

Article

Constructing a Polyimide/Zinc Sulfide Heterojunction Photocatalyst for Enhanced Photocatalytic Performance

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Abstract

Photocatalytic decomposition of water to produce hydrogen and the degradation of organic pollutants are among the most ideal strategies for addressing energy shortages and environmental pollution. Moreover, constructing organic–inorganic heterojunctions based on surface interactions is one of the most effective strategies for enhancing photocatalytic activity. In this work, a novel II-type polyimide/zinc sulfide (PI/ZnS) heterojunction photocatalyst was successfully synthesized for the first time through a simple hydrothermal method. The influence of PI in the PI/ZnS composite material was systematically studied. The 1PI/ZnS composite shows the highest rate (587.7 $\mu\text{mol/g/h}$) of photocatalytic water splitting for hydrogen production, which is approximately 19% higher than the value of ZnS (492.5 $\mu\text{mol/g/h}$), and it is 34.6 times the PI value (16.95 $\mu\text{mol/g/h}$). The degradation efficiency of the 3 PI/ZnS composite is nearly 35.5 times that of PI and nearly 1.9 times that of ZnS. The enhancement in the photocatalytic activity of the PI/ZnS photocatalyst is mainly attributed to the dense interface and II-type heterojunction between the PI and ZnS, which effectively improves the spatial separation efficiency of photogenerated carriers. This study demonstrates that the nanostructured II-type heterojunction in the PI/ZnS composite can significantly improve the photocatalytic performance of polyimide photocatalysts.

Keywords: polyimide; zinc sulfide; photocatalysis

1. Introduction

In the context of the increasingly scarce global energy resources and the continuous environmental pollution, efficient conversion of new energy sources and environmental purification have attracted great attention. Photocatalytic technology has received extensive attention due to its green and sustainable characteristics. It can not only utilize solar energy to degrade organic pollutants but also produce hydrogen through the photolysis process of water. Therefore, it is regarded as an effective approach to simultaneously address energy and environmental issues [1–3].

Since TiO_2 was reported to have the property of photocatalytic water splitting to produce hydrogen in 1972, research on photocatalytic has developed rapidly [4]. As a typical inorganic semiconductor, TiO_2 has the advantages of good stability, non-toxicity, and low cost. Therefore, many scholars have carried out extensive research in the field of organic pollutant degradation and photolysis of water to produce hydrogen [5]. However, traditional inorganic semiconductors generally have problems such as a narrow visible



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light absorption range and rapid recombination of photogenerated electrons and holes, which limit their practical applications [6].

In recent years, organic polymer semiconductors have gradually attracted the attention of researchers due to their advantages of adjustable band structure, strong visible light absorption capacity, and easy design of molecular structure [7]. Among them, graphitic carbon nitride (g-C₃N₄), as a new type of organic polymer semiconductor photocatalyst, has been found to efficiently degrade organic pollutants and decompose water to produce hydrogen [8,9]. g-C₃N₄ was widely applied in various fields such as photocatalytic water splitting for H₂ production, the degradation of organic pollutants, and the reduction of CO₂ [10,11]. Polyimide (PI), as another typical conjugated polymer, has shown promising application prospects in visible light-driven photocatalysis due to its good thermal stability, chemical stability, and suitable band structure [12]. However, pure polyimide still has some shortcomings, such as the high recombination rate of photogenerated carriers, slow interfacial charge transport, and a small specific surface area, all of which will affect its photocatalytic performance. Therefore, choosing another semiconductor with a bandgap structure that matches that of PI to construct a heterojunction in order to facilitate interface charge transfer and inhibit electron-hole recombination is considered an effective strategy for enhancing photocatalytic activity [13,14].

The bandgap of zinc sulfide (ZnS) is approximately 3.3 eV [15]. ZnS has certain photocatalytic applications due to its environmental friendliness and stable structure [16]. However, ZnS typically has a narrow light response range due to its wide bandgap, is prone to decomposition under acidic conditions, and has a high recombination rate of photogenerated carriers [14,17]. It is reported that ZnS can form heterojunctions with g-C₃N₄ to promote the spatial separation of photogenerated carriers, thereby enhancing photocatalytic performance [18,19].

Fortunately, PI has a conjugated structure similar to that of g-C₃N₄, and thus is regarded as an ideal photocatalytic material [20]. So far, the research on the construction of heterojunctions by combining ZnS with g-C₃N₄ has a certain foundation. For instance, Zhu et al. [21] controlled the bandgap by doping phosphorus elements in g-C₃N₄ and then formed a heterojunction with ZnS. The degradation rate constant of the synthesized PCN/ZnS photocatalyst has significantly increased, demonstrating significantly enhanced photocatalytic activity. However, there are currently no research reports on the formation of heterojunctions through PI modification of ZnS to enhance its ability for photocatalytic water splitting for hydrogen production and the degradation of organic pollutants.

Based on the above discussions, considering the structural similarity between PI and g-C₃N₄ as well as their excellent comprehensive performance, the composite of PI and ZnS is constructed to form a new heterojunction photocatalytic material. This is expected to further enhance the light response ability and carrier separation efficiency of ZnS and provide new research ideas for the development of efficient and stable new photocatalytic systems.

