



Article Facile Construction of 2D/2D ZnIn₂S₄-Based Bifunctional Photocatalysts for H₂ Production and Simultaneous Degradation of Rhodamine B and Tetracycline

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Abstract: A two-dimensional/two-dimensional (2D/2D) TiO₂/ZnIn₂S₄ photocatalyst was reasonably proposed and constructed by a two-step oil bath-hydrothermal method. TiO₂ nanosheets uniformly grown on the surface of ZnIn₂S₄ nanosheets and a synergetic effect between the TiO₂ and ZnIn₂S₄ could highly contribute to improving the specific surface area and hydrophilicity of ZnIn₂S₄ as well as accelerating the separation and transfer of photon-generated e^- -h⁺ pairs, and thus enhancing the visible-light photocatalytic degradation and H₂ evolution performance of ZnIn₂S₄. Rhodamine B (RhB) and tetracycline (TC) were simultaneously selected as the target pollutants for degradation in the work. The optimum photocatalytic RhB and TC degradation properties of TiO₂/ZnIn₂S₄-10 wt% were almost 3.11- and 8.61-fold higher than that of pure ZnIn₂S₄, separately, while the highest photocatalytic hydrogen evolution rate was also observed in the presence of TiO₂/ZnIn₂S₄-10wt% and 4.28-fold higher than that of ZnIn₂S₄. Moreover, the possible photocatalytic mechanisms for enhanced visible-light photocatalytic degradation and H₂ evolution were investigated and proposed in detail. Our research results open an easy pathway for developing efficient bifunctional photocatalytes.

Keywords: $TiO_2/ZnIn_2S_4$; 2D/2D heterostructures; bifunctional photocatalysts; degradation; hydrogen evolution

1. Introduction

Since the concept of sustainable development was proposed, the production of clean energy and the treatment of wastewater with persistent organic pollutants have attracted increasing attention from researchers [1–4]. Compared to conventional treatment methods, photocatalysis technology by semiconductors has some advantages of clean, easy operation and high efficiency, which is considered to be promising in the territory of alleviating energy shortages and environmental crises [5,6]. Numerous scholars have been endeavoring to probe newfashioned semiconductors photocatalysts with superior activity and good stability to achieve effective hydrogen production and pollutant degradation in the past few decades [7,8]. Among the semiconductors photocatalysts, ternary metal chalcogenide semiconductors, such as $CuCo_2S_4$, $ZnIn_2S_4$, and $CaIn_2S_4$, have obtained exceeding attention in the domain of photocatalysis research owing to the advantages of small band gaps, outstanding photoconversion capacity, and good stability [9–11].



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Copyright: © 2023 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/). ZnIn₂S₄, as an outstanding representative of ternary metal chalcogenides, possesses two-dimensional (2D) nanosheet morphologies, a narrow bandgap of ca. 2.4 eV, and good stability, and thus is recognized to be a suitable candidate for visible-light photocatalytic hydrogen production and pollutant degradation [12,13]. Nonetheless, pristine ZnIn₂S₄ tends to agglomerate and displays low separation efficiency of the photogenerated electronhole pairs, which greatly restricts its photocatalytic property with hindering its application in the photocatalytic realm [14]. Therefore, it is urgently needed to surmount the drawbacks of pristine ZnIn₂S₄, and thus a series of modification strategies have been proposed. Among all of them, constructing heterojunctions with other semiconductor materials can immensely promote the separation of photogenerated electron-hole pairs, which has been demonstrated to be a productive modification strategy [15,16].

Among the semiconductor materials, TiO₂, as a wide bandgap ($E_g \sim 3.2 \text{ eV}$) semiconductor material, is widely considered as an ideal candidate to fabricate heterojunction with $ZnIn_2S_4$ due to its excellent stability, nontoxicity, and low cost [17], which has been widely applied in photocatalytic H₂ production [18], pollution degradation [19], CO₂ reduction [20], and organic synthesis [21]. More importantly, the energy band position of $ZnIn_2S_4$ is above that of TiO₂ allowing for photogenerated carriers transfer between $ZnIn_2S_4$ and TiO₂, and thus coupling $ZnIn_2S_4$ and TiO_2 contributes to addressing the shortfalls of $ZnIn_2S_4$ [22]. So far, $TiO_2/ZnIn_2S_4$ heterojunctions with different morphologies, such as $2D/3D TiO_2$ nanosheets/ZnIn₂S₄ nanostructure [23,24], 3D ZnIn₂S₄ nanosheets/TiO₂ nanobelts [25], and 1D TiO₂ nanofibers/2D ZnIn₂S₄ nanosheet heterostructure [26], have been successfully fabricated with significantly improving the separation efficiency and lifetime of carriers, and thus boosting the photocatalytic activity of $ZnIn_2S_4$. It is widely believed that the 2D/2D structure with close contacts has potential advantages of large specific surface area, excellent light absorption ability, and effective charge separation efficiency [27–29]. It was revealed that due to the 2D/2D structure, $Co_3O_4/ZnIn_2S_4$ and $TiO_2/g-C_3N_4$ photocatalysts showed efficient separation of photogenerated carriers, and thus obtaining enhanced photocatalytic properties [30,31]. Therefore, it is necessary to fabricate $2D/2D \operatorname{Ti}O_2/2n \ln_2S_4$ nanostructures and investigate the enhanced photocatalytic activity.

