

Article

The Preparation of g-C₃N₄/ZnIn₂S₄ Nano-Heterojunctions and Their Enhanced Efficient Photocatalytic Hydrogen Production

Hubing Li ^{1,2,3,4}, Yaoting Wang ^{1,2,3,4}, Song Wang ^{1,2,3,4,*} and Xin Xiao ^{2,3,4,*}

- ¹ Jiangsu Key Laboratory of Marine Bioresources and Environment, Jiangsu Ocean University, 59 Cangwu Road, Haizhou, Lianyungang 222005, China
- ² Co-Innovation Center of Jiangsu Marine Bio-Industry Technology, Jiangsu Ocean University, 59 Cangwu Road, Haizhou, Lianyungang 222005, China
- ³ Jiangsu Institute of Marine Resources Development, 59 Cangwu Road, Haizhou, Lianyungang 222005, China
- ⁴ Jiangsu Key Laboratory of Function Control Technology for Advanced Materials, Jiangsu Ocean University, 59 Cangwu Road, Haizhou, Lianyungang 222005, China
- * Correspondence: wangsong75@163.com (S.W.); xiaoxin@njjust.edu.cn (X.X.)

Abstract: Hydrogen production technology has triggered a research boom in order to alleviate the problems of environmental pollution and the pressure on non-renewable energy sources. The key factor of this technology is the use of an efficient photocatalyst. g-C₃N₄ is a typical semiconductor photocatalytic material that is non-toxic and environmentally friendly and does not cause any serious harm to human beings. Therefore, it can be applied to drug degradation and the photocatalytic production of H₂. Combined with ZnIn₂S₄, this semiconductor photocatalytic material, with a typical lamellar structure, has become one of the most promising catalysts for research due to its suitable bandgap structure and excellent photoelectric properties. In this study, 10% g-C₃N₄/ZnIn₂S₄ nano-heterojunction composite photocatalytic materials were successfully prepared by compounding ZnIn₂S₄ and g-C₃N₄ semiconductor materials with good visible-light-trapping ability. Under visible light irradiation, the photocatalytic activity of the composites was significantly better than that of pure g-C₃N₄ and ZnIn₂S₄. This is attributed to the formation of a heterojunction structure, which effectively inhibited the recombination of photogenerated carriers through the interfacial contact between the two semiconducting materials, and then improved the separation efficiency of the photogenerated electron–hole pairs, thus enhancing the catalytic activity. In this study, pure g-C₃N₄ and ZnIn₂S₄ were prepared using calcination and hydrothermal methods, and then, the composites were synthesized using ultrasonic and hydrothermal means. The differences in the structure, morphology, and hydrogen production performance of the materials before and after recombination were analyzed in detail using XRD, SEM, and FTIR characterization, which further verified that the 10% g-C₃N₄/ZnIn₂S₄ nano-heterojunction composites possessed excellent photocatalytic activity and stability, providing new possibilities for the optimization and application of photocatalytic hydrogen production technology.

Keywords: g-C₃N₄/ZnIn₂S₄; semiconductor; photocatalytic hydrogen production



Citation: Li, H.; Wang, Y.; Wang, S.; Xiao, X. The Preparation of g-C₃N₄/ZnIn₂S₄ Nano-Heterojunctions and Their Enhanced Efficient Photocatalytic Hydrogen Production. *Molecules* **2024**, *29*, 2571. <https://doi.org/10.3390/molecules29112571>

Academic Editors: Yucheng Lan and Jin Jia

Received: 4 February 2024

Revised: 28 April 2024

Accepted: 30 April 2024

Published: 30 May 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In recent years, due to the sharp increase in the world's energy consumption, the deterioration of the ecological environment is showing an increasingly serious trend, especially regarding non-renewable resources, such as oil, natural gas, and coal, which are difficult to restore after their consumption and which cause a series of environmental problems [1,2]. The most troubling aspects for humans are global climate change caused by the emissions of greenhouse gases and acid rain caused by the emissions of sulfur-containing and nitrogen-containing compounds, which have extremely negative impacts. Therefore, the development of new energy sources is urgent. Hydrogen, a clean secondary energy source, has attracted a lot of attention. In recent years, more and more attention

has been paid to the development, research, and utilization of solar energy, and many researchers and scholars have begun to decompose water by using sunlight to obtain hydrogen [3,4]. The biggest advantage of this method is maximizing the use of energy. Research has found that water can be split in the presence of a semiconductor catalyst using sunlight irradiation. The semiconductor is excited by an external force to produce photogenerated electrons and holes, which react with the water to produce hydrogen. Photocatalytic technology is crucial for solving the energy crisis, and the development of highly efficient and stable photocatalysts is key to this technology [5,6].

g-C₃N₄ is a typical semiconducting polymer with a two-dimensional lamellar structure similar to graphene's planar structure. g-C₃N₄ is considered one of the most promising semiconducting materials using visible light. It has a high value for the degradation of pollutants and the preparation of H₂ and O₂ through photocatalysis [7,8]. The photocatalytic properties of C₃N₄ materials can be improved by increasing their surface area and modulating their electronic structure. Porous 3D or exfoliated 2D C₃N₄-based materials have been successfully used in the preparation of efficient photocatalysts with a high surface area and an improved visible light absorption ability [9]. g-C₃N₄ has attracted attention in many fields because it can be prepared in a very simple way, and it has no toxic substances of its own that can cause serious damage to the human body. Additionally, it is a friendly material that does not cause serious pollution to the environment, and it can be used as an economical precursor at a low price and in the development of a wide range of applications [10–12]. As a new type of non-metallic photocatalytic material, it has been shown that g-C₃N₄ has a relatively wider absorption spectral range than traditional TiO₂ photocatalysts, and, therefore, its photocatalytic reaction is more stable than that of traditional TiO₂ [13]. Compared to traditional TiO₂ photocatalysts, its photocatalytic reaction can take place only under normal visible light. g-C₃N₄ also has a more effective ability to activate molecular oxygen compared to TiO₂, and it is able to generate photocatalytic conversion reactions for organic functional groups and superoxide radicals to meet the requirements for the photocatalytic degradation of organic pollutants [14–16]. However, pure g-C₃N₄ has a small forbidden bandwidth (2.01 eV), is very easily excited by visible light, and suffers from the disadvantage of a fast photogenerated electron–hole complexation rate, in addition to its relatively slow electron transfer rate.

ZnIn₂S₄ is a photocatalyst material belonging to an AB₂X₄ (A = Zn, Ca, Cd, and Cu; B = Al, In, and Ga; X = Se, S, and Te) semiconductor family system. With a typical layered structure, ZnIn₂S₄ is generally considered to be one of the most promising catalysts based on its excellent optical and electrical properties, suitable bandgap (2.34–2.48 eV), high visible light utilization, etc. ZnIn₂S₄ has both cubic and hexagonal crystal system structures [17–20]. Many experts and scholars have reported that ZnIn₂S₄ semiconductor photocatalytic materials with these two crystal systems are widely used for the photocatalytic preparation of H₂ and the degradation of environmental pollutants under the irradiation of visible light due to their very high catalytic activity and good chemical stability. ZnIn₂S₄ also has a suitable bandgap structure, which makes it possible to build a binary system catalyst or a multisystem catalyst with other semiconductors [1,21,22]. This can largely improve the separation efficiency of the photogenerated carriers and thus increase their migration rate, which can also improve the photocatalytic performance. In order to improve the catalytic activity of optical semiconductor photocatalysts, two catalysts with different conduction and valence bands are usually compounded into a new type of heterostructure catalyst so that the photogenerated electron–hole complex can be better suppressed and the catalytic activity can be efficiently enhanced. With its good absorbance, the composite of ZnIn₂S₄ and g-C₃N₄ can effectively promote the utilization of photogenerated carriers in the system, and the performance of the composite photocatalytic material can be improved.

At present, we are facing a variety of environmental and energy problems. An effective way to solve the problem of energy consumption is the semiconductor photocatalytic decomposition of water to produce hydrogen. Therefore, it is crucial to find a good catalyst, as the key factor of photocatalytic hydrogen production technology is a highly efficient

photocatalyst. It has been found through research that composite semiconductor materials can improve photocatalytic activity to a large extent, making this an effective method.

