material, which indicated the successful loading of TiO₂. This was consistent with the catalyst morphology design. As shown in Figure 2d, the addition of MoP did not result in any obvious morphological changes. However, the MoP content was repeatedly low.

Element mapping (Figure 3 and Table 1) confirmed that MoP/TiO₂/Co-ZnIn₂S₄ contained S, Mo, In, Zn, Ti, O, P, and Co elements. All elements were evenly distributed without visible aggregation, further demonstrating the successful synthesis of the MoP/a-TiO₂/Co-ZnIn₂S₄ composite.

Table 1. Distribution of elements in the MoP/a-TiO₂/Co-ZnIn₂S₄ composite catalyst.

	In	S	Zn	Mo	P	Ti	O	Co
wt%	53.2	26.0	10.2	2.5	0.3	1.1	6.2	0.5

The morphological characteristics of the MoP/a-TiO₂/Co-ZnIn₂S₄ photocatalyst were further investigated by TEM, as shown in Figure 4. Figure 4a shows that the MoP/a-TiO₂/Co-ZnIn₂S₄ composite system had a nanoflower-like structure and intact, non-agglomerated microspheres. Figure 4b is a partial enlargement of Figure 4a, showing a more detailed view of the ZnIn₂S₄ nanosheets, which are very thin in the nanoflower. Some MoP/TiO₂ particles were visible on the nanosheets, which showed the successful loading of MoP and TiO₂ on the surface of ZnIn₂S₄. Figure 4c shows an electron diffraction pattern of the MoP/a-TiO₂/Co-ZnIn₂S₄ photocatalyst, demonstrating its good crystallinity. Lattice fringe spacings of 0.21, 0.32 and 0.35 nm were identified in Figure 4d, which re-

spectively corresponded to MoP, ZnIn_2S_4 , and TiO_2 . This was consistent with the data in the relevant literature. Overall, this TEM analysis further demonstrated the successful preparation of $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$.

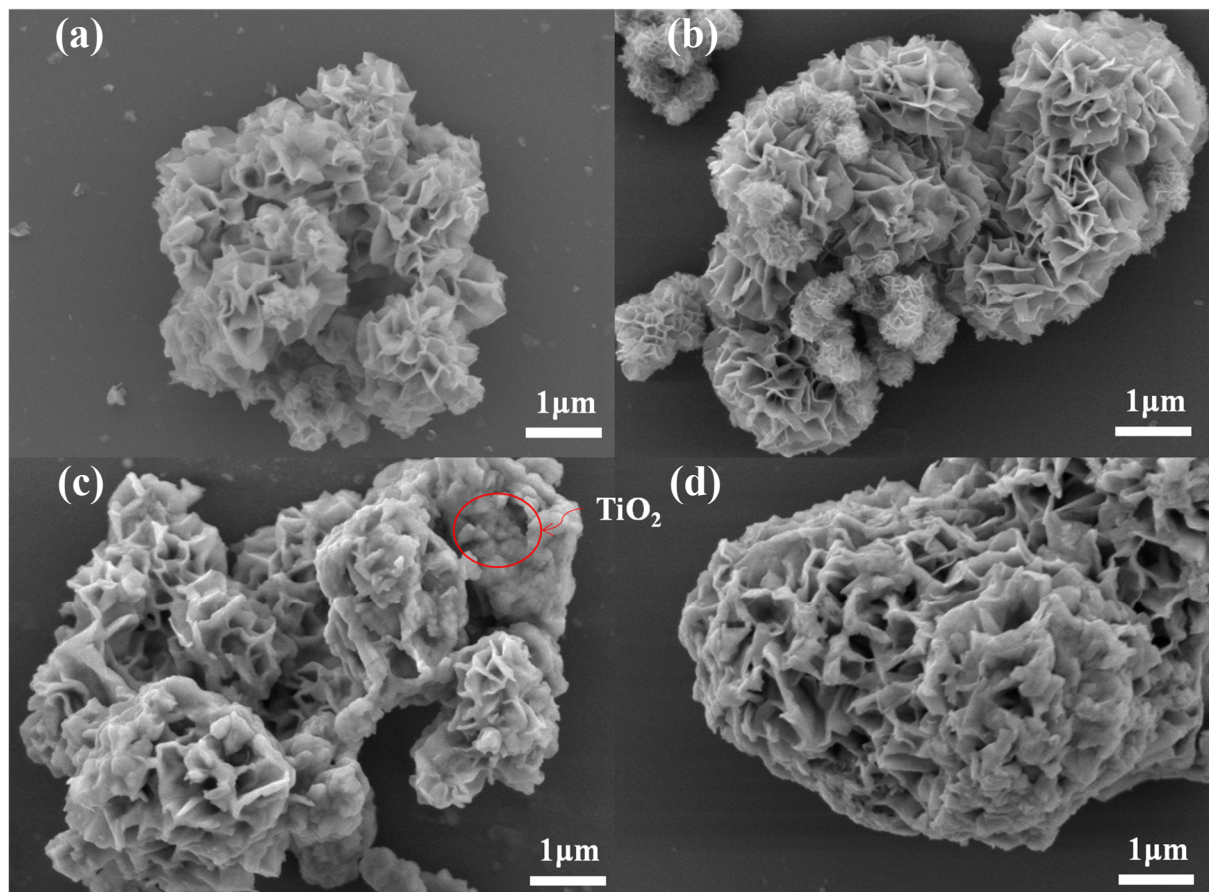


Figure 2. SEM micrographs of (a) ZnIn_2S_4 , (b) $\text{Co-ZnIn}_2\text{S}_4$, (c) $\text{a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$, and (d) $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$.