2. Experimental Section

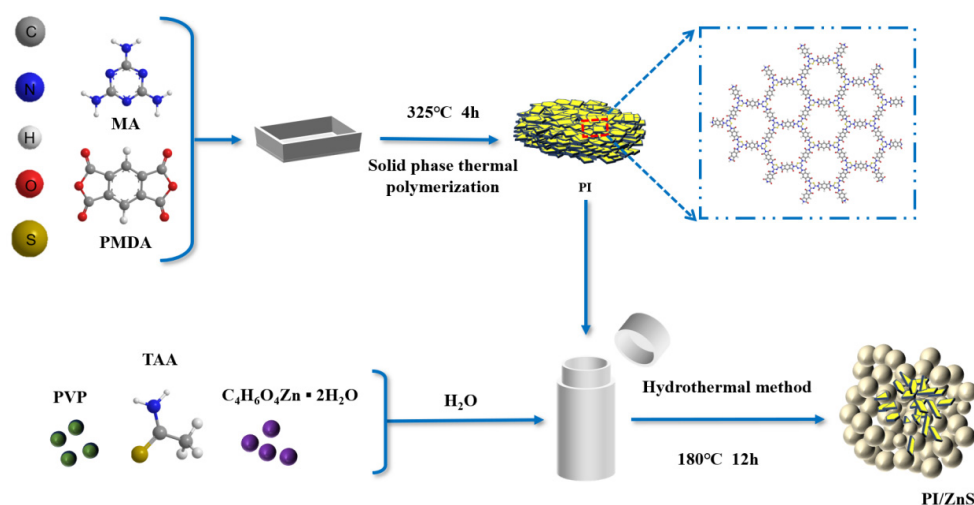
2.1. Reagents and Raw Materials

Zinc acetate (dihydrate) (C₄H₆O₄Zn·2H₂O) and thioacetamide (TAA) were procured from West Asia Chemical Technology (Shandong) Co., Ltd. (Jinan, China). Melamine (MA), pyromellitic dianhydride (PMDA) and polyvinylpyrrolidone (PVP, K = 23–27) were procured from Shanghai McLean Biochemical Co., Ltd. (Shanghai, China). Triethanolamine (TEOA) was procured from Sigma-Aldrich in St. Louis, MO, USA. Chloroplatinic acid (H₂PtCl₆) was procured from Aladdin Reagent (Shanghai) Co., Ltd. (Shanghai, China).

2.2. Synthesis of Photocatalysts

Polyimide (PI) was synthesized through solid-phase thermal polymerization, following established procedures described in the literature. Usually, 1.0 g of melamine (MA) and 1.7 g of pyromellitic dianhydride (PMDA) are weighed and ground in the same mortar. After grinding the reactant particles until they were fine and uniform, they were placed in a small porcelain boat and then placed in a tube furnace. After the nozzle was assembled and sealed, it was heated to 325 °C, with a heating rate of 2.5 °C/min, then maintained for 240 min and subsequently cooled to room temperature at a chilling rate of 2.5 °C/min. Finally, the rough product is purified, dried and ground to obtain the required PI photocatalyst.

PI/ZnS composites were prepared via the hydrothermal method. PI, 2.25 g zinc acetate dihydrate ($C_4H_6O_4Zn \cdot 2H_2O$), 0.14 g polyvinylpyrrolidone (PVP), and 1.54 g thioacetamide (TAA) were dissolved in water and dispersed in an ultrasonic bath for 10 min. Then, the suspension was stirred in a magnetic mixer at 70 °C and 900 r/min, and then transferred to the reactor. The temperature rose to 180 °C at a heating rate of 2.5 °C/min in the reactor, and the hydrothermal reaction was performed for 12 h. Finally, the soil gray PI/ZnS composite was obtained, and then further washing, drying, and grinding of the crude product to obtain the soil gray PI/ZnS composite material were performed. The preparation of pure ZnS must remove PI during the above synthesis process. By controlling the percentage of PI content, a series of composite photocatalytic materials with a PI content of 1%, 2%, 3%, 4%, and 5% were obtained, which are referred to as 1PI/ZnS, 2PI/ZnS, 3PI/ZnS, 4PI/ZnS, and 5PI/ZnS, respectively. The synthesis process of PI/ZnS compounds is shown in Scheme 1.



Scheme 1. Preparation process diagram of PI/ZnS composite.

2.3. Catalyst Characterization

Characterization of the catalysts can be found in the Supplementary Materials.

2.4. Electrochemical Testing

Photoelectrochemical testing was performed using an electrochemical analyzer (Chenhua CHI 660 D, Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). This analyzer employed the standard three-electrode system and was operated under the assistance of a xenon lamp as the light source. The three electrodes are the comparative electrode (Ag/AgCl), the auxiliary electrode (platinum electrode), and the working electrode (conducting glass with the sample). The electrolytic solution is a sodium sulfate solution (Na_2SO_4 , 0.5 mol/L, pH = 6.8). The working electrode was produced from fluorine-doped

tin oxide (FTO) pellucid conducting glass. Preparation method: We dissolved 5 mg of the sample in 1 mL of anhydrous ethanol as A, and then dissolved 20 μ L Nafion in 1 mL of absolute ethanol as B. A and B were dispersed via ultrasound for 30 min. Thereafter, they were coated on the surface of a 1×2 cm conducting glass (up to a 1/2 position). First, 50 μ L A was coated on the conductive glass, with 10 μ L each time for five cycles. After each coating, the coating was dried at a specific temperature for 1–2 min to ensure that the sample adheres to the conducting glass, and then 10 μ L of solution B was applied each time, for a total of 20 μ L on the conducting glass. Under dark conditions, the Mott–Schottky curve was measured at a frequency of 1.0 kHz. Electrochemical impedance spectroscopy (EIS) was obtained in the frequency range of 200 kHz–10 MHz.

2.5. Photocatalytic Performance Test

The photocatalytic hydrogen production activity of the catalyst samples was tested on a top-illuminated reactor using an XL-300W (Excelitas Technologies, Pittsburgh, PA, USA) (I = 20 A) xenon lamp as a full-radiation light source. A total of 50 mg of the photocatalyst was added to a mixed solution of triethanolamine (TEOA) and deionized water. The total volume of the mixed solution was 100 mL, and the volume ratio of TEOA to water was 1:9. On this basis, by adding an appropriate amount of H_2PtCl_6 as a co-catalyst, the dispersion was transferred to a beaker, ultrasonically dispersed for 10 min, and then transferred to a reactor. The reactor was irradiated for 2 h under full radiation ($\lambda > 300$ nm), and the hydrogen production rate was assessed by gas chromatography (GC9790 II, Zhejiang Fuli Analytical Instrument Co., Ltd., Taizhou, China, Fuli, TCD, Ar carrier).

The XL-300 W xenon lamp was utilized as the degradation light source, and the filter plate ($\lambda > 420$ nm) was used to emulate visible light. Methyl orange (MO) was used to simulate organic pollution to investigate the photocatalytic degradation activity of the photocatalyst. A total of 200 mg of the photocatalyst was added to the reactor and scattered in 100 mL of the prepared methyl orange solution (concentration of 40 mg/L). The circulating water system of the magnetic stirring device and the low-temperature thermostat were opened, and the sample was recorded as sample 0. After stirring for 1 h in dark environments to reach the adsorption–desorption balance, the mixed suspension (3–4 mL) sample was extracted and recorded as sample 1; the xenon lamp (300 W) was activated, and photocatalytic degradation was carried out. The mixed suspension (3–4 mL) samples were extracted every 1 h. The above samples were filtered by an MCE 0.45 μ m filter, and then the absorbency was determined at 464 nm by using a UV–visible spectrophotometer (Mapada, Shanghai, China, UV-1800).