In the present work, pure $g\text{-C}_3\text{N}_4$ nanoflakes were prepared through calcination, and then, pure ZnIn_2S_4 was prepared using the hydrothermal method to study their respective photocatalytic properties. Then, 10% $g\text{-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$ nano-heterojunction composites were prepared by loading $g\text{-C}_3\text{N}_4$ nanoflakes onto ZnIn_2S_4 using the hydrothermal method. A series of characterization tests were carried out to analyze the morphologies and differences in the hydrogen production properties of the materials before and after composition in order to obtain better photocatalytic materials.

2. Results and Discussion

2.1. X-ray Diffraction (XRD) Analysis

Figure 1 shows the XRD patterns of the different samples, from which we can see that there are diffraction peaks at $2\theta = 21.5^\circ$ and $2\theta = 27.6^\circ$ for the photocatalytic materials that we prepared. The characteristic peaks at $2\theta = 27.6^\circ$ correspond to the crystalline surface (002) of $g\text{-C}_3\text{N}_4$, and the characteristic diffraction peaks at $2\theta = 27.39^\circ$, 47.60° , and 56.69° for the prepared ZnIn_2S_4 samples can be found in the XRD pattern of the material prepared [23,24]. The XRD patterns of the prepared ZnIn_2S_4 samples show characteristic diffraction peaks at $2\theta = 27.39^\circ$, 47.60° , and 56.69° , and the cell structure of ZnIn_2S_4 is hexagonal according to the cell parameters. The images show that the addition of $g\text{-C}_3\text{N}_4$ did not affect the structure of ZnIn_2S_4 . The XRD patterns of the 10% $g\text{-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$ samples are similar to those of ZnIn_2S_4 , which indicates that we successfully prepared 10% $g\text{-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$ nano-heterojunction composite photocatalytic materials and that the $g\text{-C}_3\text{N}_4$ was homogeneously loaded onto the ZnIn_2S_4 photocatalytic material [25,26].

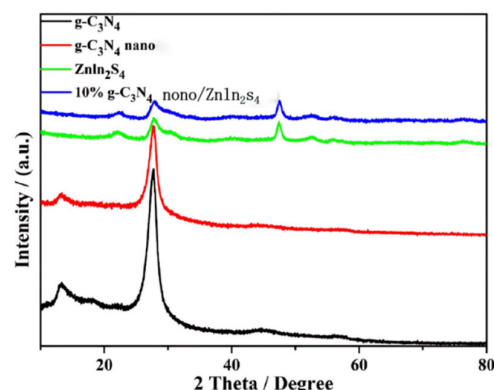


Figure 1. XRD patterns of $g\text{-C}_3\text{N}_4$, nano $g\text{-C}_3\text{N}_4$, ZnIn_2S_4 , and 10% nano $g\text{-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$.

2.2. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) Analyses

Figures 2 and 3 show the SEM and TEM images of the $g\text{-C}_3\text{N}_4$ and nano $g\text{-C}_3\text{N}_4$ samples, respectively, and Figure 4 shows the SEM and TEM images of the ZnIn_2S_4 and 10% $g\text{-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$ nano-heterojunctions. In Figures 2 and 3, it can be seen that the $g\text{-C}_3\text{N}_4$ that we prepared had an irregular layered structure, while nano $g\text{-C}_3\text{N}_4$ was a lamellar thin nanosheet. Figure 4 shows that the ZnIn_2S_4 sample material had a microspherical pleated structure, while the micrograph of the 10% $g\text{-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$ nanohybrid junction material obtained after their composite shows that the lamellar $g\text{-C}_3\text{N}_4$ grew tightly on the microspherical pleated layers of the ZnIn_2S_4 . This kind of structure, with obvious lattice stripes, can shorten the diffusion distance of the light-generated carriers, which greatly improves its ability to capture photons, thus improving the photocatalytic performance to a certain extent.

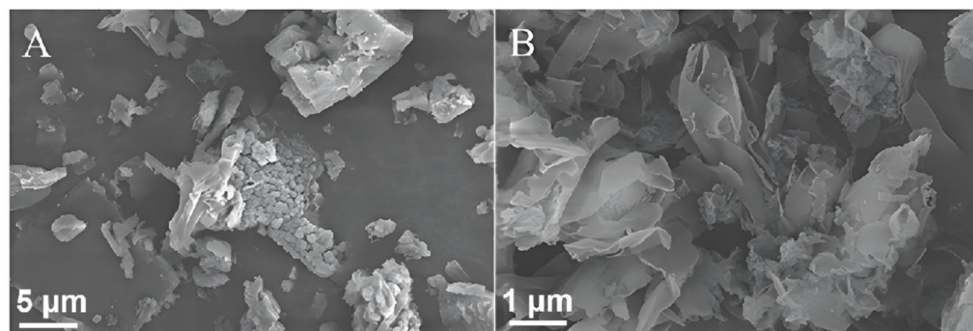


Figure 2. (A) SEM image of $g\text{-C}_3\text{N}_4$ and (B) SEM image of nano $g\text{-C}_3\text{N}_4$.

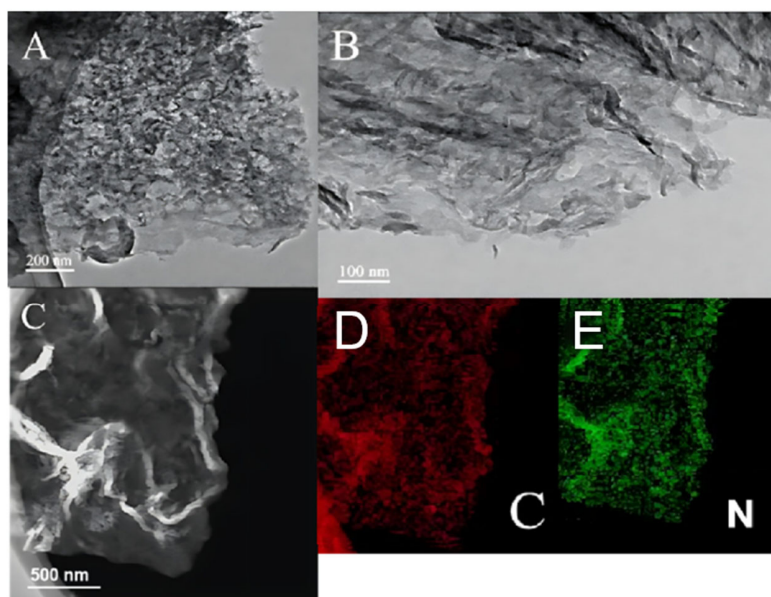


Figure 3. (A) TEM image of $g\text{-C}_3\text{N}_4$, (B) TEM image of nano $g\text{-C}_3\text{N}_4$, (C) dark-field image, and (D,E) mapping of nano $g\text{-C}_3\text{N}_4$.

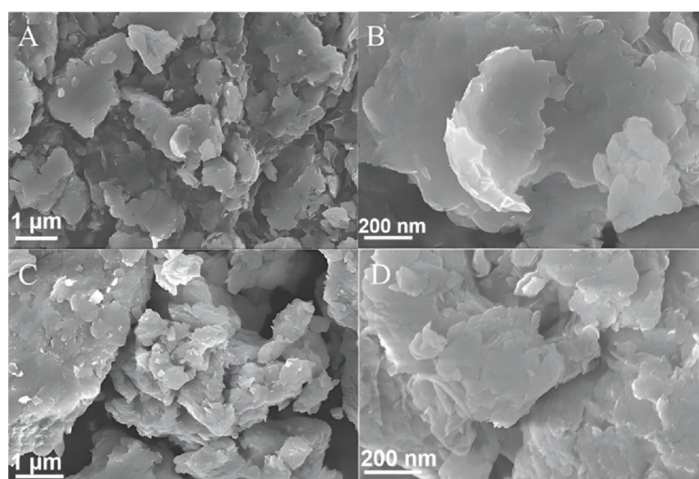


Figure 4. (A,B) SEM images of ZnIn_2S_4 and (C,D) SEM images of 10% nano $g\text{-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$.