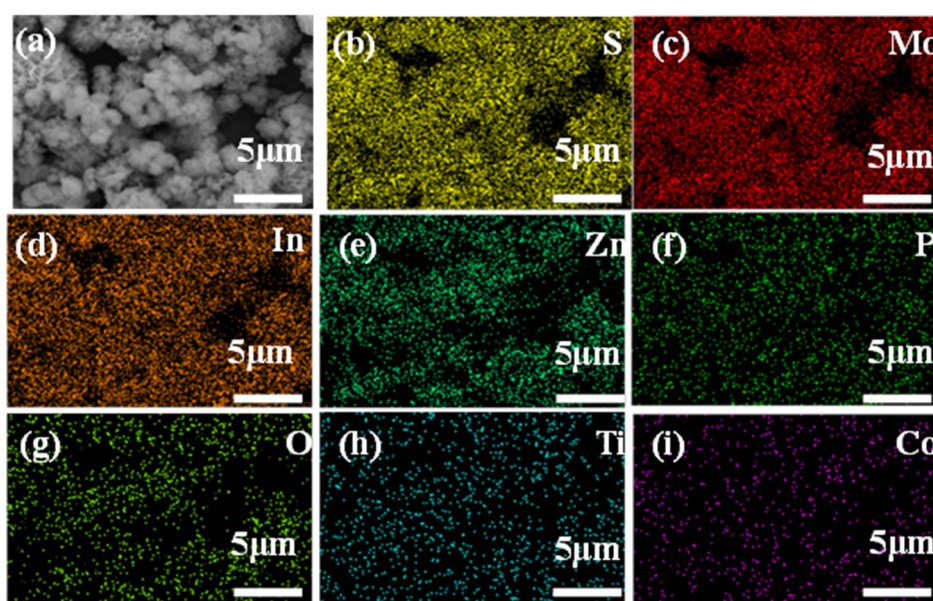


Figure 3. Elemental mapping of the $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ composite catalyst. (a) scanning area, (b) S, (c) Mo, (d) In, (e) Zn, (f) P, (g) O, (h) Ti, (i) Co.

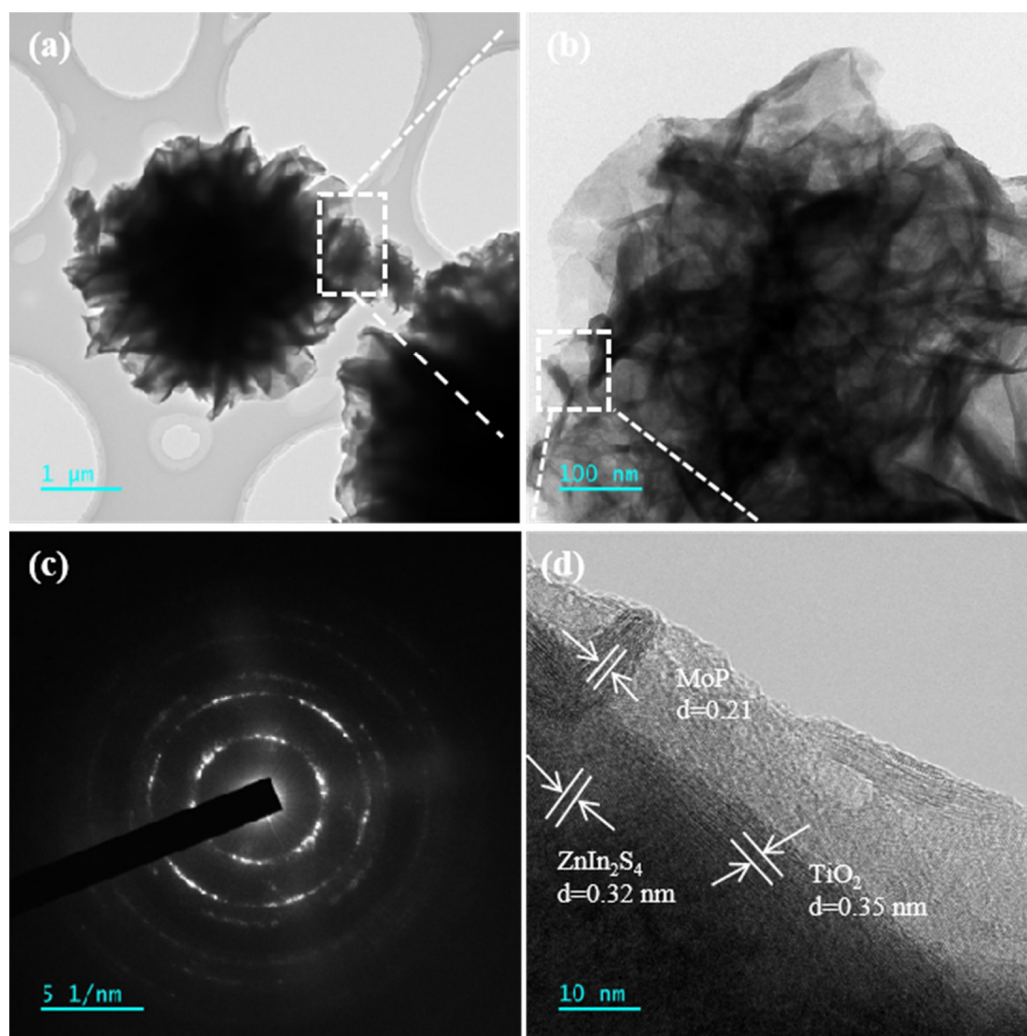


Figure 4. (a,b) TEM micrographs, (c) electron diffraction pattern, and (d) high-resolution TEM micrograph showing the lattice fringe spacing of MoP/a-TiO₂/Co-ZnIn₂S₄.

The catalyst samples were investigated by X-ray diffraction, as shown in Figure 5. Characteristic diffraction peaks were visible at 8.52°, 21.3°, 29.1°, and 49.3° for all four catalysts, and these peaks were consistent with standard cards JCPDS 49–1562 and JCPDS 48–1778. ZnIn₂S₄ is a direct bandgap semiconductor with a layered (according to card NO. 48–1778, $a = b = c = 10.6$, $\alpha = \beta = \gamma = 90^\circ$) and trigonal structure (ICSD-JCPDS card NO. 49–1562, $a = b = 3.85$, $c = 24.68$, $\alpha = 37.01^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$), as shown in Figure 5. All polymorphs show certain photocatalytic performance under visible light, while the hexagonal ZnIn₂S₄ has better photocatalytic performance. The cubic ZnIn₂S₄ is a direct cubicspinel phase when the S atoms in the unit cell are ABC stacking [36]. The diffraction peak positions did not significantly shift upon modification, which indicated that the ZnIn₂S₄ was not significantly affected. The shape of the ZnIn₂S₄ peaks did not change after TiO₂ loading and no separate TiO₂ peaks were identified, indicating that partly amorphous TiO₂ was synthesized. The diffraction peaks also did not change after the addition of MoP, indicating the successful preparation of the composite MoP/a-TiO₂/Co-ZnIn₂S₄ catalyst.