3. Results and Discussion

3.1. Structure and Morphology Analysis

To clarify the crystal phase structure and phase composition of the samples, X-ray powder diffraction (XRD) was employed to test PI, ZnS, and the PI/ZnS composite. The results are shown in Figure 1. In the diffraction pattern of pure ZnS, three relatively strong and sharp diffraction peaks at 2θ values of approximately 28.5° , 47.5° , and 56.3° can be observed [22], corresponding to the (111), (220), and (311) crystal planes of the cubic crystal structure of ZnS (PDF#05-0566), respectively. This indicates that the prepared ZnS has a typical cubic crystal structure. The higher peak intensity and narrower peak width indicate that ZnS has good crystallinity, and high crystallinity can effectively reduce the recombination of photogenerated carriers, thereby significantly improving its photocatalytic activity [23,24]. The XRD pattern of PI shows a wide and diffuse diffraction peak in the range of 20 – 30° , indicating that PI is an amorphous structure [12]. The disordered structure of PI endows it with a large specific surface area, which contributes to the uniform

dispersion of ZnS particles in PI. For PI/ZnS composites, the diffraction peaks of ZnS can still be observed in the XRD pattern, indicating that the crystal structure of ZnS is retained in the composites [25]. However, compared with ZnS, these diffraction peaks are slightly broadened, and the intensity is reduced, indicating that the dispersion of ZnS in PI is significantly improved and the grain size is reduced. The diffraction peak intensities and full width at half maximum (FWHM) values of the (111), (220), and (311) characteristic crystal planes in the XRD spectra of samples with different doping amounts of PI-loaded ZnS and PI/ZnS were fitted. The results are summarized in Table S1. Comparative analysis found that with the increase in PI doping amount, the diffraction peak intensity of the sample decreased regularly. Taking the (111) crystal plane as an example, the peak intensity of ZnS is 18,013.30. When the PI doping amount is 5%, the intensity decreases to 14,873.3, and the attenuation effect is significant. At the same time, the FWHM of the diffraction peak gradually increases with the increase in PI doping amount, and the FWHM of the crystal plane increases from 0.73 to 0.96, indicating that the grain size of the sample decreases. These analysis results confirm the decrease in diffraction peak intensity and the broadening of half peak width. It is worth noting that in the XRD spectrum of the PI/ZnS composite material, the characteristic diffraction peaks related to PI are not prominent. The possible reason for this is that the proportion of PI is relatively low, and it also has good dispersion in the composite system. The enhancement in the uniformity of ZnS dispersion can promote the formation of more active sites, thereby increasing the number of active centers that can participate in the reaction in the PI/ZnS composite material [26].

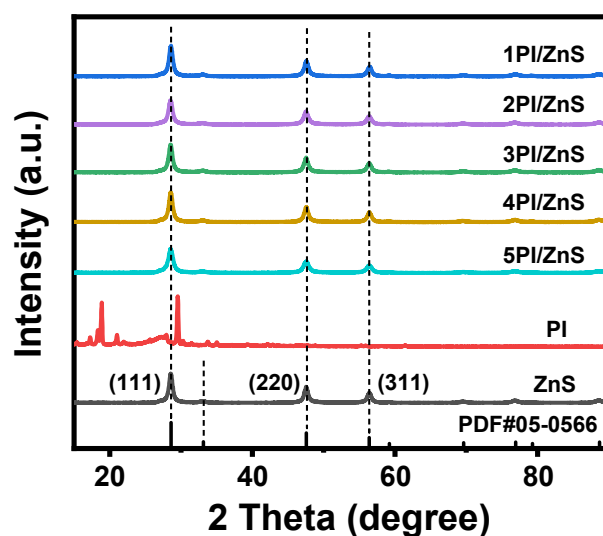


Figure 1. XRD patterns of ZnS, PI, and PI/ZnS composite.

The surface morphology of PI, ZnS and the 3PI/ZnS composite was characterized by SEM, and the relationship between different morphological features and photocatalytic performance was analyzed. As shown in Figure 2a, PI exhibits a typical two-dimensional layered structure [12]. This unique lamellar structure not only facilitates the anisotropic transport of electrons [27]. Moreover, it can effectively increase the specific surface area of the PI/ZnS composite, providing more available active centers for catalytic reactions. As displayed in Figure 2b, the ZnS sample exhibits a relatively obvious nanospherical structure [22], accompanied by significant agglomeration. Due to the agglomeration of particles, the exposed surface area of the material may decrease accordingly [26], which will have an adverse effect on the separation efficiency of photogenerated carriers and the migration process. It is worth noting that, as can be seen from the morphology image of the 3PI/ZnS composite material (Figure 2c), the two-dimensional PI nanosheets

are uniformly dispersed within the ZnS nanocrystals, thereby forming a heterojunction structure with excellent interface contact. This heterostructure has multiple synergistic effects. Firstly, the layered structure of the PI is conducive to the formation of continuous charge transmission channels, enabling the electrons and holes generated by light to be separated and transported more effectively and reducing their recombination. Secondly, the heterojunction formed between PI and ZnS can achieve energy band matching, broaden the spectral response range, and significantly improve the efficiency of light absorption and utilization within the visible light range. In addition, by introducing PI, it is possible to effectively inhibit the agglomeration of ZnS nanoparticles [22].

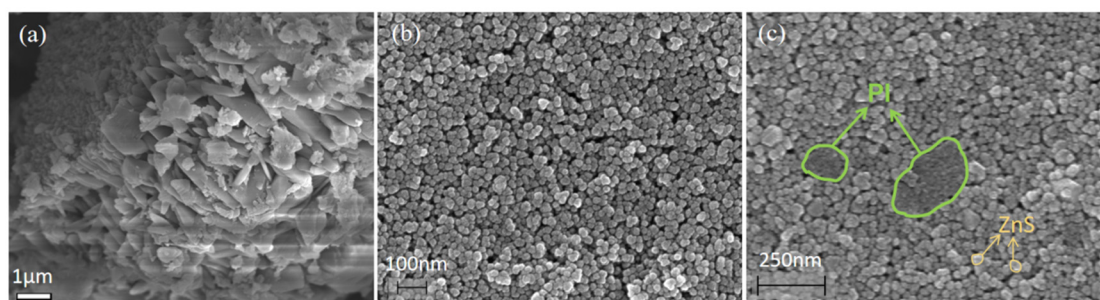


Figure 2. SEM morphological characterization images of different samples: (a) PI; (b) ZnS; (c) 3PI/ZnS.