2.3. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Figure 5 shows the infrared spectra of the catalysts prepared in this experiment, in which it can be seen that there was a clear absorption band at $2900\text{--}3500\text{ cm}^{-1}$ for $g\text{-C}_3\text{N}_4$, which was caused by the hydroxyl group of H_2O and N-H in the layered structure of

g-C₃N₄. There was also a characteristic peak at 810 cm^{−1}, which was due to the stretching and vibration of the molecules of the triazinane cyclic analogs. The absorption band at 1130–1240 cm was caused by hydroxyl group absorption in the structure of the sample, and the characteristic peak at 1250–1650 cm was due to the skeleton vibration of the aromatic heterocyclic compounds. The characteristic peaks at 1300–1600 cm^{−1} were due to the adsorption of water molecules by the hydroxyl groups on the surface of the samples. The absorption peaks at g-C₃N₄ were all in the nano-heterojunctions of the g-C₃N₄/ZnIn₂S₄. According to the spectra, the composite 10% nano g-C₃N₄/ZnIn₂S₄ nano-heterojunction contained the telescopic vibration modes of both the ZnIn₂S₄ and g-C₃N₄ samples, which indicates that the nano-heterojunction prepared in this experiment contained the presence of the components of ZnIn₂S₄ and g-C₃N₄. This further verifies that the composite photocatalytic material of the 10% nano g-C₃N₄/ZnIn₂S₄ nano-heterojunction was successfully prepared.

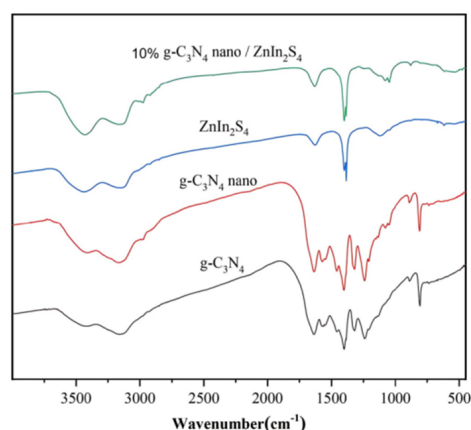


Figure 5. FTIR spectra of g-C₃N₄, nano g-C₃N₄, ZnIn₂S₄, and 10% nano g-C₃N₄/ZnIn₂S₄.

2.4. Photoluminescence (PL) Analysis

Photoluminescence (PL) and time-resolved fluorescence decay properties are important tools used to explore the rate of charge generation, separation, and complexation, as the intensity of fluorescence is closely related to the complexation of electrons and holes. Figure 6a compares the fluorescence intensities of g-C₃N₄, nano g-C₃N₄, ZnIn₂S₄, and 10% nano g-C₃N₄/ZnIn₂S₄. It can be clearly seen that ZnIn₂S₄ has almost no obvious absorption peak at the excitation wavelength of 375 nm due to its optical nature. The emission peaks of the 10% nano g-C₃N₄/ZnIn₂S₄ composites are relatively weak, which is most likely due to the effective charge transfer between 10% nano g-C₃N₄ and ZnIn₂S₄.

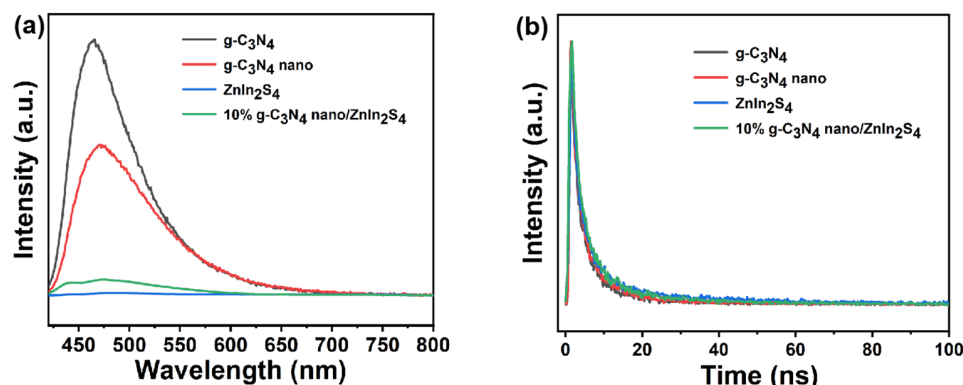


Figure 6. (a) Steady-state photoluminescence spectra of different samples. (b) Time-resolved photoluminescence decay spectra of g-C₃N₄, nano g-C₃N₄, ZnIn₂S₄, and 10% nano g-C₃N₄/ZnIn₂S₄.

The time-resolved fluorescence decay spectra also provide a strong basis for evaluating the separation efficiency of photogenerated charge carriers. Figure 6b shows the time-resolved fluorescence decay curves of the samples evaluated using the double-exponential fitting equation as follows: $I(t) = A_1 \times \exp(\frac{-t}{\tau_1}) + A_2 \times \exp(\frac{-t}{\tau_2})$. The average lifetime is $\tau_{ave} = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$. In the figure, it can be seen that the fluorescence lifetime of the pure g-C₃N₄ was relatively short, only 7.2 ns. In contrast, the fluorescence average lifetime of 10% nano g-C₃N₄/ZnIn₂S₄ reached 8.9 nanoseconds, which is nearly 16% longer than the 7.5 nanoseconds of ZnIn₂S₄. The increase in the average lifetimes of the composite photocatalysts ZnIn₂S₄ and 10% nano g-C₃N₄/ZnIn₂S₄ compared to g-C₃N₄ suggests that the 2D/2D VDW heterojunction effectively created more high-speed charge transfer paths, which promoted the efficient transfer of photogenerated charges and consequently enhanced the photocatalytic hydrogen production activity.

2.5. X-ray Photoelectron Spectroscopy (XPS) Analysis

XPS further confirmed the composition of the 10% nano g-C₃N₄/ZnIn₂S₄ sample. Figure 7a shows that the C 1s spectrum of nano g-C₃N₄ has two characteristic peaks located at 288.42 and 284.76 eV. These peaks correspond to the sp²-hybridized carbon-containing defects (N-C=N) and graphitic carbon in the carbon-containing aromatic ring of the sp² bonds (C-C, C=C). Typically, the C 1s peak at 284.76 eV originates from carbon-based impurities, which are generated during high-temperature treatment [27–29]. This impurity peak increases in intensity as the amount of cyanuric acid increases [30]. Figure 7b shows that the Zn 2p XPS spectrum of ZnIn₂S₄ has two significant peaks located at 1022.56 and 1044.83 eV, which correspond to Zn 2p_{3/2} and Zn 2p_{1/2}, respectively, while the 10% Zn 2p_{1/2} peaks are located at 1022.56 and 1044.83 eV, respectively. Meanwhile, the Zn 2p characteristic peaks corresponding to nano 10% g-C₃N₄/ZnIn₂S₄ show a slight shift to 1022.12 and 1045.21 eV, respectively. Similarly, Figure 7c shows that the In 3d spectra of ZnIn₂S₄ has two characteristic peaks located at 445.25 and 452.82 eV, which correspond to In 3d_{5/2} and In 3d_{3/2}. Similar to the above, the positions of the In 3d peaks corresponding to 10% nano g-C₃N₄/ZnIn₂S₄ show a small decrease, shifting to 445.12 and 452.4 eV, respectively. In addition, the N 1s spectrum of nano g-C₃N₄ shown in Figure 7d reveals three characteristic peaks at 401.01, 400.03, and 398.73 eV, which correspond to the amino group (C-N-H), the tertiary nitrogen N-(C)₃ group, and the sp²-bonded N (C-N=C), respectively [31,32]. Notably, both the N 1s and C 1s characteristic signals of nano g-C₃N₄ were slightly shifted to higher binding energies after forming a heterojunction with the ZnIn₂S₄ nanosheets, which could be attributed to the transfer of some of the electrons from the N and C to the S of ZnIn₂S₄. In addition, the observed peak at 397.21 eV in the N 1s spectrum of 10% nano g-C₃N₄/ZnIn₂S₄ may be related to the N-S bonding, which further proves the existence of a strong interfacial interaction between nano g-C₃N₄ and ZnIn₂S₄ [33]. Figure 7e shows that the binding energies of S 2p_{3/2} and S 2p_{1/2} are located at 161.92 and 163.11 eV, respectively, which are related to S^{2−} in ZnIn₂S₄ [34]. Similarly, the binding energies at 161.72 and 162.82 eV of 10% nano g-C₃N₄/ZnIn₂S₄ are lower than those of ZnIn₂S₄. Both the binding energy and the peak intensities of S 2p in 10% nano g-C₃N₄/ZnIn₂S₄ become smaller, and, theoretically, the increase in the binding energy is attributed to the decrease in the electron density, resulting in a weakening of the electron shielding effect. On the contrary, the electron density increase leads to a decrease in the binding energy, which is due to the enhancement of the electron shielding effect [35].