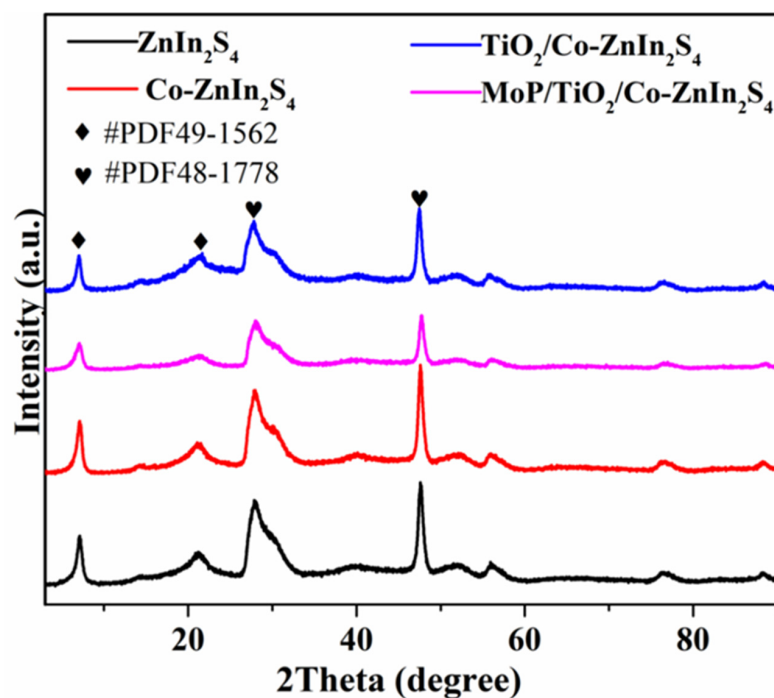


Figure 5. XRD patterns of the ZnIn_2S_4 , $\text{Co-ZnIn}_2\text{S}_4$, $\text{a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$, and $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ photocatalysts.

Figure 6a,b shows the N_2 adsorption–desorption isotherms and pore size distributions of ZnIn_2S_4 , $\text{Co-ZnIn}_2\text{S}_4$, $\text{a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ and $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$. All four isotherms were identified as type IV, and they contained H3 hysteresis loops. Moreover, the catalysts exhibited pore sizes ranging from 10 to 100 nm. As shown in Table 2, the specific surface area slightly changed after catalyst modification. Specifically, $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ showed a slight increase in specific surface area compared with pure ZnIn_2S_4 . The pore volume of $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ was also slightly higher than that of pure ZnIn_2S_4 . This was consistent with the SEM image shown in Figure 2c, in which some of the TiO_2 nanoparticles were supported on the ZnIn_2S_4 nanosheets. Therefore, the addition of TiO_2 and the MoP co-catalyst led to an increase in adsorption pore volume. Consequently, more adsorption and active sites were generated on the photocatalyst surface. Moreover, the modified catalysts exhibited lower pore sizes because TiO_2 was distributed between the ZnIn_2S_4 petals, which reduced the pore size.

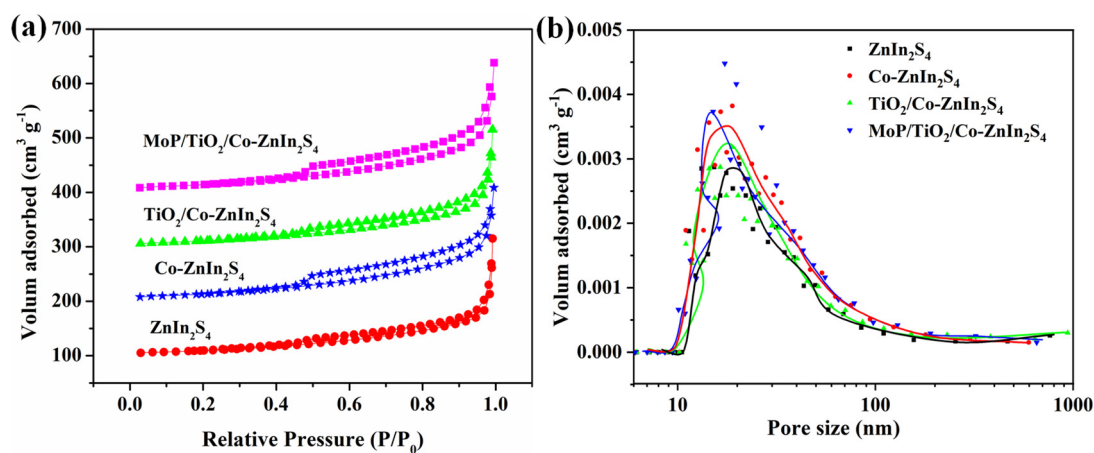
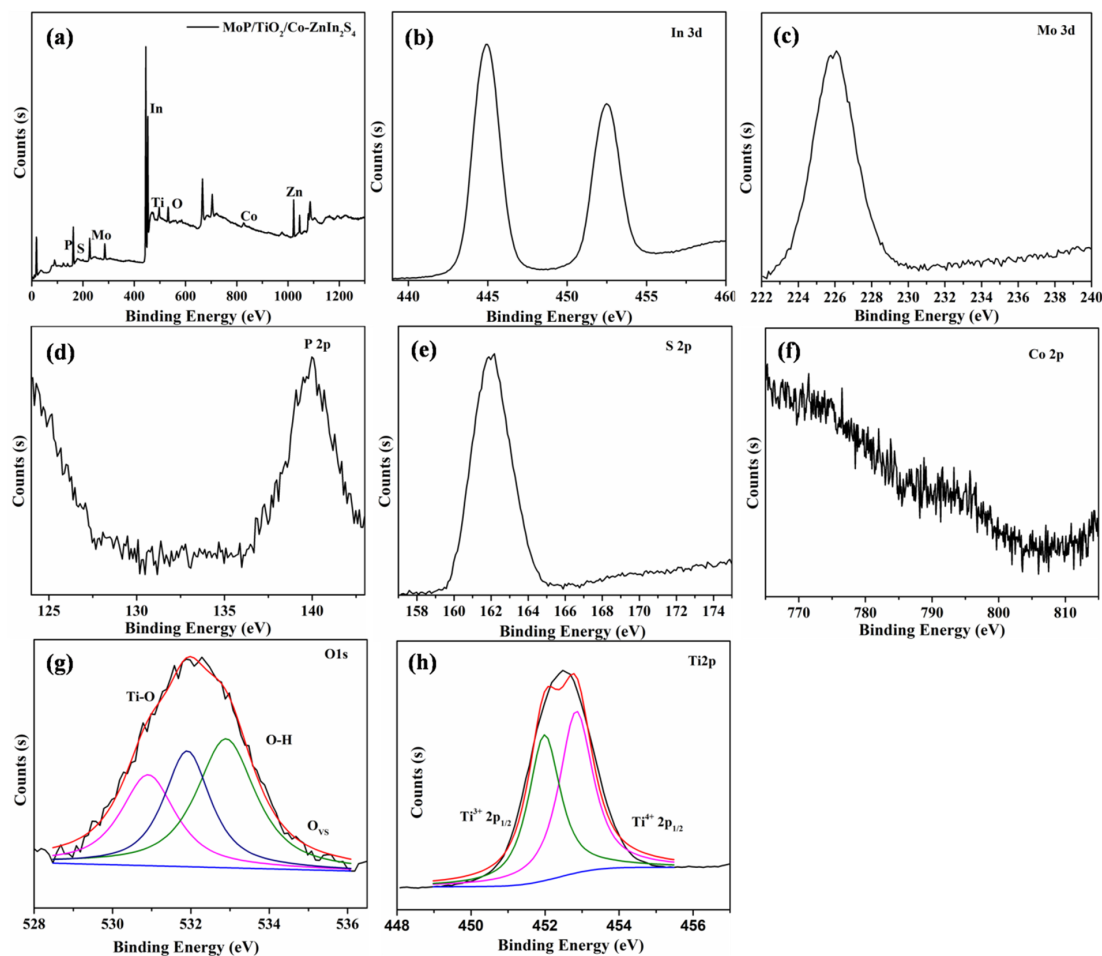