To further explore the morphologies and structures of the samples, the morphologies of the prepared ZnS and 3PI/ZnS samples were analyzed by HR-TEM. As shown in Figure 3a, ZnS exhibits a typical nanoparticle structure, which is consistent with the morphology obtained from the SEM analysis. The clear lattice stripe spacing in Figure 3b is approximately 0.32 nm, corresponding to the (111) crystal plane of ZnS [22]. Meanwhile, Figure 3c,d show the TEM images of ZnS and the 3PI/ZnS composite, respectively, confirming the existence of the morphologies of the PI nanosheets and ZnS nanoparticles in the PI/ZnS composite. At the same time, the SAED pattern of ZnS is displayed in Figure 3e,f, which shows the crystal planes corresponding to ZnS (111), (220), and (311) [23]. These results correspond to the XRD results shown in Figure 1. Interestingly, the results shown in Figure 3g indicate that there is a distinct boundary between the ZnS nanoparticles and the PI layer, and the PI has been embedded into a large number of ZnS nanoparticles. These ZnS particles have clear lattice stripes, and the spacing of the lattice stripes is consistent with that shown in Figure 3f. Figure 3f also shows that PI does not break the crystal structure of ZnS and improves the dispersity [28]. Figure 3i further presents the EDS surface scan distribution results of the C, N, O, S and Zn elements in the 3PI/ZnS composite material. It can be seen that the red part represents the distribution of C elements, while the blue and green parts are the distributions of N and O elements, all of which are derived from PI. The cyan and yellow colors represent the distribution of Zn and S elements, respectively, which are completely consistent with the distribution of ZnS. Furthermore, after the PI/ZnS composite system was constructed, the agglomeration of ZnS nanoparticles was effectively alleviated.

The FTIR spectra of PI, ZnS, and the PI/ZnS composites are depicted in Figure S1. In the infrared spectra of the PI/ZnS composites, with the gradual increase in PI loading percentage, the characteristic spectra of the PI/ZnS composites did not change significantly, indicating that the introduction of PI did not destroy the crystal structure of ZnS. ZnS, as a typical wide bandgap semiconductor, usually exhibits a zinc blende crystal structure, and its characteristic infrared absorption peaks are mainly distributed in the wavenumber range of 400–500 cm^{-1} [12]. The black dotted line-labeled peak at 1680 cm^{-1} corresponds to the characteristic vibration absorption peak of the H-O-H bond. With the increase in

PI doping percentage from 1% to 5%, the characteristic infrared absorption peaks of the PI/ZnS composites in the wavenumber range of $1500\text{--}1400\text{ cm}^{-1}$ and $1650\text{--}1720\text{ cm}^{-1}$ did not change. No obvious PI characteristic absorption peaks were observed in the composite material. This is mainly due to the low doping amount of PI and its good dispersion within the PI/ZnS composite system.

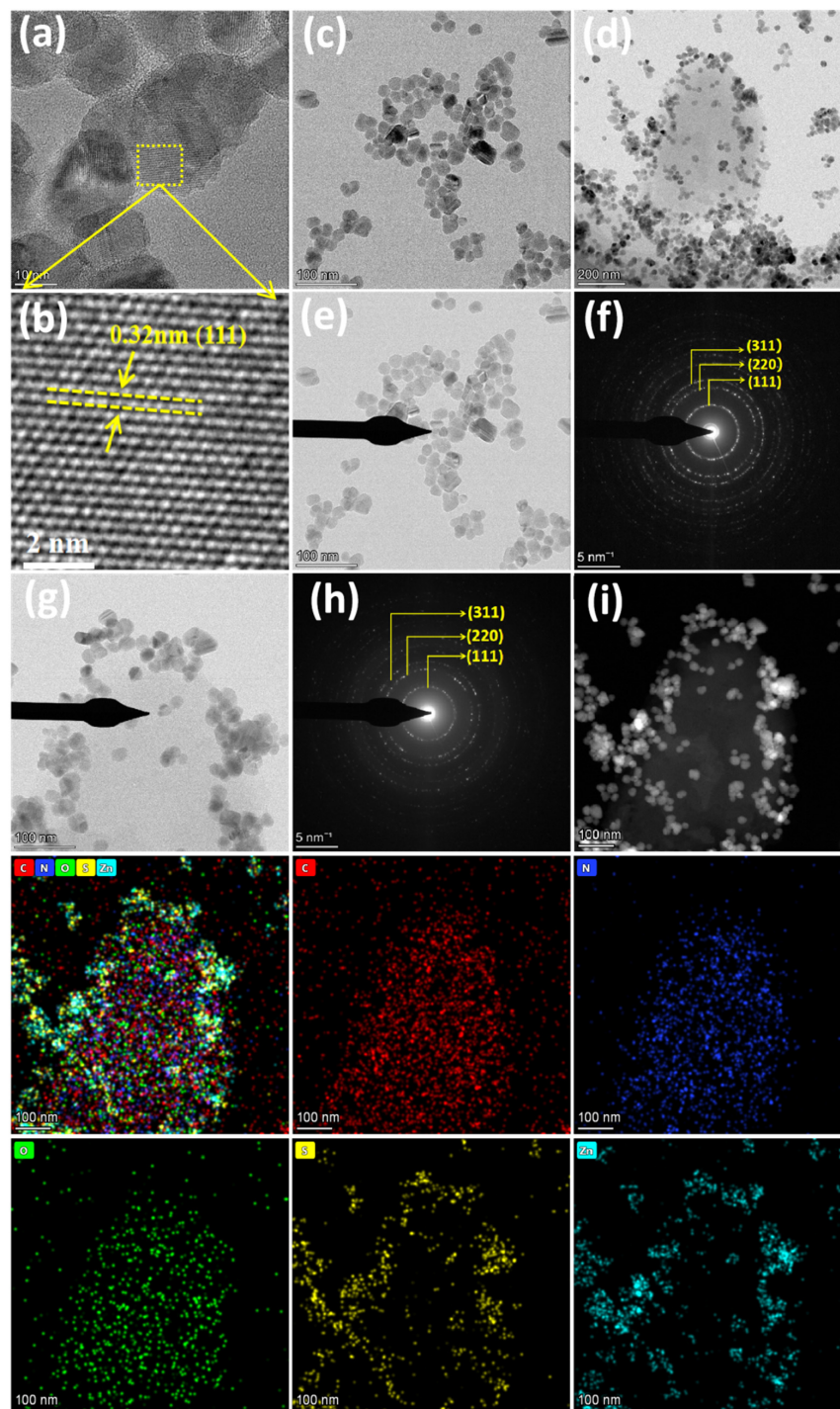


Figure 3. Images of (a,b) HR-TEM, (c) TEM, (e) TEM, and (f) SAED patterns for ZnS; (d,g) TEM images, (h) SAED patterns, and (i) EDS mapping of C, N, O, S, and Zn elements for 3PI/ZnS composite.