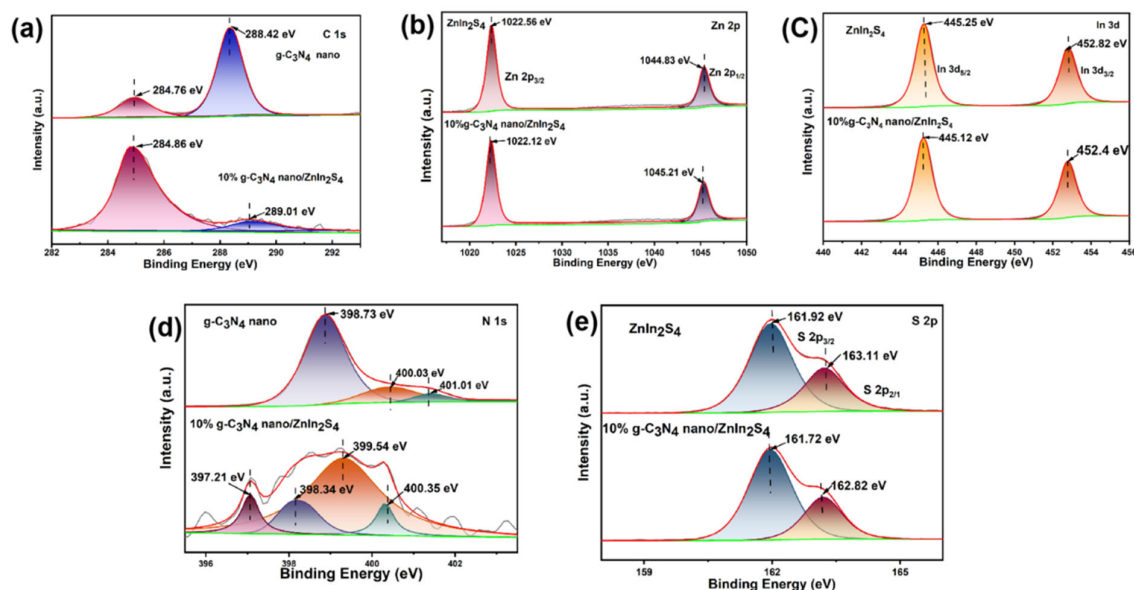


Figure 7. (a) High-resolution XPS spectra of C 1s of g-C₃N₄ and 10% nano g-C₃N₄/ZnIn₂S₄, (b) high-resolution XPS spectra of Zn 2p of ZnIn₂S₄ and 10% nano g-C₃N₄/ZnIn₂S₄, (c) high-resolution XPS spectra of In 3d of ZnIn₂S₄ and 10% nano g-C₃N₄/ZnIn₂S₄, (d) high-resolution XPS spectra of N 1s of g-C₃N₄ and 10% nano g-C₃N₄/ZnIn₂S₄, (e) high-resolution XPS spectra of S 2p of ZnIn₂S₄ and 10% nano g-C₃N₄/ZnIn₂S₄.

2.6. UV–Visible Diffuse Reflectance Spectroscopy

Figure 8a shows the UV–Vis diffuse reflectance spectroscopy of the different samples. The pristine ZnIn₂S₄ had a broad visible absorption range, with an absorption boundary at about 480 nm, whereas the pure g-C₃N₄ exhibited an absorption range from UV to visible, with a steep absorption boundary at about 400 nm. Significant red-shifting of the absorption boundaries of the ZnIn₂S₄ and 10% nano g-C₃N₄/ZnIn₂S₄ composites occurred compared to pure g-C₃N₄, implying that these complexes trapped visible light more efficiently. Figure 8b shows the band gaps of the different samples. We calculated the band gap values of the materials by applying the Kubelka–Munk method (the specific formula is $(\alpha h\nu)^2 = K(h\nu - E_g)$, where $h\nu$ represents the photon energy, K is a constant, α is the absorption coefficient, and E_g represents the bandgap energy). By observing the Tauc curves, we obtained the bandgap energies of g-C₃N₄, nano g-C₃N₄, ZnIn₂S₄, and 10% nano g-C₃N₄/ZnIn₂S₄, which were about 2.84, 2.76, 2.4, and 2.31 eV, respectively.

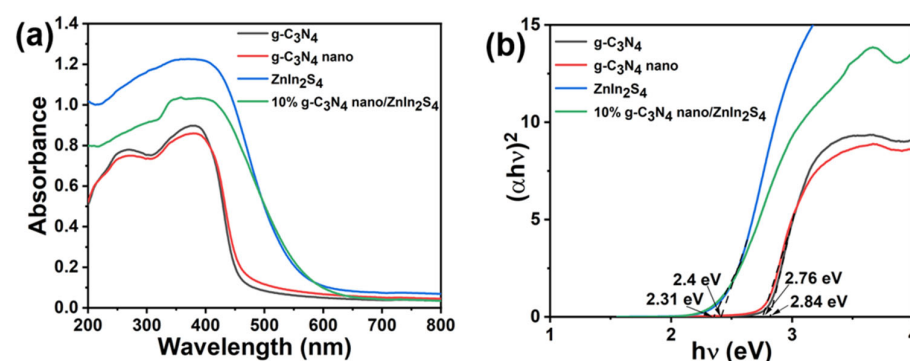


Figure 8. (a) UV–Vis diffuse reflectance spectra of g-C₃N₄, nano g-C₃N₄, ZnIn₂S₄, and 10% nano g-C₃N₄/ZnIn₂S₄; (b) band gaps of g-C₃N₄, nano g-C₃N₄, ZnIn₂S₄, and 10% nano g-C₃N₄/ZnIn₂S₄.

2.7. N₂ Adsorption–Desorption Isotherm

Using N₂ adsorption–desorption isotherms, the specific surface areas and pore size distributions of the g-C₃N₄, nano g-C₃N₄, ZnIn₂S₄, and 10% nano g-C₃N₄/ZnIn₂S₄ com-

posites were studied. Table 1 shows that the average pore sizes of these materials were 20.05 nm, 19.1 nm, 10.56 nm, and 9.79 nm, respectively, indicating that the ZnIn_2S_4 and the composite had smaller pore sizes, and the average pore size was reduced due to the increase in mesopores. In terms of the specific surface area, 10% nano $\text{g-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$ exhibited the largest specific surface area of $90.57 \text{ m}^2/\text{g}$, which is beneficial for increasing the contact area with pollutants and promoting photocatalytic reactions. Additionally, the pore volumes of these materials were $0.07 \text{ m}^3/\text{g}$, $0.09 \text{ m}^3/\text{g}$, $0.18 \text{ m}^3/\text{g}$, and $0.24 \text{ m}^3/\text{g}$, respectively. An increase in the pore volume helps to enhance the adsorption capacity of the catalyst, thereby accelerating the catalytic degradation of pollutants. Figure 9 presents the adsorption–desorption isotherms of $\text{g-C}_3\text{N}_4$, nano $\text{g-C}_3\text{N}_4$, ZnIn_2S_4 , and 10% nano $\text{g-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$. All samples exhibited characteristic IV adsorption isotherms with H3 hysteresis loops, indicating the presence of mesoporous structures.