Enlightened by the aforementioned studies, we attempt to design and synthesize the $TiO_2/ZnIn_2S_4$ nanocomposites with intimate contacted 2D/2D structure by growing TiO_2 nanosheets on the surfaces of $ZnIn_2S_4$ nanosheets. The synergistic effect between TiO_2 and $ZnIn_2S_4$ promoted the photogenerated carriers' separation as well as enhanced specific surface area and hydrophilicity. As a result, the as-obtained composite photocatalysts showed significantly enhanced photocatalytic H₂ production rate and pollution removal efficiency with excellent reusability. The charge separation and transfer mechanism on the contact interface of TiO_2 and $ZnIn_2S_4$ for the superior photocatalytic performance was analyzed in-depth. This study provides a promising path for the construction of highly efficient photocatalysts for simultaneous application in energy- and environment-related areas.

2. Materials and Methods

2.1. Chemicals

HF (40% aqueous solution), tetraisopropyl titanate (TIPT, \geq 95.0%), NaOH (\geq 99.0%), chromic chloride (CdCl₃, \geq 99.0%), and indium chloride (InCl₃, \geq 99.9%) were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). RhB (\geq 99.0%), TC (\geq 99.0%), Thioacetamide (TAA, \geq 99.0%), anhydrous ethanol (\geq 99.7%), hydrochloric acid (HCl, 36.5%), and zinc chloride (ZnCl₂, \geq 98.0%) were commercially available from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ethylenediamine tetraacetic acid disodium (EDTA-2Na, \geq 99.5%), p-Benzoquinone (BQ, \geq 99.5%), tertiary butyl alcohol (t-BuOH, \geq 99.5%), and triethanolamine (TEOA, \geq 98.0%) were supplied by Shanghai Zhanyun Chemical Co., Ltd. (Shanghai, China). All chemicals were utilized as received. The distilled water was obtained using Water Purification System.

2.2. Synthesis of ZnIn₂S₄ Nanosheets

 $ZnIn_2S_4$ was prepared via an oil-bath process according to the former literature [12]. 272 mg of $ZnCl_2$, 442 mg of $InCl_3$, and 300 mg of TAA were dissolved into 50 mL of deionized water (pH = 2.5), and heated at 80 °C for 2 h. After cooling, $ZnIn_2S_4$ could be obtained by separating, washing, and drying under a vacuum at 60 °C overnight. Finally, 500 mg of $ZnIn_2S_4$ was dispersed into 100 mL of methanol with continuous ultrasound treatment.

2.3. Synthesis of $TiO_2/ZnIn_2S_4$ Nanosheets

The specific reaction process was illustrated in Figure 1. Firstly, 10 mL of HF was slowly dropped into a 100 mL of Teflon-lined autoclave reactor containing 25 mL of tetrabutyl titanate and heated at 200 °C for 40 h. After cooling, the precipitates were thoroughly separated by centrifugation and then dried under vacuum at 60 °C for overnight. Subsequently, the precipitates (3.1 mg, 15.5 mg, 18.6 mg, and 31 mg) and ZnIn₂S₄ dispersion liquid (19.6 mL, 18 mL, 17.6 mL, and 16 mL) were added in 0.1 M NaOH solution under stirring for 24 h, separately, then washed with deionized water till the pH = 7 and dried at 100 °C in a vacuum drying chamber. Finally, TiO₂/ZnIn₂S₄ composites with different weight percent of TiO₂ (2 wt%, 10 wt%, 12 wt% and 20 wt%) were obtained via the procedure and marked as TiO₂/ZnIn₂S₄-2 wt%, TiO₂/ZnIn₂S₄-10 wt%, TiO₂/ZnIn₂S₄-10 wt%, also utilized to synthesize blank TiO₂ in the absence of ZnIn₂S₄.