Figure 6. (a) N_2 adsorption–desorption isotherms and (b) pore size distributions of the ZnIn_2S_4 , $\text{Co-ZnIn}_2\text{S}_4$, $\text{a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$, and $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ photocatalysts.

Table 2. Specific surface area, pore volume, and average pore diameter of ZnIn₂S₄, Co-ZnIn₂S₄, a-TiO₂/Co-ZnIn₂S₄, and MoP/a-TiO₂/Co-ZnIn₂S₄.

Sample	Specific Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (nm)
ZnIn ₂ S ₄	41.293	0.3346	162.1
Co-ZnIn ₂ S ₄	53.453	0.3242	121.3
TiO ₂ /Co-ZnIn ₂ S ₄	46.669	0.3346	143.4
MoP/a-TiO ₂ /Co-ZnIn ₂ S ₄	53.250	0.3703	139.1

The chemical state and chemical composition of the MoP/a-TiO₂/Co-ZnIn₂S₄ composite was analyzed by XPS. As shown in Figure 7, the XPS survey spectrum confirmed the presence of P, Mo, Ti, Zn, In and S elements in this composite photocatalyst. This was consistent with the EDS test results. The binding energy peaks at 445.1 eV, 225.9 eV, 139.8 eV and 161.9 eV were attributed to In 3d, Mo 3d, P 2p and S 2p signals, respectively. This indicated the presence of MoP, TiO₂ and ZnIn₂S₄ in the MoP/a-TiO₂/Co-ZnIn₂S₄ composite photocatalyst. In the Ti 2p spectrum, the two main peaks near 458.7 eV and 464.5 eV were attributed to Ti 2p_{3/2} and Ti 2p_{1/2}. These peaks were generated by the Ti⁴⁺ oxidation state of TiO₂. A single O 1s peak near 530.0 eV was deconvoluted into three peaks. The peak at 530.0 eV was attributed to the presence of oxygen vacancies, and the peaks at 530.8 and 532.4 eV were caused by Ti–OH. This demonstrated that the synthesized TiO₂ was amorphous and that the presence of this TiO₂ increased the oxygen vacancy concentration of the catalyst. These results conclusively demonstrate that the MoP/a-TiO₂/Co-ZnIn₂S₄ composite photocatalyst was successfully prepared.

**Figure 7.** XPS spectra of the MoP/a-TiO₂/Co-ZnIn₂S₄ composite catalyst.

UV-vis diffuse reflectance spectra of $\text{TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ were obtained using different TiO_2 loading times to explore the effect of TiO_2 on catalytic activity, as shown in Figure 8a. These spectra were denoted as $X\text{-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$, where X represents the number of minutes. With increasing TiO_2 loading time, the light absorption intensity and range of this composite catalyst first increased and then decreased. In particular, at 20 min, the absorption side band of $a\text{-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ shifted to the right, and the highest absorption was achieved at this time. Therefore, $20\text{-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ was selected as the basis for subsequent experiments. Figure 8b shows UV-vis diffuse reflectance spectra of ZnIn_2S_4 , $\text{Co-ZnIn}_2\text{S}_4$, $a\text{-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ and $\text{MoP}/a\text{-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$. The absorption edge of pure ZnIn_2S_4 synthesized in this study was 480 nm. As shown, the spectrum significantly changed after Co doping, reaching 500 nm. However, almost the same absorption was demonstrated after the addition of amorphous TiO_2 . The absorption edge of $\text{MoP}/a\text{-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ was widened to about 518 nm, indicating that the MoP was photocatalyzed by the load. The band gap energies of ZnIn_2S_4 , $\text{Co-ZnIn}_2\text{S}_4$, $a\text{-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ and $\text{MoP}/a\text{-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ were calculated using the curves shown in Figure 8b. As shown in Figure 8c, the band gap energy of $\text{MoP}/a\text{-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ was 2.7 eV. This analysis demonstrated the broader light absorption range and enhanced photocatalytic activity of the $\text{MoP}/a\text{-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ composite photocatalyst.