During the XPS analysis process, the C1s signal located at 284.6 eV was selected as the energy correction reference, which was used to correct the binding energy positions of different elements. Based on the XPS spectra, a systematic discussion was conducted on the

chemical composition, valence state changes, and possible interface interactions in the PI, ZnS, and 3PI/ZnS composite. The C1s spectrum is shown in Figure 4a. The pure PI sample exhibits sp² hybridization (C–C/C=C) and carbonyl (C=O) characteristic peaks at 284.6 eV and 287.9 eV, respectively [28]. In the composites, the C=O peak shifted to the low-binding-energy direction to 287.8 eV, which indicated that there was a significant electron transfer between PI and ZnS. The N 1s spectrum is shown in Figure 4b, which further confirms this inference. The characteristic peaks of PI are located at 399.4 (–NH–) and 398.1 eV (C–N), and the C–N peak shifts to 398.3 eV after recombination, indicating that the electron cloud density of nitrogen atoms is redistributed. The Zn 2p spectrum is shown in Figure 4c. The pure ZnS material exhibits a typical Zn 2p characteristic double peak at 1020.9 eV (Zn 2p^{3/2}) and 1044.0 eV (Zn 2p^{1/2}) [17]. After recombination, these characteristic peaks shift to 1021.4 eV and 1044.5 eV in the direction of high binding energy, respectively, confirming that the electron cloud density of Zn atoms decreases. The peak shift can also be observed in the S 2p spectrum (starting at 160.8 eV and 161.8 eV); Figure 4d further confirms the interfacial charge transfer phenomenon, indicating that a strong interaction heterojunction interface is formed between PI and ZnS [29]. It is worth noting that the chemical shifts observed in the C 1s and N 1s spectra indicate that the PI skeleton structure can be used as an efficient electron transport channel to enhance the photocatalytic activity of the PI/ZnS composite. At the same time, XPS results confirmed that the composite process did not lead to a significant change in the chemical state of the PI/ZnS composite, showing excellent structural stability.

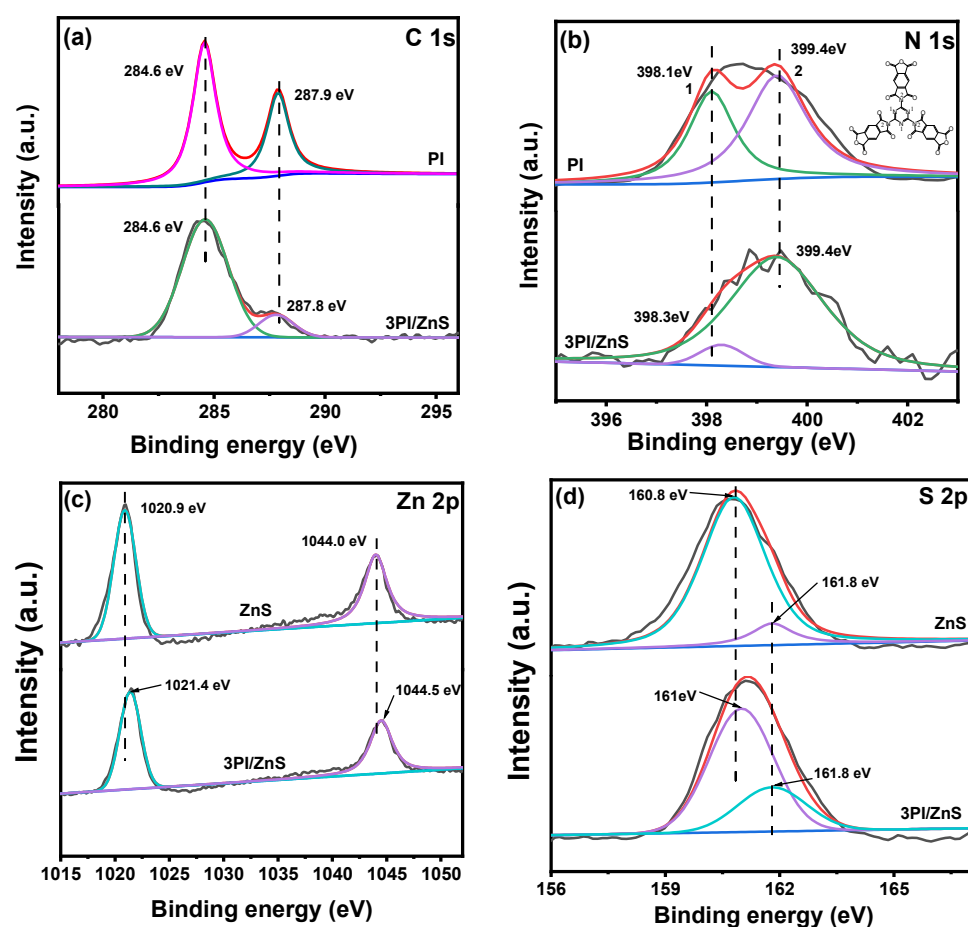


Figure 4. XPS spectra for (a) C 1s, (b) N 1s, (c) Zn 2p, and (d) S 2p of PI, ZnS, and 3PI/ZnS composite.