Figure 1. Schematic illustration for the formation process of TiO₂/ZnIn₂S₄ composites.

2.4. Characterization

The crystal phases were investigated via an X-ray diffractometer (XRD, XRD-6100, Shimadzu, Kyoto, Japan) using Cu-K α radiation ($\lambda = 1.5406$ A). The morphologies and lattice properties were analyzed by scanning electron microscopy (SEM, Sigma, Carl Zeiss, Oberkochen, Germany) and transmission electron microscopy (TEM, JEM2100, JEOL, Kyoto, Japan). The specific surface areas were determined by the physical adsorption of N_2 on a Micromeritics (ASAP 2020, Micromeritics, Atlanta, GA, USA) using the Brunauer-Emmett-Teller (BET) equation. The chemical state was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Thermo Fisher, Waltham, MA, USA). The light absorption as well as charge separation and transfer efficiency were studied by ultraviolet-visible diffuse reflection spectroscopy (UV-vis DRS, Lambda 750, PerkinElmer, Waltham, USA), photoluminescence spectroscopy (PL, ZolixLSP-X500A, Zolix, Beijing, China), fluorescence lifetime spectrophotometer (C11367, Quantaurus-Tau, Hamamatsu, Japan), and threeelectrode photoelectrochemical cell system (CHI660E, Chenghua, Shanghai, China). The water contact angles were measured by a contact angle meter (HARKE-SPCA, HARKE, Beijing, China). TOC analyzer (TOC-2000, Metash, Shanghai, China) was utilized to investigate the total organic carbon (TOC) of the residual solution.

2.5. Density Functional Theory (DFT) Calculation

To calculate the band gaps and work functions of TiO_2 and $ZnIn_2S_4$, the model of TiO_2 (1 × 2 × 1 supercell) and $ZnIn_2S_4$ (1 × 1 × 2 supercell) were first built and given in Figure S1. Subsequently, the calculations were performed by utilizing the Vienna ab initio Simulation Package (VASP), which implements the DFT with a generalized gradient

approximation (GGA) and super-soft pseudopotential method. Calculations were carried out by utilizing the Predew–Burke–Ernzerhof (PBE) scheme. The electron wave functions were described by the projector augmented wave (PAW) method with a cutoff energy of 300 eV and a K-point of $2 \times 3 \times 2$.

2.6. Photocatalytic Hydrogen Generation

The photocatalytic hydrogen experiments were conducted in an automatic online gas analysis system (Labsolar-6A, Perfectlight, Beijing, China). A Xenon lamp of 300 W (PLS-SXE 300C, λ > 420 nm) was employed to supply the visible-light source. During the process, 20 mg of as-fabricated photocatalysts were added into a 60 mL of mixed solution (50 mL deionized water and 10 mL of TEOA) without adding H₂PtCl₆, and then the reaction container was installed into the photocatalytic reaction instrument and the distance between the light source and the solution was about 16 cm. Ahead of starting the reaction, the entire installation was vacuumed to remove the air until the system pressure was beneath 1.0 Kpa. Then, turned on the light source and operated the program, automatic sampling every 60 min. In the whole reaction process, the temperature of circulating cooling water was always controlled at about 5 °C. Finally, the generated blended gas was transferred to gas chromatography (GC9790) equipped with a TCD detector (LabSolar-IIIAG, Perfectlight, Beijing, China) to further detect and calculate the production of hydrogen. To investigate the reusability of the binary heterostructure, recycled hydrogen production was carried out four times using $TiO_2/ZnIn_2S_4$ -10 wt% as the photocatalyst. The apparent quantum efficiencies (AQE) for H₂ evolution of λ = 400, 420, and 500 nm were determined in a 75 mL Pyrex glass reactor. The apparent quantum efficiency (AQE) could be determined using the following equation:

$$AQE = \frac{2 \times \text{the number of } H_2 \text{ evolved molecules}}{\text{the number of incident photons}} \times 100\%$$