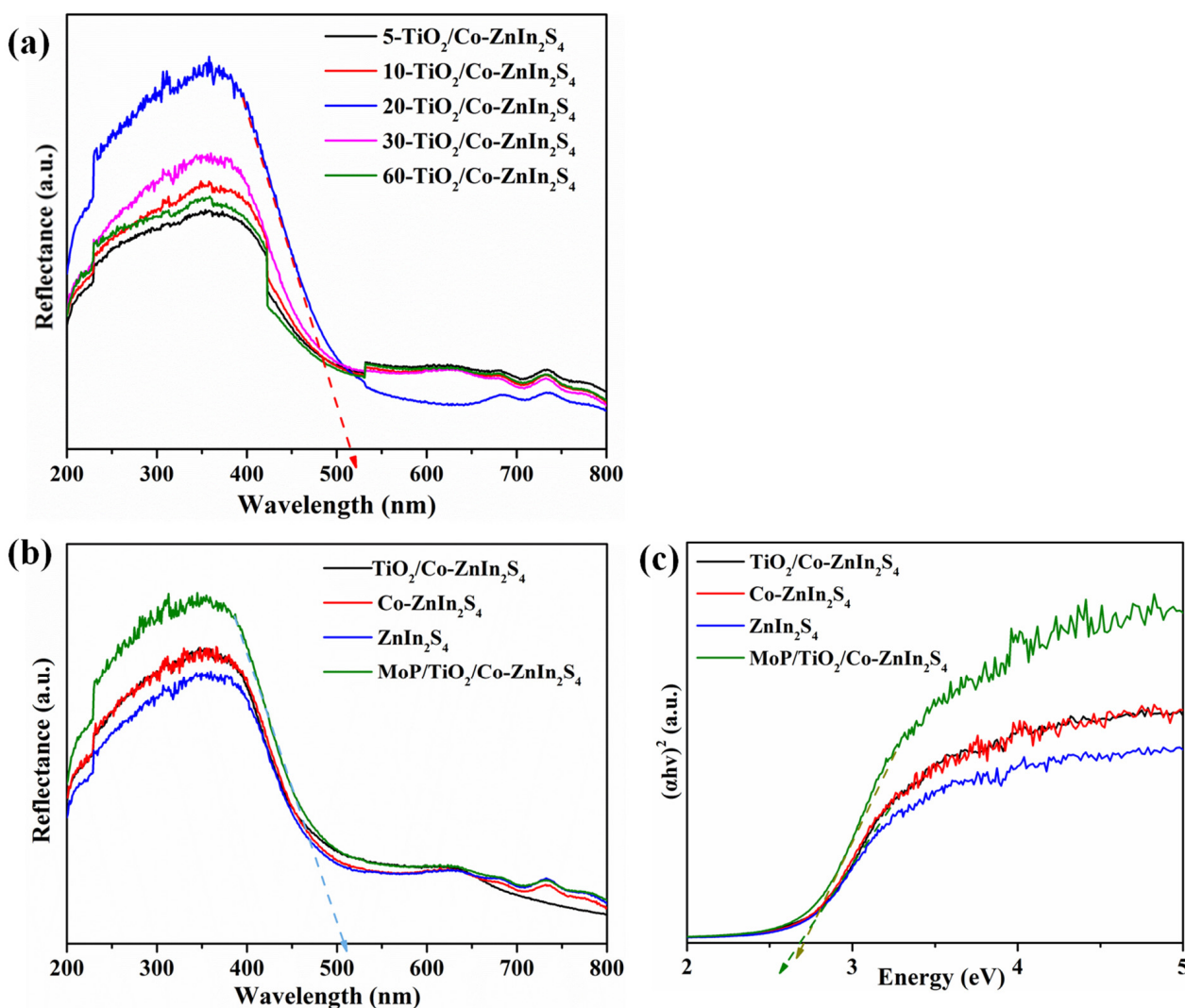


Figure 8. (a) UV-vis diffuse reflectance spectra of $a\text{-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ at different times; (b) UV-vis diffuse reflectance spectra and (c) bandgaps of ZnIn_2S_4 , $\text{Co-ZnIn}_2\text{S}_4$, $a\text{-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$, and $\text{MoP}/a\text{-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$.

2.2. Photoelectrochemical Performance

The photoelectrical properties of the catalysts were characterized in order to study their photocatalytic activity. Figure 9a shows that the photocurrent starting positions of all the catalysts were significantly earlier than their dark current starting positions. In addition, compared with $\text{Co-ZnIn}_2\text{S}_4$, the initial positions of $\text{TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ and $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ were slightly shifted to the left. These results indicate that the composite catalyst had a lower activation energy and enhanced photocatalytic performance. Linear scan voltammetry curves of ZnIn_2S_4 , $\text{Co-ZnIn}_2\text{S}_4$, $\text{a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$, and $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ were obtained under both light and dark conditions, as shown in Figure 9b. This shows the photocurrent densities of ZnIn_2S_4 , $\text{Co-ZnIn}_2\text{S}_4$, $\text{a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ and $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$, which exhibited photocurrents of $1 \mu\text{A}/\text{cm}^2$, $3 \mu\text{A}/\text{cm}^2$, $4 \mu\text{A}/\text{cm}^2$ and $4.5 \mu\text{A}/\text{cm}^2$, respectively. This showed that Co doping significantly improved the performance of ZnIn_2S_4 . Moreover, the separation efficiency of photogenerated electron-hole pairs was also significantly improved by the addition of TiO_2 supported on the ZnIn_2S_4 nanosheets. In addition, $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ had a higher photocurrent density, therefore exhibiting more efficient carrier separation and transfer efficiency. The electrochemical impedance spectra shown in Figure 9c demonstrate that $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ had lower high-frequency semicircles than $\text{Co-ZnIn}_2\text{S}_4$ or $\text{a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ as well as lower resistance. This further indicated that $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ had more efficient carrier separation and transfer efficiency. The line increase of curves $\text{Co-ZnIn}_2\text{S}_4$, $\text{a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ and $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ indicates that the charge transfer resistance decreases sequentially, which is also consistent with the higher carrier separation and transfer efficiency.