To further evaluate the surface properties of PI, ZnS and the 3PI/ZnS composite, the BET method was employed for characterization and analysis. As shown in Figure 5a, the

characterization results of N_2 adsorption–desorption isotherms reveal that the prepared PI, ZnS, and the 3PI/ZnS composite all exhibit typical type IV isotherm characteristics [30], which are in line with the characteristic curve of the IUPAC classification standard, i.e., mesoporous. In the region where the relative pressure P/P_0 exceeds 0.8, the typical H_3 -type lagging loop characteristics can be observed, which confirms the existence of a typical slit-like pore structure of the material [31]. The results of the BET test show that the specific surface area of the original PI material is only $4.33 \text{ m}^2/\text{g}$, while that of pure ZnS reaches $40.42 \text{ m}^2/\text{g}$. Compared with a single component, the specific surface area of the 3PI/ZnS composite further increases to $49.34 \text{ m}^2/\text{g}$, which is approximately 11.40 times that of pure PI, indicating that the formation of the composite system can effectively enhance the specific surface area of the material. It has increased by approximately 22.1% compared to ZnS. As displayed in Figure 5b, the test results of the Barrett–Joyner–Halenda (BJH) pore size distribution indicate that 3PI/ZnS exhibits a wider pore size distribution than ZnS, and exhibits a significantly enhanced pore volume in the mesoporous region (2–50 nm). In order to verify this phenomenon, the average pore size data of ZnS, PI and 3PI/ZnS samples were supplemented. The results are shown in Table S2. The data comparison shows that the pore size of the composite material is larger than that of pure ZnS. This optimized hierarchical pore structure is conducive to the construction of efficient electron transport channels and provides rich surface-active sites [32,33]. In contrast, PI exhibits a relatively flat distribution curve, indicating that it has fewer mesopores and micropores. The large specific surface area and hierarchical pore structure exhibited by the PI/ZnS composite are mainly attributed to the synergistic effect between the PI nanosheets and the ZnS nanoparticles. The uniformly dispersed ZnS nanoparticles not only effectively inhibit the agglomeration of PI layers, but also construct a large number of heterogeneous interface contacts [34]. This structural feature can significantly promote the spatial separation of photogenerated carriers, prolong the lifetime of electron–hole pairs, and provide sufficient active sites, thus exhibiting excellent performance in photocatalytic applications.

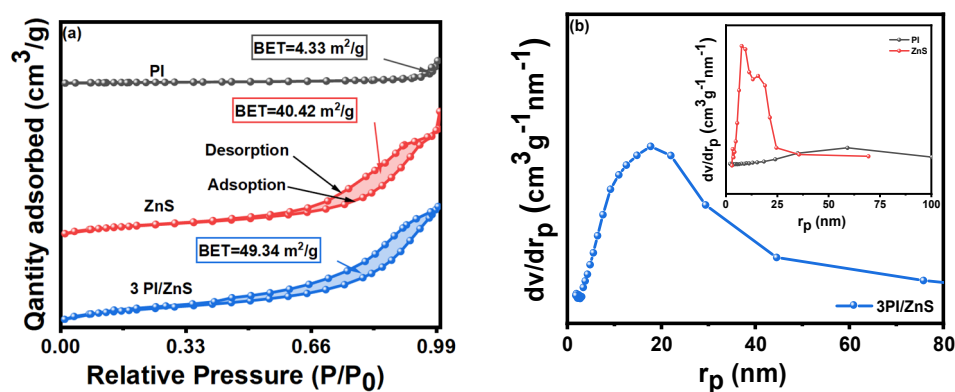


Figure 5. (a) Nitrogen adsorption–desorption analysis of PI, ZnS, and 3PI/ZnS composite and (b) BJH diagram.

3.2. Optical and Electronic Properties

To investigate the light absorption properties of PI, ZnS and PI/ZnS composites, their spectra were characterized and analyzed using UV-Vis diffuse reflectance spectroscopy. As shown in Figure 6a, PI/ZnS not only retains the strong absorption of ZnS in the ultraviolet region, but also enhances it in the visible region compared with PI, indicating that PI/ZnS has a wider light absorption range [29]. Obviously, as the PI content increases, the red shift of the optical absorption edges of the PI/ZnS composites occurs more significantly than that of ZnS, and the absorption of visible light is significantly enhanced. The electronic structure calculation uses the Kubelka–Munk function to obtain the fundamental state bandgap

energy. As shown in Figure 6b, the bandgap of PI is 2.76 eV, and the bandgap of ZnS is 3.30 eV, demonstrated by drawing the corresponding diagram of $(\alpha h\nu)^2$ and $h\nu$. The results of electrochemical analysis show that when the Mott–Schottky curve shows a positive slope, it indicates that the sample is an n-type semiconductor; when the curve shows a negative slope, it indicates that the sample is a p-type semiconductor [35]. As shown in Figure 6c, the conduction band (CB) position in the PI/ZnS system is determined by Mott–Schottky curve detection. Based on the Mott–Schottky test results and combined with the empirical relationship (CB potential = flat band potential -0.2 eV) between the flat band potential and conduction band potential of n-type semiconductors, the conduction band potentials of ZnS and PI were determined to be -0.81 eV [36] and -0.84 eV, respectively. Further, by calculating according to the relationship between bandgap energy and band position ($E_g = E_{CB} + E_{VB}$), the valence band potentials of PI and ZnS were determined to be 1.92 eV and 2.49 eV, respectively. The band structure diagram constructed by combining the above results is shown in Figure 6d.