2.7. Photodegradation Activity Evaluation

The visible-light photocatalytic degradation activity was evaluated by the degradation of fresh TC (10 mg/L) and RhB (30 mg/L) solution. The light source was provided by 500 W Xenon light (PLS-SXE 500C) equipped with a UV cutoff filter ($\lambda > 420$ nm). Firstly, 10 mg of photocatalyst was dispersed into the 50 mL of TC solution and 50 mL of RhB solution, respectively. Then, the above-mentioned solution was transferred to the photocatalytic reaction apparatus (XPA-7) and kept stirring in the dark for 60 min to obtain an adsorptiondesorption equilibrium. After turning on the Xenon light, the photocatalytic degradation reaction was starting. At a given interval, a 4 mL aliquot of mixture was taken out utilizing a syringe with a needle and then filtrated using a 0.22 µm Millipore filter to obtain the residual solution, the concentration of which at the maximum absorption wavelength (355 nm for TC and 554 nm for RhB) was monitored using a PerkinElmer UV-vis spectrophotometer (Lambda 35). Moreover, the recycled photodegradation experiments were carried out four times using $TiO_2/ZnIn_2S_4$ -10 wt% as the photocatalyst at the same condition. Once the degradation experiment was over, the remaining sample in the beaker was immediately recycled by separation, washing, and drying for the next cyclic degradation experiment. The degradation efficiency (De %) was calculated by the equation:

De % =
$$\frac{C_0 - C_t}{C_0} \times 100\%$$

In the formula, C_0 and C_t denote the concentrations at the initial time and after each stage of degradation, separately. As for the trapping experiments, equal amounts (1.0 mM) of scavengers were added to the TC solution to capture active radicals.

3. Results and Discussions

The text continues here. The XRD patterns were used to recognize the phase composition and the structure of samples, and the results are exhibited in Figure 2. The diffraction peaks observed at 21.6°, 27.7°, 47.2°, 52.7°, and 55.6° can be well attributed to the (006), (102), (110), (116), and (022) crystal planes of hexagonal $ZnIn_2S_4$ (JCPDS No. 72-0773) [32]. For pure TiO₂, a set of diffraction peaks located at 25.3° (101), 37.8° (004), 48.1° (200), 54.1° (105), 55.1° (211) and 62.8° (204) are consistent with the anatase TiO₂ (JCPDS No. 21-1272) [33]. The diffraction peaks of $ZnIn_2S_4$ and TiO₂ can be seen simultaneously in the XRD patterns of TiO₂ / ZnIn₂S₄ composites, the characteristic peak intensities of TiO₂ generally increased, while the diffraction peaks of $ZnIn_2S_4$ gradually decrease with the increased content of TiO₂. Further, no other peaks of the third (impurity) phase are detected in all XRD patterns, implying the successful construction of the TiO₂ / ZnIn₂S₄ composites.



Figure 2. XRD patterns of the as-prepared ZnIn₂S₄, TiO₂, and TiO₂/ZnIn₂S₄ composites.

SEM and TEM were utilized to observe the morphology of the catalysts. As displayed in Figure 3a, pristine TiO₂ showed a 2D nanosheet structure with different sizes. As for pure ZnIn₂S₄, a nanoflower-like structure assembled by the large number of nanosheets can be seen in Figure 3b. After coupling ZnIn₂S₄ with TiO₂, SEM (Figure 3c) and TEM (Figure 3d) images indicate TiO₂ nanosheets grow on the surface of ZnIn₂S₄ nanosheets, forming an intimate 2D/2D contact interface between ZnIn₂S₄ and TiO₂. The elemental distribution in the TiO₂/ZnIn₂S₄ composite was analyzed using SEM-energy-dispersive X-ray spectroscopy (Figure S3), and the result confirmed the homogeneous coexistence of Ti, O, Zn, In, and S elements. Moreover, high-resolution TEM analysis was conducted to investigate the microstructure information of the TiO₂/ZnIn₂S₄-10 wt% composite, and the result is depicted in Figure 3e, the lattice fringes with d spacings of 0.352 and 0.322 nm can be seen, which can be assigned to TiO₂ (101) and ZnIn₂S₄ (102) facets, separately [34,35]. The above results further indicate the successful formation of the TiO₂/ZnIn₂S₄ hybrid.