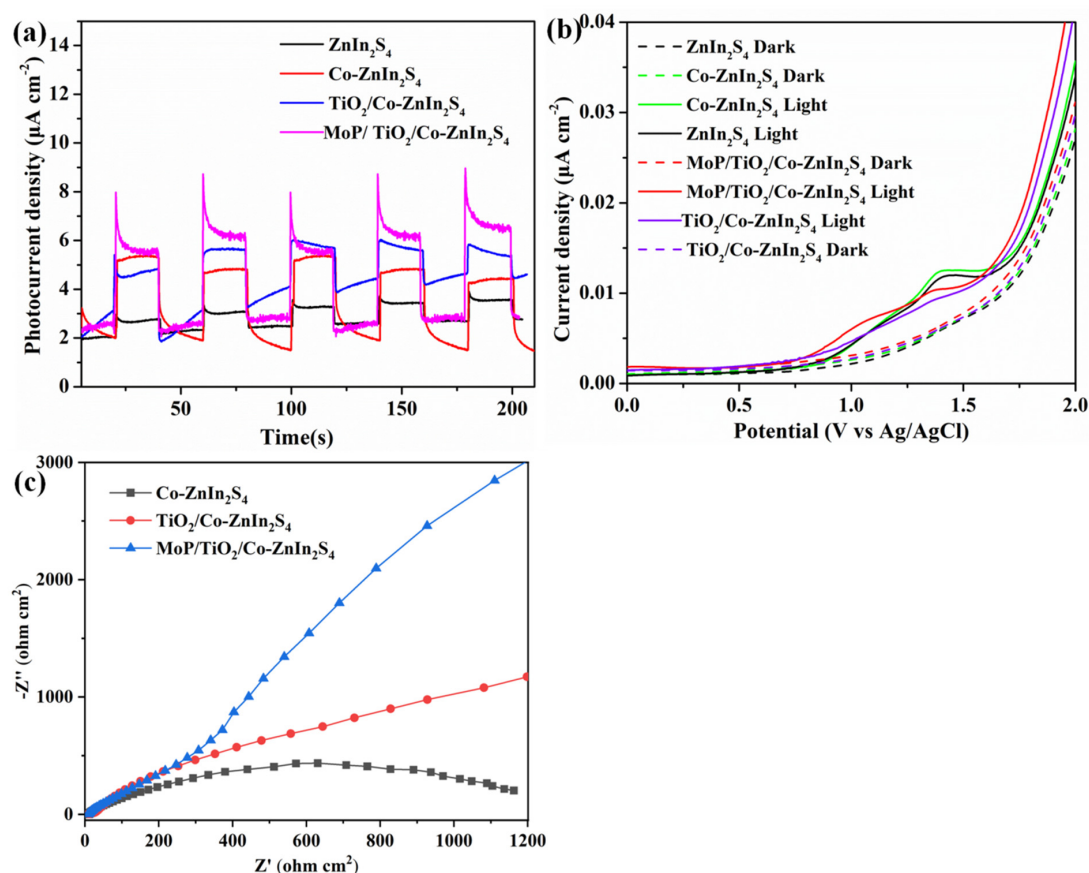


Figure 9. (a) Photocurrent response curves of $\text{Co-ZnIn}_2\text{S}_4$, $\text{a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$, and $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$; (b) linear scanning voltammograms and photocurrent response curves of ZnIn_2S_4 , $\text{Co-ZnIn}_2\text{S}_4$, $\text{a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$, and $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$; (c) EIS curves of $\text{Co-ZnIn}_2\text{S}_4$, $\text{a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$, and $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$.

2.3. Photocatalytic Hydrogen Production Performance

The hydrogen production performance of the prepared catalysts was investigated, as shown in Figure 10. With increasing illumination time, hydrogen production increased for all four catalysts. As shown in Figure 10a, to explore the influence of the supported TiO_2 on catalytic activity, the photocatalytic hydrogen production performances of a- $\text{TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ samples prepared by loading TiO_2 for different amounts of time were also investigated. The optimal hydrogen production rate of $3.88 \text{ mmol}\cdot\text{g}^{-1}$ was achieved by using 20- $\text{TiO}_2/\text{Co-ZnIn}_2\text{S}_4$, which was consistent with the UV-vis spectra shown in Figure 8a. The hydrogen production rates of ZnIn_2S_4 , $\text{Co-ZnIn}_2\text{S}_4$, a- $\text{TiO}_2/\text{Co-ZnIn}_2\text{S}_4$, $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ and P25 are shown in Figure 10b. As can be seen, Co doping, the addition of TiO_2 , and the addition of MoP all led to enhanced hydrogen evolution. It also can be seen from Figure 10b that the hydrogen production using non-noble metal co-catalyst MoP ($7.42 \text{ mmol}\cdot\text{g}^{-1}$) is approximately twice as much as using Pt co-catalyst ($3.88 \text{ mmol}\cdot\text{g}^{-1}$). In addition, it can be observed from Figure 10b,c that the hydrogen production capacity and hydrogen production rate of Pt/P25 at 2.5 h is 6.43 mmol/g and $2.55 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, respectively. As shown in Figure 10c, the highest hydrogen production rate of $2.96 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ was achieved by $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$; in contrast, the sample $\text{Pt/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ achieved $1.55 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$. Each modification step (Co doping, addition of supported TiO_2 , addition of MoP co-catalyst) further enhanced the hydrogen evolution rate compared with the unmodified ZnIn_2S_4 . These results showed that the $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ composite photocatalyst had excellent hydrogen production performance. It can be seen that the hydrogen production efficiency of the $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ without Pt is still higher in comparison to that of P25 powder.

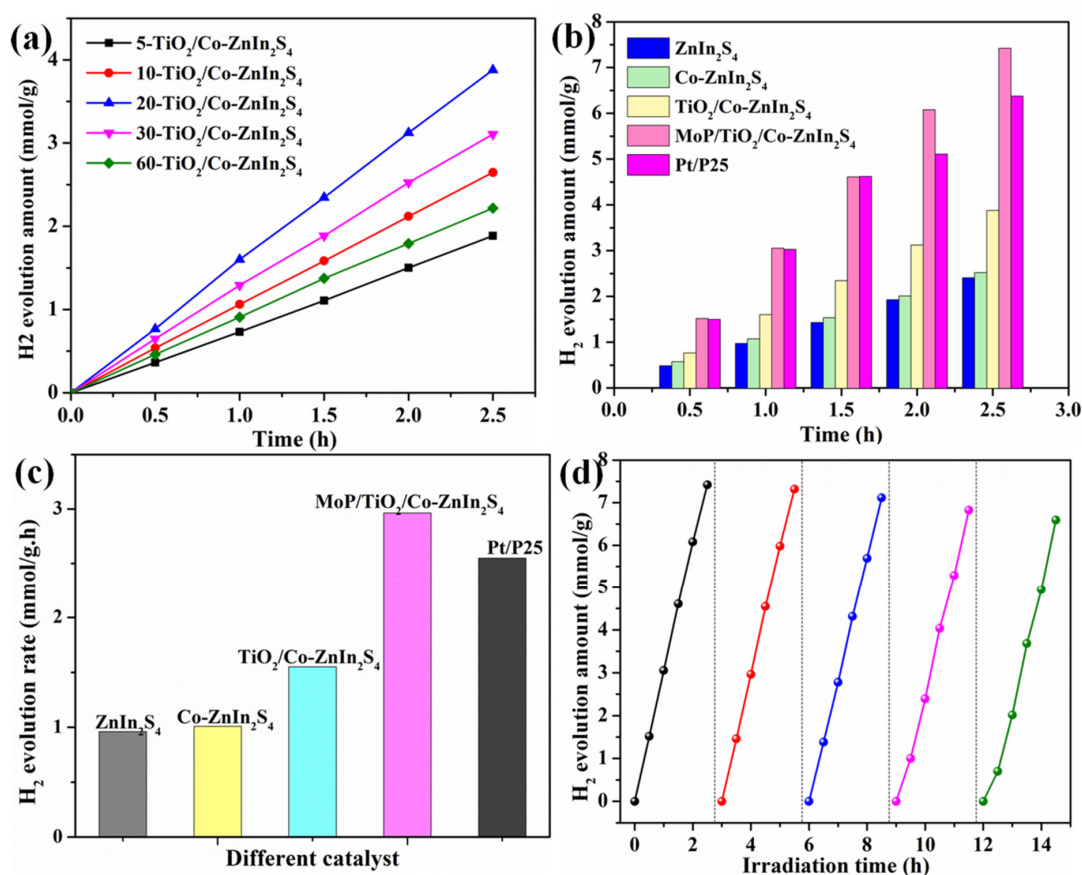


Figure 10. (a) Hydrogen production yields of a- $\text{TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ samples prepared in different amounts of time for TiO_2 loading. (b) Hydrogen production yields of the prepared catalysts with increasing reaction time. (c) Hydrogen production rates of the prepared catalysts. (d) Hydrogen production of $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ across 5 cycles.