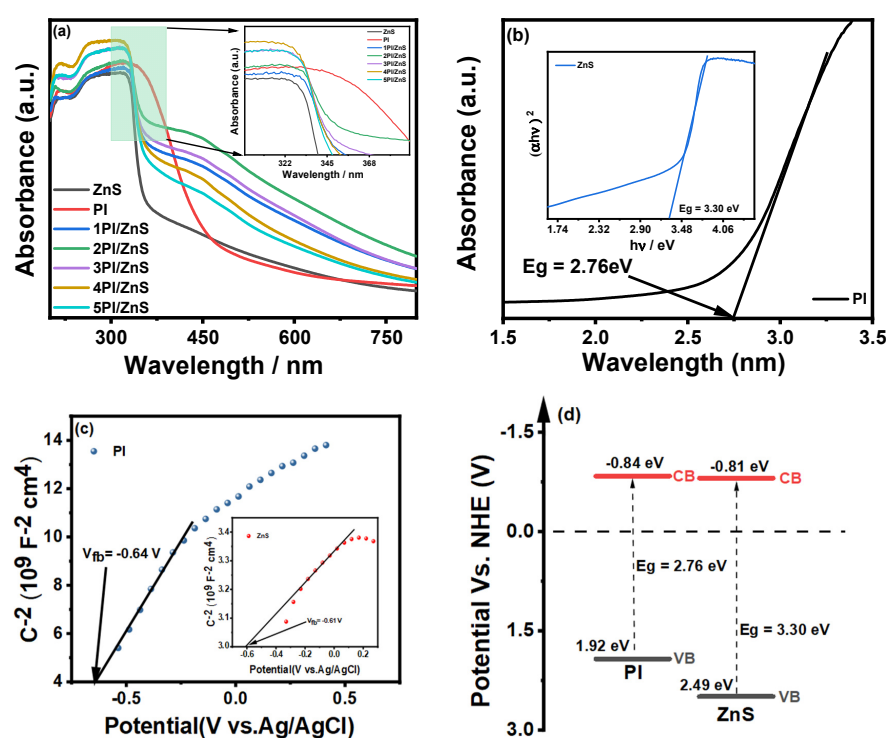


Figure 6. (a) UV-Vis diffuse reflectance spectra of PI, ZnS, and PI/ZnS. (b) Correspondence between $(\alpha h\nu)^2$ and $h\nu$. (c) Mott–Schottky curves of PI and ZnS. (d) Band structure diagrams of PI and ZnS.

When the photocatalyst is irradiated by light with energy higher than its bandgap width, the valence band electrons are excited and transitioned to the conduction band to form excited state carriers. When the excited state electrons return to the ground state, the energy is released in the form of fluorescence. Therefore, the decrease in photoluminescence intensity is closely related to the inhibition of the recombination process of photogenerated carriers. The characterization results of photoluminescence (PL) spectra illustrate the energy conversion characteristics of PI, ZnS, and PI/ZnS composites. As shown in Figure 7, both ZnS and PI exhibit a high photoluminescence response, and ZnS exhibits the strongest characteristic emission peak at $\lambda = 429$ nm, which is attributed to its band edge emission and surface defect state radiation recombination. With the introduction of PI, PI/ZnS composites showed an obvious fluorescence quenching phenomenon, and the effect was related to the doping percentage of PI. It is worth noting that the change in PI content has a significant impact on the PL strength of the composite material. As the PI proportion

increases, the fluorescence intensity first decreases and then increases. Among them, the 3PI/ZnS composite shows the lowest PL fluorescence intensity, indicating that the recombination process of photogenerated carriers is effectively suppressed under this composite proportion. In terms of photocatalytic applications, the 3PI/ZnS heterostructure composite exhibits multiple synergistic advantages. Through the precise regulation of the heterostructure, an efficient charge separation channel is constructed, which significantly inhibits the recombination of photogenerated carriers, thereby achieving the improvement in photocatalytic efficiency [37].

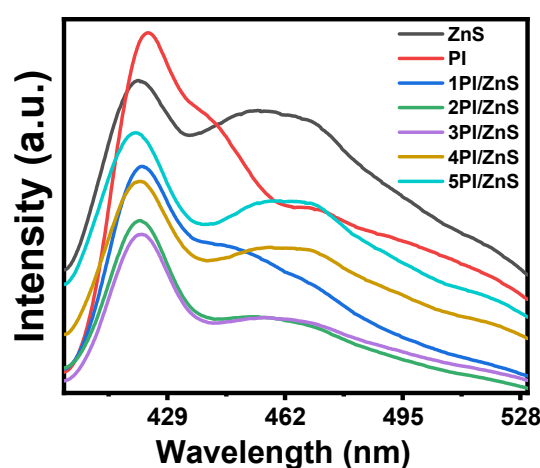


Figure 7. Comparison diagram of photoluminescence spectra of PI, ZnS and PI/ZnS composite.

To further elucidate the photocatalytic reaction mechanism and investigate the transport behavior of charge carriers, EIS and photocurrent response tests were conducted on PI, ZnS, and the 3PI/ZnS composite. As shown in Figure 8a, the EIS Nyquist diagram reveals the electrochemical properties of PI, ZnS, and the 3PI/ZnS composite. Among them, the 3PI/ZnS composite exhibits a significantly reduced charge transfer impedance (the smallest arc radius) [38], showing better electrochemical properties than pure PI and ZnS. This result indicates that the interfacial synergy between PI and ZnS effectively optimizes electron transport and promotes the separation and migration of photogenerated carriers. Under the periodic switching lights, the photocurrent potential curve is drawn, as shown in Figure 8b. Compared with pure PI and ZnS, the 3PI/ZnS composite exhibits higher photocurrent density in the whole potential range, indicating that it has a more efficient photogenerated charge separation ability and lower electron–hole pair recombination rate. This enhanced photocurrent response can be attributed to the synergistic effect between PI and ZnS [17]. ZnS is a typical type of wide-bandgap semiconductor with excellent light absorption capability. The introduction of PI can effectively regulate the energy band structure of the PI/ZnS composite, and by constructing a heterojunction interface, it promotes the separation and migration of photogenerated carriers, thereby improving the charge transport efficiency.

3.3. Photocatalytic Activity and Mechanism

To evaluate the photocatalytic activities of the prepared samples, the photocatalytic hydrogen production performances of PI, ZnS, and PI/ZnS composites were systematically evaluated. Triethanolamine (TEOA) was used as a hole sacrificial agent to compare its photocatalytic hydrogen production activity under simulated sunlight irradiation conditions ($\lambda > 300$ nm, 10 vol% TEOA aqueous solution) [39]. As shown in Figure 9, with the increase in PI doping percentage, the photocatalytic hydrogen production rate of PI/ZnS increases first and then decreases. The 1PI/ZnS composite exhibits the strongest photocatalytic

hydrogen production rate, and its hydrogen production rate reaches $587.71 \mu\text{mol/g/h}$, which is about 19% higher than that of ZnS ($492.58 \mu\text{mol/g/h}$) and 34.61 times higher than that of PI ($16.95 \mu\text{mol/g/h}$). The main reasons for the significant improvement in photocatalytic performance include the following aspects. The PI/ZnS heterojunction was constructed by precisely controlled interface engineering, which realized the directional electron transfer from the ZnS conduction band to PI and further promoted the spatial separation efficiency of charge. The introduction of PI not only significantly improves the specific surface area and dispersibility of the PI/ZnS composite, but also provides rich photocatalytic active sites. It also enhances the light absorption and light response in the visible light region through the interface charge transfer effect [40]. It is particularly noteworthy that when the mass ratio of PI is optimized to 1%, the composite exhibits the best photocatalytic activity.