XPS was explored to be aware of the surface element composition and chemical state of the TiO₂/ZnIn₂S₄-10 wt% composite. As shown in Figure 4a, the XPS survey spectrum of TiO₂/ZnIn₂S₄ reveals the coexistence of Ti, O, S, Zn, and In elements, which is in keeping with the EDS test results. Figure 4b presents the XPS spectrum of O 1s, two characteristic peaks located at 530.6 and 531.92 eV can be attributed to the Ti-O bond and the –OH group, respectively [36]. The high-resolution XPS spectra of Ti 2p showed two characteristic peaks located at 458.34 and 463.89 eV (Figure 4c), assigning to Ti $2p_{3/2}$ and Ti $2p_{1/2}$, separately [37]. In the high-resolution S 2p spectrum (Figure 4d), the binding energies of 161.06 and 162.31 eV can be assigned to the S $2p_{3/2}$ and S $2p_{1/2}$, respectively, suggesting the occurrence of S^{2–} [38]. In Figure 4e, the peaks centered at 444.30 and 452.40 eV are ascribed to In $3d_{5/2}$ and In $3d_{3/2}$, assigning to In³⁺ binding state [39]. As for Zn 2p (Figure 4f), the peaks centered at 1021.34 and 1044.36 eV ascribed to $2p_{3/2}$ and $2p_{1/2}$, respectively, which proves the existence of Zn²⁺ [40].



Figure 3. SEM images of TiO_2 (**a**), $ZnIn_2S_4$ (**b**), and $TiO_2/ZnIn_2S_4$ -10wt% (**c**); TEM image (**d**) and HR-TEM image (**e**) of $TiO_2/ZnIn_2S_4$ -10 wt%.



Figure 4. XPS spectra of as-synthesized $TiO_2/ZnIn_2S_4$ -10 wt% heterostructure: (**a**) survey scan, (**b**) O 1s, (**c**) Ti 2p, (**d**) S 2p, (**e**) In 3d, and (**f**) Zn 2p.

The specific surface area and water contact angles were measured to investigate the adsorption performance of photocatalysts, and the results are displayed in Figure 5. The nitrogen adsorption-desorption isotherms of TiO₂, ZnIn₂S₄, and TiO₂/ZnIn₂S₄-10 wt% showed type IV isotherms with the hysteresis loop of mesoporous structures (Figure 5a), the specific surface area of TiO₂/ZnIn₂S₄-10 wt% was larger than that of TiO₂ and ZnIn₂S₄. It can be seen that the average pore sizes are between 2 and 50 nm (Figure 5b), which further confirmed the formation of a mesoporous structure. Meanwhile, water contact angles of TiO₂, TiO₂/ZnIn₂S₄, and ZnIn₂S₄ were also measured to analyze the hydrophilicity and hydrophobicity of prepared materials. It can be observed from Figure 5c–e that contact angles of ZnIn₂S₄, TiO₂/ZnIn₂S₄-10 wt% and TiO₂ were, respectively, 72.9°, 15.6°, and 8.9°, manifesting the hydrophilicity of ZnIn₂S₄ can be improved by coupling with TiO₂. These results illustrated that interface contact exists between pollutants and the photocatalysts owing to the enhanced specific surface area and hydrophilicity, and thus it is expected to obtain excellent photocatalytic performance.



Figure 5. Nitrogen adsorption-desorption isotherms (**a**) and the corresponding pore size distribution plots (**b**) of bare TiO₂, ZnIn₂S₄, and TiO₂/ZnIn₂S₄-10 wt% samples; Water contact angles of ZnIn₂S₄ (**c**), TiO₂/ZnIn₂S₄-10 wt% (**d**), and TiO₂ (**e**).

The photoabsorptive behavior of TiO₂, $ZnIn_2S_4$, and TiO₂/ $ZnIn_2S_4$ -10 wt% was detected via UV-vis DRS spectra as shown in Figure 6a, the absorption wavelength of pristine $ZnIn_2S_4$ with steep edge was at approximate 560 nm in the visible-light areas, which presented favorable absorption capacity both in the visible and UV light, while the absorption edge of absolute TiO_2 was located in about 406 nm. The photoabsorption ability of $TiO_2/ZnIn_2S_4$ -10 wt% exhibits a very close absorption profile with $ZnIn_2S_4$ with slightly diminished absorption and blue-shifted absorption edge, suggesting the introduction of TiO_2 has a slight influence on the light absorption property of $ZnIn_2S_4$. As depicted in Figure 6b,c, the band gaps of TiO₂ and ZnIn₂S₄ were calculated as 3.24 and 2.48 eV based on the equation: $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$ [41], which were roughly matched with the results of DFT calculation (Figure S3). Valence band XPS (VB-XPS) of TiO₂ and $ZnIn_2S_4$ were also conducted to further understand the band structure of TiO₂ and $ZnIn_2S_4$. As demonstrated in Figure 6d, the E_{VB-XPS} values of pure TiO₂ and $ZnIn_2S_4$ were 2.95 and 1.49 eV, respectively. Therefore, the VB potentials of the normal hydrogen electrode (E_{VB-NHE} , pH = 7) of TiO₂ and ZnIn₂S₄ were determined to be 2.71 and 1.25 eV based on the $E_{VB vs. NHE} = \phi + E_{VB-XPS} - 4.44$, where ϕ is the work function (4.2 eV) of the XPS analyzer [42], while the E_{CB vs. NHE} values of TiO₂ and ZnIn₂S₄ could be computed as -0.53 and -1.23 eV using the equation: $E_{CB} = E_{VB} - E_g$ [43]. Therefore, the overall band structure positions of TiO₂ and ZnIn₂S₄ can be obtained and shown in Figure S4.