Photocatalytic stability across multiple cycles is another important factor that influences the practical application of photocatalysts. Therefore, the MoP/a-TiO₂/Co-ZnIn₂S₄ composite catalyst was tested for cyclic hydrogen production. As shown in Figure 10d, after use in three cycles, the hydrogen production only decreased by 5%, indicating that it has good cycle stability. However, after 5 cycles, a slight decline in activity was observed (decline rate of 13.5%). This indicated a certain degree of catalytic stability. The degradation between cycles 3 and 4 (decline rate of 4.2%) was greater than that between cycles 1 and 2 (decline rate of 2.1%) due to the photocorrosion of ZnIn₂S₄.

2.4. Mechanism of Photocatalytic Hydrogen Evolution

According to the band gap structures and Fermi level of TiO₂ and ZnIn₂S₄, the possible transfer processes of photogenerated electron–hole pairs are proposed in Figure 11 [37]. The photogenerated electrons in the CB of ZnIn₂S₄ migrate to the CB of TiO₂ while the photoexcited holes in the VB of TiO₂ transfer to the VB of ZnIn₂S₄. The E_{CB} of the photogenerated electrons is lower than the E_0 redox (H^+/H_2). The presumed process is, therefore, not feasible in this photocatalytic process. Another possible reaction mechanism is shown in Figure 11. In the photocatalytic reaction, the solid–solid contact interface between ZnIn₂S₄ and TiO₂ serves as the combination center of the photogenerated electrons in the CB of TiO₂ and the photogenerated holes in the VB of ZnIn₂S₄ [38]. The photogenerated electrons involved in the reaction have a stronger reduction ability than that of pure TiO₂, thus performing a better photocatalytic activity for HER. The photogenerated holes in the VB of TiO₂ oxidize water to O₂, while the photogenerated electrons in the CB of ZnIn₂S₄ simultaneously reduce H^+ to H₂. In summary, all of the above analyses show that the electron transfer process is identified as an S-scheme mechanism in this study.

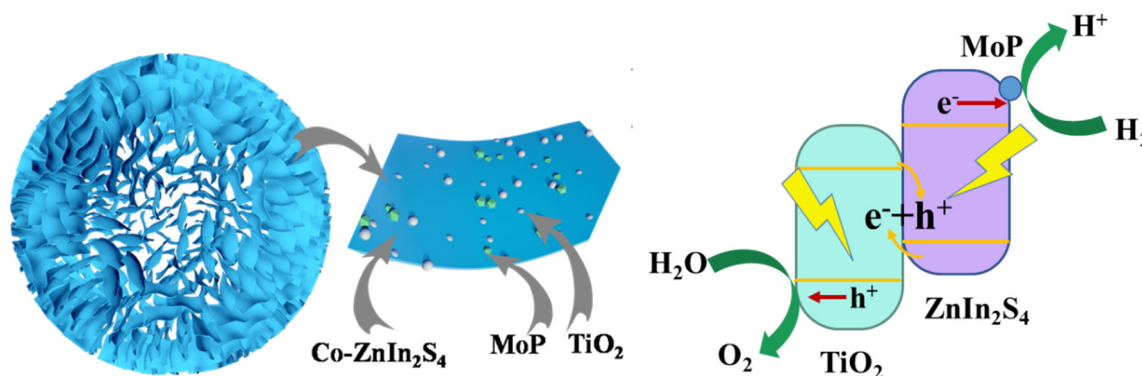


Figure 11. Composition diagram and photocatalytic reaction mechanism of MoP/a-TiO₂/Co-ZnIn₂S₄.

3. Experimental Section

3.1. Materials and Characterization

Zinc chloride (ZnCl₂, AR), indium chloride (InCl₃, AR), thioacetamide (TAA, AR), nickel chloride hexahydrate (NiCl₂·6H₂O, AR), tungsten chloride (WCl₆, AR), polyethylene glycol (HO(CH₂CH₂O)_nH, AR), melamine (C₃N₃(NH₂)₃, AR), and sodium citrate dehydrate (C₆H₅Na₃O₇·2H₂O, AR) were purchased from Shanghai Macklin Biochemical Co. (Shanghai, China). Triethanolamine (TEOA, AR) was purchased from Tianjin Beichen Founder Reagent Factory (Tianjin, China). Ethyl alcohol (CH₃CH₂OH, AR) was provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All materials were used as received.

Sample morphologies were analyzed using scanning electron microscopy (SEM, JSM-7900F, JEOL, Tokyo, Japan) coupled with energy-dispersive X-ray spectroscopy (OXFORD MAX-80, Oxford, UK). Transmission electron microscopy (TEM) was performed using a JSM-2100plus (JEOL, Tokyo, Japan). X-ray diffraction (XRD, Bruker (Billerica, MA, USA), D8 Advance) was used for crystal structure analysis. XRD patterns were obtained in the 2θ range of 20–90° with a scanning rate of 6°/min. Surface compositions were investigated by X-ray photoelectron spectroscopy (XPS) using an AMICUS ESCA3200 (Philadelphia,

PA, USA). The XPS spectra were corrected using the C1s peak at 284.8 eV. Ultraviolet-visible (UV-vis) diffuse reflectance spectra (DRS) were obtained in the 200–800 nm range by a UV-vis spectrophotometer (Shimadzu UV-2450, Kyoto, Japan). Photoluminescence (PL) spectra were collected using an Perkin-Elmer LS50B (Buckinghamshire, UK) with a 380 nm excitation wavelength at room temperature. BET surface areas and porosity were measured via nitrogen adsorption–desorption experiments using a Micromeritics ASAP 2020 (Micromeritics, Norcross, GA, USA).