Table 1. Pore structure parameters of $\text{g-C}_3\text{N}_4$, nano $\text{g-C}_3\text{N}_4$, ZnIn_2S_4 , and 10% nano $\text{g-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$ samples.

Sample	$S_{\text{BET}} (\text{m}^2 \cdot \text{g}^{-1})$	$V_{\text{Total}} (\text{m}^3 \cdot \text{g}^{-1})$	$D_{\text{Average}} (\text{nm})$
$\text{g-C}_3\text{N}_4$	6.9	0.07	20.05
$\text{g-C}_3\text{N}_4$ nano	9.36	0.09	19.1
ZnIn_2S_4	65.85	0.18	10.56
10% $\text{g-C}_3\text{N}_4$ nano/ ZnIn_2S_4	90.57	0.24	9.79

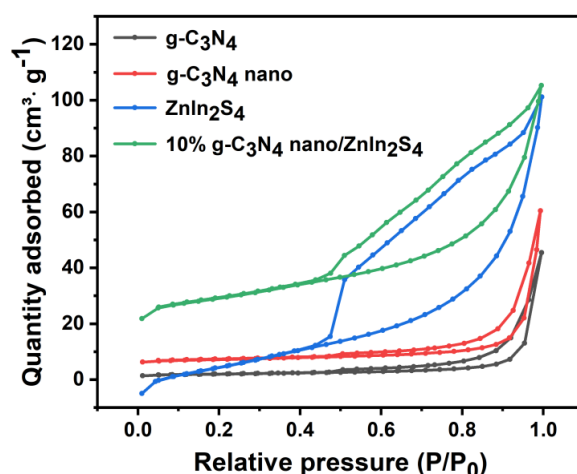


Figure 9. N_2 adsorption–desorption isotherms of $\text{g-C}_3\text{N}_4$, nano $\text{g-C}_3\text{N}_4$, ZnIn_2S_4 , and 10% nano $\text{g-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$ samples.

2.8. Photocatalytic Activity Studies

Figure 10 shows the photocatalytic hydrogen production of the different samples under visible light illumination for 5 h, as well as the rate of hydrogen production. It can be seen that the hydrogen production of both the $\text{g-C}_3\text{N}_4$ and the $\text{g-C}_3\text{N}_4$ nanosheets was low and negligible compared to that of the ZnIn_2S_4 and 10% nano $\text{g-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$. This was due to the high recombination rate of the photogenerated carrier in the graphene-like layered structure of $\text{g-C}_3\text{N}_4$. The 10% nano $\text{g-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$ sample material, obtained by loading 10% $\text{g-C}_3\text{N}_4$ nanoflakes onto the ZnIn_2S_4 semiconductor material, possessed a relatively high hydrogen yield. In Figure 6B, it can be seen that the hydrogen yield of $\text{g-C}_3\text{N}_4$ was $32.7372 \mu\text{mol g}^{-1} \text{ h}^{-1}$, whereas that of the 10% $\text{g-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$ nanohybrid junction photocatalytic material was as high as $4772.6404 \mu\text{mol g}^{-1} \text{ h}^{-1}$, which is equivalent to 100 times that of the $\text{g-C}_3\text{N}_4$ photocatalytic material. This also means that the 10% $\text{g-C}_3\text{N}_4/\text{ZnIn}_2\text{S}_4$ nano-heterojunction prepared in this experiment possessed high photocatalytic activity. This is due to the fact that the hetero-junction structure formed by the composite of $\text{g-C}_3\text{N}_4$ and ZnIn_2S_4 semiconductors effectively inhibits the recombination

of photogenerated carriers, thus improving the photocatalytic performance of the material to a large extent.

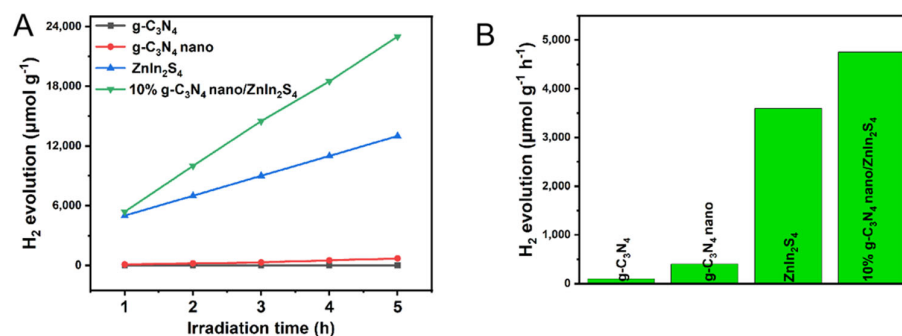


Figure 10. (A) Photocatalytic hydrogen production of different samples under visible light for 5 h. (B) Hydrogen production rates of different samples.

2.9. Stability Analysis of 10% g-C₃N₄/ZnIn₂S₄ Nano-Heterojunction

Based on the above experiments and analyses, it is clear that the 10% g-C₃N₄/ZnIn₂S₄ nanohybrid junction composites prepared in this experiment can effectively improve the photocatalytic activity. However, in real life and production, developing materials with high catalytic activity is only one of the goals of our research; their practicality is an indicator that we cannot ignore. Therefore, while pursuing high catalytic activity, we should also ensure that the prepared photocatalytic materials have a long life and stability. In this experiment, we also investigated the stability of the 10% g-C₃N₄/ZnIn₂S₄ nano-heterojunction composite photocatalytic materials for hydrogen production, as shown in Figure 11A,B. After three cycles of experimental testing, with 5 h of irradiation each time, the test results show that the catalytic activity of the sample catalysts did not decrease significantly during the test, which indicates that the 10% g-C₃N₄/ZnIn₂S₄ nano-heterojunction composite photocatalytic materials prepared in this experiment have a long life and stability. The ZnIn₂S₄ nano-heterojunction catalytic material did not decompose under visible light irradiation and still maintained its high catalytic activity, which also strongly verifies that the composites prepared in this experiment have high stability and reusability.

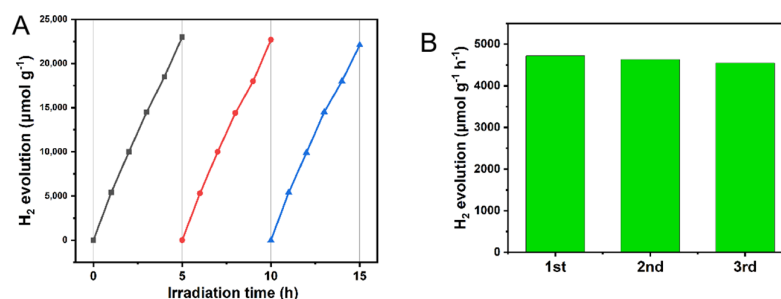


Figure 11. (A) Cyclic hydrogen production plot of prepared 10% nano g-C₃N₄/ZnIn₂S₄. (B) Cyclic hydrogen production rate plot.