To uncover the positive influence of constructing heterojunction on the catalytic performances of $ZnIn_2S_4$, the separation and migration behaviors of photogenerated charges were deeply investigated. First, the PL spectra of $ZnIn_2S_4$ and $TiO_2/ZnIn_2S_4$ -10 wt% were measured to monitor the recombination process of photoinduced charge carriers. Generally, the dramatically reduced PL intensity is regarded as a signal of effective charge separation [44]. As shown in Figure 7a, $TiO_2/ZnIn_2S_4$ -10 wt% exhibited a lower PL intensity than $ZnIn_2S_4$, suggesting a higher separation efficiency of photogenerated carriers in $TiO_2/ZnIn_2S_4$ -10 wt% composite. The time-resolved photoluminescence (TRPL) spectra were also acquired to investigate the detailed information about the decay behavior of photogenerated carriers, and the results are shown in Figure 7b. The average fluorescence lifetime (τ_{avg}) of $TiO_2/ZnIn_2S_4$ -10 wt% (581 ps) was longer than pristine $ZnIn_2S_4$ (543 ps), implying that the coupling $ZnIn_2S_4$ with TiO_2 can helpfully prevent the recombination of photoinduced carriers and obtain a longer fluorescence lifetime. To further clarify the en-

hanced photogenerated charge transfer and separation efficiency, the photoelectrochemical performance was characterized and analyzed by transient photocurrent responses and EIS tests. As demonstrated in Figure 7c, the TiO₂/ZnIn₂S₄-10 wt% showed a higher photocurrent density than ZnIn₂S₄, and the average photocurrent density of TiO₂/ZnIn₂S₄-10 wt% was raised to be 2.11 mA·cm⁻², approximately 1.5-fold larger than that of pristine ZnIn₂S₄ (1.39 mA·cm⁻²), implying that the construction of TiO₂/ZnIn₂S₄ composite can promote the photoexcited charge carrier transfer. Furthermore, the EIS plot of TiO₂/ZnIn₂S₄-10 wt% composite exhibited a smaller semicircle than pristine ZnIn₂S₄, as observed in Figure 7d, manifesting a lesser electric resistance and more efficient charge transfer process existing in the TiO₂/ZnIn₂S₄-10 wt% composite. These optical and photoelectrochemical properties demonstrated that the formation of TiO₂/ZnIn₂S₄ heterojunction was capable of elevating the separation and transfer efficiency of photogenerated carriers, thus obtaining the enhanced photocatalytic performance.

The visible-light photocatalytic H₂ generation activities of TiO₂, ZnIn₂S₄, and TiO₂/ ZnIn₂S₄ composites were evaluated in the presence of TEOA sacrificial reagent. As shown in Figure 8a, pure $ZnIn_2S_4$ possessed a low photocatalytic performance due to the high recombination rate of photoexcited charge carriers and photocorrosion, while pristine TiO₂ had almost no catalytic activity, which could be attributed to its wide bandgap [45]. Notably, the photoactivity of $ZnIn_2S_4$ was gradually improved along with the introduction of TiO₂. Among all composites, the $TiO_2/ZnIn_2S_4$ -10 wt% composite showed the optimal H₂ rate of $650 \ \mu mol/h/g$, which was 4.28-fold higher than that of pristine ZnIn₂S₄ (Figure 8b). The recycling tests were also conducted in the same reaction condition to investigate the durability performance of $TiO_2/ZnIn_2S_4$ -10 wt% photocatalyst. As is demonstrated in Figure 8c, the H₂ production amount throughout four successive cycles barely changed. Moreover, the crystal structure and morphology of TiO₂/ZnIn₂S₄-10 wt% showed no noticeable changes by comparing the XRD pattern (Figure S5a) or SEM image (Figure S5b) of a used sample with the fresh sample. These test results manifested that the $TiO_2/ZnIn_2S_4$ -10 wt% composite possesses good photocatalytic stability. To further clarify the driving force in the photocatalytic process, the AQEs of TiO₂/ZnIn₂S₄-10 wt% photocatalyst at 400, 420, and 500 nm were calculated as 1.3, 1.1, and 0.1%, respectively (Figure 8d), which exhibits a similar trend with the adsorption spectrum, indicating that the H_2 production reaction is a photocatalytic driven process.