3.2. Steps for Preparation of MoP/a-TiO₂/Co-ZnIn₂S₄ Flower-like Composite Photocatalysts

3.2.1. Preparation of Co-ZnIn₂S₄ Catalyst

A total of 0.136 g zinc chloride, 0.586 g indium chloride, and 0.301 g thioacetamide were weighed and added to 80 mL ethylene glycol. This mixture was stirred and centrifugally sonicated to dissolve the solid compounds. The solution was then transferred to a 100 mL hydrothermal kettle and heated in an oven at 180 °C for 2 h. After the reaction, the reaction solution was removed from the hydrothermal kettle and left to stand for 0.5 h. Next, centrifugation was used to obtain the solid product. The sample was then crushed with agate mortar to obtain ZnIn₂S₄. Doped Co-ZnIn₂S₄ was obtained by repeating this experimental procedure with the addition of 0.0069 g Co(NO₃)₂·6(H₂O).

3.2.2. Preparation of a-TiO₂/Co-ZnIn₂S₄ Catalyst

A total of 80 mg Co-ZnIn₂S₄ was added to 20 mL isopropanol. Then, 100 µL tetra-butyltitanate and 20 µL water were then added dropwise under stirring. Five samples were prepared and stirred for 5 min, 10 min, 20 min, 30 min and 60 min for the control test. These samples were centrifuged three times using isopropanol and then dried at 60 °C in an oven. The dried samples were ground and heated in a muffle furnace at 120 °C for 1 h to obtain a-TiO₂/Co-ZnIn₂S₄.

3.2.3. Preparation of MoP/a-TiO₂/Co-ZnIn₂S₄ Catalyst

A mixture of 1 g Na₂MoO₄·2H₂O and 10 g NaH₂PO₂ was ground in a mortar for 0.5 h until no crystal particles remained, and then transferred to a tubular furnace, under Ar protection at 400 °C (heating rate 10 °C/min), and calcined for 1 h to obtain MoP. A 2 mg/mL MoP solution was then prepared. Next, 0.5 g a-TiO₂/Co-ZnIn₂S₄ and 1.25 mL MoP solution were magnetically stirred for 0.5 h. MoP/a-TiO₂/Co-ZnIn₂S₄ was obtained by drying the resulting product in an oven at 60 °C followed by crushing with a mortar.

3.3. Photocatalysis and Photoelectrochemical Performance Measurements

3.3.1. Hydrogen Production Performance

Photocatalytic experiments were performed using an online photocatalytic hydrogen evolution system (Meiruichen, Beijing, China MC-SCO₂II-AG) at 5 °C using a 300 W Xe lamp equipped with a AM1.5G cutoff filter positioned 20 cm away from the reactor. A total of 10 mg of catalyst was dispersed in 100 mL of 0.1 M Na₂S and 0.1 M Na₂SO₃ solution and the mixture was stirred in vacuum for 30 min. We first ran tests in the dark for one hour to confirm no H₂ production. Hydrogen evolution, detected by an online gas chromatography (using FL9790, Fuli, Zhjiang, TCD with nitrogen as a carrier gas and 5 Å molecular sieve column) was observed only under light irradiation. At the end of the photocatalytic reaction, which lasted for 2.5 h, the reactor was refilled with 10 mL of Na₂S and Na₂SO₃ solutions and degassed. Then, 10 mg of P25 was dispersed in 100 mL of CH₃OH/H₂O solution, and 0.1 mL (1 mg/mL) of chloroplatinic acid was added.

3.3.2. Photoelectrochemical Performance

A CHI760E electrochemical workstation and a standard three-electrode system (platinum sheet, saturated silver chloride electrode, and the loaded FTO substrate) were used to analyze the catalysts. An aqueous 0.5 mol/L Na₂SO₄ solution was used as the electrolyte for transient photocurrent testing and electrochemical impedance spectroscopy (EIS) testing.

A xenon lamp light source system with an AM1.5G filter was used to simulate daylight for photocurrent testing.

Photocatalytic hydrogen production experiments were performed using a vacuum photocatalytic carbon dioxide reduction system with a xenon light source to simulate daylight. A working electrode for photochemical measurements was prepared using 7.5 mg of sample (ZnIn_2S_4 , $\text{Co-ZnIn}_2\text{S}_4$, $\text{a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ and $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$), which was sonicated for 30 min in a mixture containing 375 μL of ultrapure water, 125 of ethanol and 30 μL of naphthol. Then, 30 μL of the resulting suspension was used to drop-coat FTO glass, which was then heated for 30 min at 300 $^\circ\text{C}$ under Ar. A 1 cm $\times$ 1 cm glass substrate was then ultrasonicated first in acetone, then in ethanol and finally in water (15 min each step), after which it was dried by a flow of Ar. PEC measurements were conducted using a single compartment quartz cell with three electrodes. Data were recorded by the workstation equipment containing photoanode, saturated Ag/AgCl and 1 cm $\times$ 1 cm Pt piece as working, reference and counter electrodes, respectively. We used 0.2 M Na_2SO_4 with pH = 6.5 as electrolyte. PEC tests were conducted using a 150 W Xenon lamp equipped with a standard AM 1.5G filter. Quartz cell was positioned 10 cm away from the light source. The recorded potential was converted to reference hydrogen electrode (RHE) potentials using the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + \text{pH} * 0.059 + 0.195 \text{ V}$$

Linear sweep voltammetry (LSV) was conducted at 10 mV/s scan rate in the -0.4 – 1.2 V scan range relative to the Ag/AgCl electrode. EIS was performed under Xe lamp at 0 V with AC potential ranging from 100 K to 0.1 Hz.

4. Summary

In summary, a $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ composite photocatalyst was successfully prepared by a facile hydrothermal method. The Co dopant in the flower-like ZnIn_2S_4 broadened the absorption band edge of the composite catalyst. Amorphous TiO_2 and $\text{Co-ZnIn}_2\text{S}_4$ were combined to form a heterojunction, which improved the photocarrier separation efficiency and the stability of the catalyst. More importantly, the introduction of amorphous TiO_2 created oxygen vacancies, which further improved the carrier density. Finally, the non-noble metal catalyst MoP nanoparticles were introduced into the system as co-catalysts, which became the hydrogen production sites and realized high-efficiency hydrogen production. The flower-like $\text{MoP/a-TiO}_2/\text{Co-ZnIn}_2\text{S}_4$ composite photocatalyst exhibited a hydrogen production rate of $2.96 \text{ mmol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$, which was $0.98 \text{ mmol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$ of that of the pure ZnIn_2S_4 . Therefore, this catalyst shows great promise for the green production of hydrogen. Moreover, this study also provides new insight into the design and underlying mechanism of direct Z-schemes for enhanced photocatalysis.

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Conflicts of Interest: We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company.

Sample Availability: Samples of the compounds are available from the authors.

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