2.10. Mechanism Analysis

The Schottky barrier formed at the metal/semiconductor interface promotes electron–hole separation in photocatalysis, while the metal acts as an electron sink. The photoinduced electrons in noble metals and holes in the VB of semiconductors participate in subsequent redox reactions. The whole process increases the charge carrier lifetime and improves the photocatalytic activity. The unique localized surface plasmon resonance (LSPR) of noble metal NPs can boost photocatalytic activity by increasing the incoming photon absorption. Furthermore, the facile tunability of LSPR (i.e., by adjusting the size and shape) allows for a broad spectrum of light absorption [36]. Conduction band (CB) potentials of -0.58 and

−1.28 V (relative to the NHE) were calculated for 10% nano g-C₃N₄/ZnIn₂S₄ and g-C₃N₄, respectively, based on the equation $E_{CB} = E_{VB} - E_g$, according to the bandgap energy data map in Figure 12. The energy band alignment in the figure indicates that the E_{CB} of g-C₃N₄ was more negative than that of 10% nano g-C₃N₄/ZnIn₂S₄, while the E_{VB} position of 10% nano g-C₃N₄/ZnIn₂S₄ was below that of g-C₃N₄. Due to the energy matching between 10% nano g-C₃N₄/ZnIn₂S₄ and g-C₃N₄, the transfer of the photogenerated holes or electrons between the two semiconductors is considered a type II heterostructure mechanism. Under visible light irradiation, 10% nano g-C₃N₄/ZnIn₂S₄ and g-C₃N₄ were excited and produced electron–hole pairs. The photoinduced electrons were transferred from the CB of g-C₃N₄ to the CB of 10% nano g-C₃N₄/ZnIn₂S₄ through the tight two-dimensional heterojunction interface, and then H⁺ was reduced to H₂. Photogenerated holes at the VB energy level of 10% nano g-C₃N₄/ZnIn₂S₄ can be spontaneously injected into the VB energy level of g-C₃N₄. In addition, due to the two-dimensional structure of the ultrathin g-C₃N₄ and 10% nano g-C₃N₄/ZnIn₂S₄, the photoinduced carriers are able to migrate rapidly to the surface for efficient subsequent reactions. Compared to ZnIn₂S₄ and g-C₃N₄ alone, the proper arrangement of the energy band structures in the composites facilitates the separation of photoinduced carriers and thereby promotes photocatalytic H₂ release.

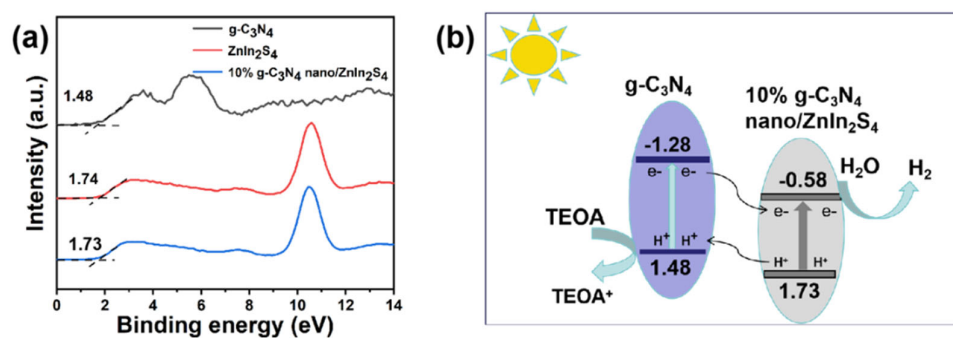


Figure 12. (a) Valence band spectra of g-C₃N₄, nano g-C₃N₄, ZnIn₂S₄, and 10% nano g-C₃N₄/ZnIn₂S₄. (b) Photocatalytic mechanism diagram of 10% g-C₃N₄/ZnIn₂S₄ nano-heterojunction.

3. Experimental Section

3.1. Preparation of Photocatalysts

3.1.1. Preparation of g-C₃N₄ Nanoflakes

We prepared g-C₃N₄ using a calcination method. The experimental steps were as follows. First, 3.0000 g of melamine was accurately weighed and then ground into a fine powder in a quartz mortar. The ground melamine was then transferred and poured into a ceramic crucible and put into a tube furnace, where it reacted for 4 h under a temperature of 550 °C (the rate of the temperature increase was 5 °C/min). Argon gas was introduced into the tube furnace, and the reaction was completed. After the tube furnace temperature was reduced to room temperature, the sample was taken out. The obtained yellow powder was the g-C₃N₄ semiconductor photocatalytic material, of which 0.5000 g was weighed and put into the tube furnace. It reacted for 2 h at a temperature of 550 °C (with a heating rate of 5 °C/min). Argon gas was introduced. At the end of the reaction, and after the temperature of the reaction system was reduced to room temperature, the obtained yellow sample was removed and ground. The light yellow powder obtained was the prepared g-C₃N₄ nanoflake photocatalytic material.

3.1.2. Preparation of ZnIn₂S₄ Material

We prepared ZnIn₂S₄ semiconductor nanomaterials with a hexagonal crystal type using the hydrothermal method; the specific steps were as follows. We weighed 1 mmol (0.2975 g) of zinc nitrate hexahydrate, 2 mmol (0.6017 g) of indium nitrate hydrate, and 6 mmol (0.4508 g) of thioacetamide, and combined them in a beaker. Then, we added 30 mL of water and mixed it well before placing the mixture into a rotor with a magnetic stirrer.

The mixed solution was transferred to a reaction kettle, and the sealed reaction kettle was placed in an electrically heated constant-temperature blast-drying oven. The temperature of the reaction system was set to 180 °C, and the reaction was carried out for 12 h. When the reaction was complete, the temperature of the constant-temperature oven was lowered to room temperature. The samples obtained from the reaction were washed with ultrapure water 3 times, and then washed with anhydrous ethanol 3 times. Then, they were placed in a drying oven at 70 °C to dry. The dried samples were ground and then dried again at 70 °C. The obtained yellow powder was the sample of ZnIn₂S₄ photocatalytic material.

3.1.3. Preparation of 10% g-C₃N₄/ZnIn₂S₄ Nano-Heterojunction Composites

We weighed out 0.0149 g of g-C₃N₄, 1 mmol (0.2975 g) of zinc nitrate hexahydrate, 2 mmol (0.6017 g) of indium nitrate hydrate, and 6 mmol (0.4508 g) of thioacetamide and placed them in a beaker. Then, we added 30 mL of water, and it was mixed under ultrasonic conditions for 20 min until a uniform solution was obtained. Then, it was put into the rotor and stirred with a magnetic stirrer for 20 min. The solution was transferred to the reaction kettle, and the sealed reaction kettle was placed in the electric constant-temperature blast-drying oven. The temperature was set to 180 °C, and the reaction time was 12 h. After the reaction was completed and the oven cooled down to room temperature, the samples obtained from the reaction were washed with ultrapure water 3 times and then washed with anhydrous ethanol 3 times, under the conditions of a centrifuge rotation speed of 8000 r/min for 3 min. Then, the samples were put into a drying oven and dried at a temperature of 70 °C. The yellow powder obtained from grinding was the 10% g-C₃N₄/ZnIn₂S₄ composite photocatalytic material sample.

3.2. Material Characterization

The powder X-ray diffraction (XRD) patterns of the as-prepared samples were analyzed using a Bruker D8 Advance X-ray diffractometer with Cu K α radiation. The Bruker D8 Advance X-ray diffractometer is manufactured by Bruker Company, Germany. Bruker's headquarters is located in Saarbrücken, Germany. The morphology was observed using a Hitachi S-4800 field emission scanning electron microscope (SEM) and a JEOL JEM 2100F transmission electron microscope (TEM). The Hitachi S-4800 Field Emission Scanning Electron Microscope (SEM) is manufactured by Hitachi Ltd., with its headquarters located in Chiyoda-ku, Tokyo, Japan. The JEOL JEM 2100F Transmission Electron Microscope (TEM) is manufactured by JEOL Ltd., which is also based in Chiyoda-ku, Tokyo, Japan. The X-ray photoelectron spectra (XPS) were recorded using a Thermo ESCALAB 250XI. The manufacturer of the Thermo ESCALAB 250XI equipment is Thermo Fisher Scientific, headquartered in Waltham, MA, USA. N₂ adsorption-desorption isotherms were recorded at 77 K using a Quantachrome Autosorb-IQ-2C analyzer. The photoluminescence (PL) spectra were measured using a FLS-980 (Edinburgh, UK). The Quantachrome Autosorb-IQ-2C is manufactured by Quantachrome Instruments, with its headquarters located in Boca Raton, FL, USA. The FLS-980 fluorescence spectrometer is manufactured by Edinburgh Instruments, headquartered in Livingston, UK.