Figure 6. (a) UV–vis DRS of TiO₂, ZnIn₂S₄ and TiO₂/ZnIn₂S₄-10 wt%; energy bandgap of (b) TiO₂ and (c) ZnIn₂S₄; (d) VB-XPS of TiO₂ and ZnIn₂S₄.



Figure 7. PL spectra (**a**), TRPL curves (**b**), transient photocurrent responses (**c**), and EIS plots (**d**) over bare $ZnIn_2S_4$ and $TiO_2/ZnIn_2S_4$ -10 wt% samples.



Figure 8. (a) Photocatalytic HER activity (a) and H_2 evolution rates (b) of all samples. (c) Cycling experiments of $TiO_2/ZnIn_2S_4-10$ wt%. (d) AQEs and DRS spectrum of $TiO_2/ZnIn_2S_4-10$ wt%.

To confirm the performance multiformity of the as-prepared samples, the photocatalytic degradation capacities of all samples were also investigated by using colorless TC and colored RhB as the simulated organic pollutants. The TC and RhB photodegradation curves of TiO₂, ZnIn₂S₄, and TiO₂/ZnIn₂S₄ composites were illustrated in Figures 9a and S6a, respectively. Almost no changes in the concentration of TC and RhB were noticed in the absence of a catalyst, suggesting that the self-degradation process could be ignored. The pure TiO₂ displayed weak degradation activities within 60 min, while ZnIn₂S₄ showed high degradation activities than TiO_2 due to a wider visible-light response range. With respect to the $TiO_2/ZnIn_2S_4$ composites, all composites showed better photocatalytic performance than TiO₂ and ZnIn₂S₄. Among them, TiO₂/ZnIn₂S₄-10 wt% possessed the optimum performance, and almost 95% of TC and 93% of RhB could be degraded. The photocatalytic activity was enhanced when the mass content of TiO_2 increased from 2% to 10%, then decreased as TiO₂ content further increased to 12% or even more, which may be attributed to excessive TiO₂ shielding the light absorption. To obtain the reaction rate constant "k", the photodegradation curves were further kinetically fitted by using the pseudo-first-order equation: $-\ln (C/C_0) = kt$, the results were displayed in Figures 9b and S6b, separately. The k value of $TiO_2/ZnIn_2S_4$ -10 wt% composite was highest compared with other samples and was up to 0.04115 min^{-1} for TC and 0.04168 min^{-1} for RhB, which was almost 111 and 190 fold that of pure TiO₂, and 26 and 6.65 fold that of individual ZnIn₂S₄. Meanwhile, the mineralization capacities of all kinds of photocatalysts were investigated by TOC measurement. As demonstrated in Figures 9c and S6c, the TOC removal efficiencies of $TiO_2/ZnIn_2S_4$ composites distinctly overtopped TiO₂ and ZnIn₂S₄ under the irradiation of visible light. Among them, the TiO₂/ZnIn₂S₄-10 wt% composite showed the highest TOC removal efficiency (83.5% for TC and 85.6 for RhB), which formed the correspondence with its doughty photocatalytic degradation abilities, and confirmed that the $TiO_2/ZnIn_2S_4$ had high mineralization capacities. To determine the reusability of $TiO_2/ZnIn_2S_4-10$ wt% in the photocatalytic process, the photocatalytic cycle experiments were performed to investigate the reusable performance. As shown in Figures 9d and S6d, the photodegradation efficiency scarcely had changed after undergoing four consecutive cycles. In addition, the XRD pattern (Figure S7a,c) and SEM image (Figure S7b,d) of $TiO_2/ZnIn_2S_4$ -10 wt% illuminated the crystal structure and morphology of TiO₂/ZnIn₂S₄-10 wt% before and after photodegradation cycling remained unchanged. The results demonstrated the splendid degradation stability of $TiO_2/ZnIn_2S_4$ -10 wt% during the photocatalytic process.