3.3. Photocatalytic Performance Test

In this experiment, we used a Labsilar-III (AG) photolyzed water hydrogen system, produced by Beijing Porphyry Technology Co. (Beijing, China). This photolyzed water system has a vacuum system and an online system, and the experiment was carried out at atmospheric pressure to produce hydrogen for online sampling and testing to ensure the accuracy and consistency of the experiment. When the semiconductor is irradiated with energy greater than or equal to its forbidden bandwidth, the valence electrons within the semiconductor are excited, jumping to the conduction band, which causes photogenerated electron-hole separation. In this experiment, the photocatalytic hydrogen production test was carried out under the irradiation condition of a xenon lamp filtering out the ultraviolet light instead of sunlight, and the reaction device was in a vacuum state. Triethanolamine

was used as the hole sacrificial agent, chloroplatinic acid was the co-catalyst, and the xenon lamp current was 15 mA. When the conduction band potential of the semiconductor material tested is more negative than the hydrogen electrode potential, its valence band potential is more positive than the oxygen electrode potential, and a redox reaction can occur to reduce the water to hydrogen. The experimental feeding time interval was one hour to obtain the amount of hydrogen prepared using photocatalysis for each sample. This cycle was used until the reaction was complete, and the photocatalytic activity of each sample was analyzed based on the test data.

4. Conclusions

In this experiment, g-C₃N₄/ZnIn₂S₄ nano-heterojunction composites were prepared using a combination of ultrasonication and hydrothermal methods, and g-C₃N₄, prepared using the calcination method, was loaded onto ZnIn₂S₄ catalytic material. Then, the composites were characterized using XRD, SEM, UV, and FTIR, and the compositions of the composites were verified, i.e., g-C₃N₄/ZnIn₂S₄ nano-heterojunction composites were successfully prepared. Under visible light irradiation, the composite material showed higher photocatalytic activity compared to pure g-C₃N₄ and ZnIn₂S₄. This was due to the heterojunction structure formed by the interfacial contact of the two semiconducting materials, g-C₃N₄ and ZnIn₂S₄, which effectively inhibited the recombination of the photogenerated carriers and improved the separation efficiency of the photogenerated electron–hole pairs, thus increasing the catalytic activity. At the same time, the heterojunction structure made the composite material more efficient and stable.

Author Contributions: H.L.: Conceptualization, Investigation, Validation, Formal analysis, Writing—original draft. Y.W.: Conceptualization, Investigation, Formal analysis, Writing—original draft. S.W.: Conceptualization, Validation, Writing—review & editing, Funding acquisition, Supervision, Project administration. X.X.: Conceptualization, Validation, Writing—review & editing, Funding acquisition, Supervision, Project administration. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Key Research and Development Program of China (Grant No. 2022YFC2807505). This work was also supported by the Lianyungang Postdoctoral Research Foundation (LYG20230017) and the Research Program of “521 Project” of Lianyungang City of China.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data presented are available in this article.

Conflicts of Interest: The authors declare that they have no conflicts of interest.

References

1. Shi, X.; Mao, L.; Yang, P.; Zheng, H.; Fujitsuka, M.; Zhang, J.; Majima, T. Ultrathin ZnIn₂S₄ nanosheets with active (110) facet exposure and efficient charge separation for cocatalyst free photocatalytic hydrogen evolution. *Appl. Catal. B Environ.* **2020**, *265*, 118616. [\[CrossRef\]](#)
2. Sun, Z.; Zhu, M.; Lv, X.; Liu, Y.; Shi, C.; Dai, Y.; Wang, A.; Majima, T. Insight into iron group transition metal phosphides (Fe₂P, Co₂P, Ni₂P) for improving photocatalytic hydrogen generation. *Appl. Catal. B Environ.* **2019**, *246*, 330–336. [\[CrossRef\]](#)
3. Zhang, B.; Shi, H.; Yan, Y.; Liu, C.; Hu, X.; Liu, E.; Fan, J. A novel S-scheme 1D/2D Bi₂S₃/g-C₃N₄ heterojunctions with enhanced H₂ evolution activity. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *608*, 125598. [\[CrossRef\]](#)
4. Zhang, F.; Zhu, Y.; Lin, Q.; Zhang, L.; Zhang, X.; Wang, H. Noble-metal single-atoms in thermocatalysis, electrocatalysis, and photocatalysis. *Energy Environ. Sci.* **2021**, *14*, 2954–3009. [\[CrossRef\]](#)
5. Zhao, W.; Li, Y.; Zhao, P.; Zhang, L.; Dai, B.; Xu, J.; Huang, H.; He, Y.; Leung, D.Y. Novel Z-scheme Ag-C₃N₄/SnS₂ plasmonic heterojunction photocatalyst for degradation of tetracycline and H₂ production. *Chem. Eng. J.* **2021**, *405*, 126555. [\[CrossRef\]](#)
6. Zuo, G.; Wang, Y.; Teo, W.L.; Xie, A.; Guo, Y.; Dai, Y.; Zhou, W.; Jana, D.; Xian, Q.; Dong, W.; et al. Ultrathin ZnIn₂S₄ nanosheets anchored on Ti₃C₂TX MXene for photocatalytic H₂ evolution. *Angew. Chem.* **2020**, *132*, 11383–11388. [\[CrossRef\]](#)

7. Chen, T.; Zhang, J.; Ge, H.; Li, M.; Li, Y.; Duan, T.; He, R.; Zhu, W. Efficient extraction of uranium in organics-containing wastewater over g-C₃N₄/GO hybrid nanosheets with type-II band structure. *J. Hazard. Mater.* **2020**, *384*, 121383. [[CrossRef](#)] [[PubMed](#)]
8. Gao, S.; Liu, S.; Wang, D.; Zhu, C.; Shi, W.; Tao, H.; Wang, X.; Yang, F. Boosting carrier separation over ultrathin g-C₃N₄ by f-ionic intercalation for improved photocatalytic activity. *Appl. Surf. Sci.* **2024**, *644*, 158808. [[CrossRef](#)]
9. Jang, D.; Lee, S.; Kwon, N.H.; Kim, T.; Park, S.; Jang, K.Y.; Yoon, E.; Choi, S.; Han, J.; Lee, T.W.; et al. Preparation of carbon nitride nanotubes with P-doping and their photocatalytic properties for hydrogen evolution. *Carbon* **2023**, *208*, 290–302. [[CrossRef](#)]
10. Gorai, D.K.; Kuila, S.K.; Oraon, A.; Kumar, A.; Suthar, M.; Mitra, R.; Biswas, K.; Roy, P.; Ahmad, M.I.; Kundu, T.K. A facile and green synthesis of Mn and P functionalized graphitic carbon nitride nanosheets for spintronics devices and enhanced photocatalytic performance under visible-light. *J. Colloid Interface Sci.* **2023**, *644*, 397–414. [[CrossRef](#)]
11. Guo, S.; Tang, Y.; Xie, Y.; Tian, C.; Feng, Q.; Zhou, W.; Jiang, B. P-doped tubular g-C₃N₄ with surface carbon defects: Universal synthesis and enhanced visible-light photocatalytic hydrogen production. *Appl. Catal. B Environ.* **2017**, *218*, 664–671. [[CrossRef](#)]
12. Lin, P.; Shen, J.; Yu, X.; Liu, Q.; Li, D.; Tang, H. Construction of Ti₃C₂ MXene/O-doped g-C₃N₄ 2D-2D Schottky-junction for enhanced photocatalytic hydrogen evolution. *Ceram. Int.* **2019**, *45*, 24656–24663. [[CrossRef](#)]
13. Li, Y.; Yin, Z.; Ji, G.; Liang, Z.; Xue, Y.; Guo, Y.; Tian, J.; Wang, X.; Cui, H. 2D/2D/2D heterojunction of Ti₃C₂ MXene/MoS₂ nanosheets/TiO₂ nanosheets with exposed (001) facets toward enhanced photocatalytic hydrogen production activity. *Appl. Catal. B Environ.* **2019**, *246*, 12–20. [[CrossRef](#)]
14. Kasinathan, M.; Thiripuranthagan, S.; Sivakumar, A. A facile fabrication of Br-modified g-C₃N₄/rGO composite catalyst for enhanced visible photocatalytic activity towards the degradation of harmful dyes. *Mater. Res. Bull.* **2020**, *130*, 110870. [[CrossRef](#)]
15. Li, Z.; Chen, Q.; Lin, Q.; Chen, Y.; Liao, X.; Yu, H.; Yu, C. Three-dimensional P-doped porous g-C₃N₄ nanosheets as an efficient metal-free photocatalyst for visible-light photocatalytic degradation of Rhodamine B model pollutant. *J. Taiwan Inst. Chem. Eng.* **2020**, *114*, 249–262. [[CrossRef](#)]
16. Zhao, D.; Wang, Y.; Dong, C.L.; Huang, Y.C.; Chen, J.; Xue, F.; Shen, S.; Guo, L. Boron-doped nitrogen-deficient carbon nitride-based Z-scheme heterostructures for photocatalytic overall water splitting. *Nat. Energy* **2021**, *6*, 388–397. [[CrossRef](#)]
17. Sun, M.; Zhao, X.; Zeng, Q.; Yan, T.; Ji, P.; Wu, T.; Wei, D.; Du, B. Facile synthesis of hierarchical ZnIn₂S₄/CdIn₂S₄ microspheres with enhanced visible light driven photocatalytic activity. *Appl. Surf. Sci.* **2017**, *407*, 328–336. [[CrossRef](#)]
18. Xu, S.; Dai, J.; Yang, J.; You, J.; Hao, J. Facile synthesis of novel CaIn₂S₄/ZnIn₂S₄ composites with efficient performance for photocatalytic reduction of Cr(VI) under simulated sunlight irradiation. *Nanomaterials* **2018**, *8*, 472. [[CrossRef](#)] [[PubMed](#)]
19. Wang, Y.; Liu, Y.; Tian, F.; Bao, S.; Sun, C.; Yang, W.; Yu, Y. MnIn₂S₄ nanosheets growing on rods-like β-MnO₂ via covalent bonds as high-performance photocatalyst for boosting Cr(VI) photocatalytic reduction under visible light irradiation: Behavior and mechanism study. *J. Colloid Interface Sci.* **2022**, *625*, 264–277. [[CrossRef](#)]
20. Zhang, M.; Arif, M.; Hua, Y.; Qiu, B.; Mao, Y.; Liu, X. Direct Z-scheme α-MnO₂@MnIn₂S₄ hierarchical photocatalysts with atomically defined junctions for improved photocatalytic activities. *Nanoscale Adv.* **2021**, *3*, 812–822. [[CrossRef](#)]
21. Wang, S.; Guan, B.Y.; Wang, X.; Lou, X.W.D. Formation of hierarchical Co₉S₈@ZnIn₂S₄ heterostructured cages as an efficient photocatalyst for hydrogen evolution. *J. Am. Chem. Soc.* **2018**, *140*, 15145–15148. [[CrossRef](#)] [[PubMed](#)]
22. Yang, H.; Cao, R.; Sun, P.; Yin, J.; Zhang, S.; Xu, X. Constructing electrostatic self-assembled 2D/2D ultra-thin ZnIn₂S₄/protonated g-C₃N₄ heterojunctions for excellent photocatalytic performance under visible light. *Appl. Catal. B Environ.* **2019**, *256*, 117862. [[CrossRef](#)]
23. Mohamed, N.A.; Ismail, A.F.; Kiong, T.S. g-C₃N₄/La₂O₃ nanocomposite as a photo-electrocatalyst in solar water splitting. *Surf. Interfaces* **2024**, *44*, 103639. [[CrossRef](#)]
24. Rajavaram, R.; Vattikuti, S.P.; Shim, J.; Liu, X.; Hoai, N.T.; Dang, N.N. Enriched photocatalytic and photoelectrochemical activities of a 2D/0D g-C₃N₄/CeO₂ nanostructure. *Nanoscale Adv.* **2023**, *5*, 6489–6500. [[CrossRef](#)] [[PubMed](#)]
25. Xu, H.; Xiao, R.; Huang, J.; Jiang, Y.; Zhao, C.; Yang, X. In situ construction of protonated g-C₃N₄/Ti₃C₂ MXene Schottky heterojunctions for efficient photocatalytic hydrogen production. *Chin. J. Catal.* **2021**, *42*, 107–114. [[CrossRef](#)]
26. Yang, Y.; Zeng, Z.; Zeng, G.; Huang, D.; Xiao, R.; Zhang, C.; Zhou, C.; Xiong, W.; Wang, W.; Cheng, M.; et al. Ti₃C₂ MXene/porous g-C₃N₄ interfacial Schottky junction for boosting spatial charge separation in photocatalytic H₂O₂ production. *Appl. Catal. B Environ.* **2019**, *258*, 117956. [[CrossRef](#)]
27. Zhu, D.; Zhou, Q. Nitrogen doped g-C₃N₄ with the extremely narrow band gap for excellent photocatalytic activities under visible light. *Appl. Catal. B Environ.* **2021**, *281*, 119474. [[CrossRef](#)]
28. Tan, S.; Xing, Z.; Zhang, J.; Li, Z.; Wu, X.; Cui, J.; Kuang, J.; Zhu, Q.; Zhou, W. Ti³⁺-TiO₂/g-C₃N₄ mesostructured nanosheets heterojunctions as efficient visible-light-driven photocatalysts. *J. Catal.* **2018**, *357*, 90–99. [[CrossRef](#)]
29. Zhu, B.; Zhang, J.; Jiang, C.; Cheng, B.; Yu, J. First principle investigation of halogen-doped monolayer g-C₃N₄ photocatalyst. *Appl. Catal. B Environ.* **2017**, *207*, 27–34. [[CrossRef](#)]
30. Lee, S.; Shin, E.Y.; Jang, D.; Choi, S.; Park, H.; Kim, J.; Park, S. Production of mesoporous carbon nitrides and their photocatalytic properties for degradation of organic pollutants. *Bull. Korean Chem. Soc.* **2022**, *43*, 1124–1129. [[CrossRef](#)]
31. Yu, H.; Shi, R.; Zhao, Y.; Bian, T.; Zhao, Y.; Zhou, C.; Waterhouse, G.I.; Wu, L.Z.; Tung, C.H.; Zhang, T. Alkali-assisted synthesis of nitrogen deficient graphitic carbon nitride with tunable band structures for efficient visible-light-driven hydrogen evolution. *Adv. Mater.* **2017**, *29*, 1605148. [[CrossRef](#)] [[PubMed](#)]

32. Dong, H.; Xiao, M.; Yu, S.; Wu, H.; Wang, Y.; Sun, J.; Chen, G.; Li, C. Insight into the activity and stability of Rh x P Nano-species supported on g-C₃N₄ for photocatalytic H₂ production. *ACS Catal.* **2019**, *10*, 458–462. [[CrossRef](#)]
33. Gao, Z.; Chen, K.; Wang, L.; Bai, B.; Liu, H.; Wang, Q. Aminated flower-like ZnIn₂S₄ coupled with benzoic acid modified g-C₃N₄ nanosheets via covalent bonds for ameliorated photocatalytic hydrogen generation. *Appl. Catal. B Environ.* **2020**, *268*, 118462. [[CrossRef](#)]
34. Li, Z.; Wang, X.; Tian, W.; Meng, A.; Yang, L. CoNi bimetal cocatalyst modifying a hierarchical ZnIn₂S₄ nanosheet-based microsphere noble-metal-free photocatalyst for efficient visible-light-driven photocatalytic hydrogen production. *ACS Sustain. Chem. Eng.* **2019**, *7*, 20190–20201. [[CrossRef](#)]
35. Zhou, M.; Wang, S.; Yang, P.; Luo, Z.; Yuan, R.; Asiri, A.M.; Wakeel, M.; Wang, X. Layered heterostructures of ultrathin polymeric carbon nitride and ZnIn₂S₄ nanosheets for photocatalytic CO₂ reduction. *Chemistry* **2018**, *24*, 18529–18534. [[CrossRef](#)]
36. Mamiyev, Z.; Balayeva, N.O. Metal sulfide photocatalysts for hydrogen generation: A review of recent advances. *Catalysts* **2022**, *12*, 1316. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.