Figure 9. Photocatalytic degradation rate (**a**), the pseudo-first-order kinetics fitted curves (**b**), and TOC removal rate (**c**) of TC over all samples; maintenance of catalytic performance of $TiO_2/ZnIn_2S_4$ -10 wt% (**d**).

The work functions (Φ) were calculated to investigate the route of charge transfer at the contact interface of ZnIn₂S₄ and TiO₂, and the results are given in Figure 10a. It was observed that the Φ of ZnIn₂S₄ is lower than that of TiO₂, and thus the photoinduced electrons could transfer from ZnIn₂S₄ to TiO₂ when ZnIn₂S₄ and TiO₂ came in contact to construct a heterojunction. Subsequently, EDTA-2Na, t-BuOH, and BQ were selected in sequence as the scavengers of h⁺, •OH, and •O₂⁻ to further identify the roles of active species during the photodegradation process. As recorded in Figure 10b, varying degrees of photocatalytic activity suppression were observed after sacrificial agents were added with an order BQ > EDTA-2Na > t-BuOH, indicating •O₂⁻ and h⁺ are main and secondary active substances, separately, while •OH has minimal impact on the photocatalytic reactions.



Figure 10. (a) Work functions of the TiO_2 (001) and $ZnIn_2S_4$ (001) surfaces; (b) photocatalytic degradation performance of TC on $TiO_2/ZnIn_2S_4$ -10 wt% with various scavengers.

The possible mechanisms for boosting photocatalytic pollutant degradation and H₂ production performances of $TiO_2/ZnIn_2S_4$ composites were proposed and illustrated in Figure 11 based on the aforementioned discussion. When TiO_2 nanosheets grew on the surface of ZnIn₂S₄ nanosheets, a closed contact interface was formed between ZnIn₂S₄ and TiO₂. Under visible-light irradiation, TiO₂ could not absorb visible light due to its large band gap energy, while the electrons on the VB of $ZnIn_2S_4$ could be easily excited to its CB and generate electron-hole pairs because of the small band gap energy. According to the DFT calculated results of work functions, the electrons would transfer from the CB of $ZnIn_2S_4$ to that of TiO₂, while h⁺ left on the VB of $ZnIn_2S_4$, which leads to the spatial separation of electrons and holes with higher redox powers. For H₂ production, the photogenerated e^- could easily reduce the surface-adsorbed protons to H_2 with h^+ being consumed by TEOA. Different from the H₂ production process, electrons on the CB of TiO₂ would firstly react with O₂ to obtain $^{\circ}O_2^{-}$ in the photodegradation process. Subsequently, the h^+ and ${}^{\bullet}O_2^-$ participated in the photodegradation reaction due to their strong oxidation ability. As a result, the improved separation efficiency of photoinduced charge carriers would provide more carriers to participate in the photocatalytic reaction process to acquire enhanced photocatalytic performance.



Figure 11. Proposed mechanisms for the photocatalytic reaction on the $TiO_2/ZnIn_2S_4$ composite.

4. Conclusions

In summary, a 2D/2D heterojunction consisting of $ZnIn_2S_4$ nanosheets and TiO_2 nanosheets was fabricated by a facile two-step synthesis method for photocatalytic H₂ evolution and pollutant degradation. The small TiO₂ nanosheets deposited on the surface of large $ZnIn_2S_4$ nanosheets, resulting in the formation of the close 2D/2D heterointerface contact, which contributes to providing sufficient and short paths for the separation and transfer of photoinduced charge. All TiO₂/ZnIn₂S₄ heterojunction photocatalysts possess higher photocatalytic activities than pure $ZnIn_2S_4$ and TiO₂. Among them, the TiO₂/ZnIn₂S₄-10 wt% photocatalyst exhibits optimal H₂ evolution rate (650 µmol/h/g) and pollution degradation efficiencies (95% for TC and 93% for RhB) with excellent photocatalytic are believed to have originated from the accelerated charges separation and transfer as well as enhanced specific surface area and hydrophilicity. This work provides a practical strategy for preparing ZnIn₂S₄-based heterojunctions to act as highly efficient bifunctional photocatalysts for energy and environmental application.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano13162315/s1, Figure S1: structure models; Figure S2: The elemental mapping images; Figure S3: Calculated band structures; Figure S4: The energy band structure; Figure S5: XRD patterns and SEM image in the recycled photocatalytic H₂ development; Figure S6: Photocatalytic degradation rate, pseudo-first-order kinetics fitted curves, TOC removal rate and maintenance of catalytic performance; Figure S7: XRD patterns and SEM images in the recycling photocatalytic degradation.

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