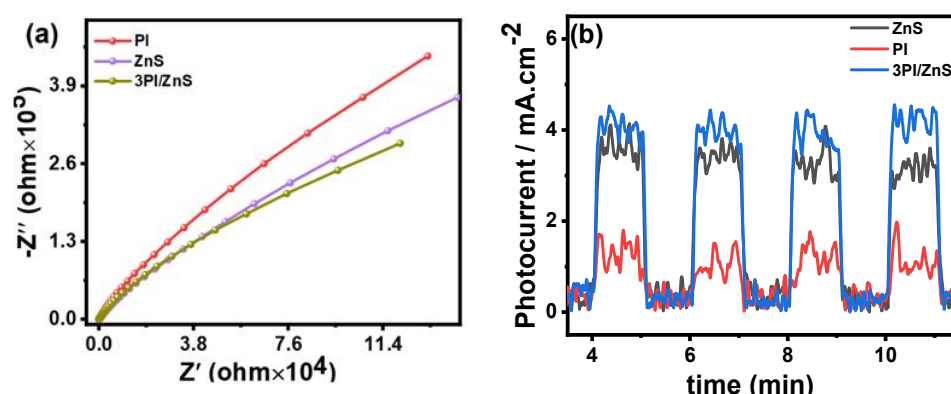


Figure 8. (a) EIS Nyquist plot of electrochemical impedance spectra; and (b) photocurrent potential curves of PI, ZnS, and 3PI/ZnS composite.

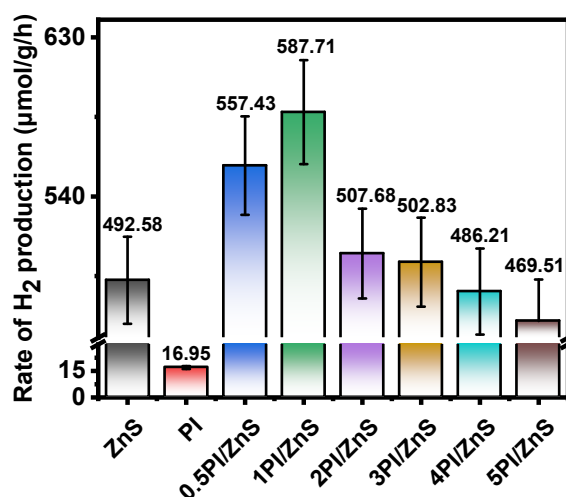


Figure 9. Comparison of hydrogen production rates by photocatalysis of PI, ZnS, and PI/ZnS composite under sunlight irradiation ($\lambda > 300 \text{ nm}$, 10 vol% aq. triethanolamine).

To further evaluate the photocatalytic activities of the prepared samples, the photocatalytic degradation of methyl orange (MO) by PI, ZnS, and PI/ZnS composites was also systematically tested. In view of the fact that MO is a classic organic pollutant [41] and has a stable structure and good oxidation resistance, it was selected as a model pollutant. In this experiment, the photocatalytic degradation of MO by the PI, ZnS, and PI/ZnS catalysts was carried out under visible light ($\lambda > 420 \text{ nm}$). As shown in Figure 10a, the photocatalytic degradation of MO by each sample was compared. In particular, the variation in the PI doping ratio will significantly affect the photocatalytic performance of the

composite material. As the content of PI increases, its photocatalytic activity shows a trend of first increasing and then decreasing. When PI loading in the composite reaches 3%, the obtained 3PI/ZnS exhibits the highest degradation activity, indicating that the optimal loading of PI is 3%. Based on the results of structural analysis (SEM, TEM, BET), UV-visible spectroscopy, and PL and EIS measurements, the 3PI/ZnS sample seems to be more conducive to charge separation. By increasing the mass percentage of PI, the photocatalytic performance of the PI/ZnS composite will decrease instead. It is generally believed that this phenomenon is attributed to excessive PI leading to excessive reduction sites on ZnS. This may hinder the efficient separation of photogenerated electron-hole pairs, thereby limiting further improvement in the separation efficiency of photogenerated carriers in the PI/ZnS composite [42]. At the same time, from Figure 10b, it can also be seen that compared with the single component, the final measured degradation efficiency of the 3PI/ZnS composite sample is nearly 35.5 times that of PI and nearly 1.9 times that of ZnS. Figure 10c displays the photocatalytic degradation kinetics of PI, ZnS and a series of PI/ZnS samples, allowing us to calculate the quasi-first-order reaction rate constant. It can be seen that the rate constant of 3PI/ZnS is the highest. The relevant data can be found in Table S3. In order to make a meaningful comparison between the developed photocatalytic system PI/ZnS and the previously reported materials, the activities of the relevant photocatalysts have been listed, as shown in Table S4. Clearly, compared with other photocatalysts, PI/ZnS exhibits the highest degradation activity through photocatalysis. Additionally, the mineralization degree of the degradation of organic pollutants was also measured. As shown in Figure 10d, the peak at a retention time $t_R = 8.85$ min corresponds to the MO solution. After 1 h of dark reaction of the 3PI/ZnS photocatalyst, no significant change in the intensity of the peak was observed, indicating that the catalyst was not adsorbed. As the irradiation time increases, the intensity of peak A gradually decreases and even disappears. This phenomenon may be attributed to the hydroxylation of the mono-methylated MO. This enhancement in photocatalytic performance is due to several aspects, namely the synergistic effect of PI on the heterojunction constructed on the surface of the ZnS sample and the dispersion of ZnS nanoparticles by the PI sheet structure. In addition, the successful construction of the PI/ZnS composite interface is also essential for obtaining efficient charge transport channels.

The stability test of the 3PI/ZnS composite under continuous 20 h illumination (Figure S2) indicated that the photocatalytic degradation of MO by this 3PI/ZnS composite hardly declined. Through the XRD patterns before and after four consecutive illumination reaction cycles (Figure S3), it was found that the XRD diffraction peak positions of the sample were consistent with those of the fresh sample; no new peaks or peak shifts were observed, confirming that the crystal structure remained stable without collapse or phase transformation. These results demonstrate the excellent stability of the PI/ZnS composite.

To further elucidate the formation and role of active species during the MO photocatalytic degradation process, electron spin resonance (ESR) tests were conducted on ZnS, PI, and the 3PI/ZnS composite [43]. Figure 11 shows the ESR free radical capture spectra of ZnS, PI, and the 3PI/ZnS composite under dark and light conditions with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a free radical scavenger for ESR signal measurement. As shown in Figure 11a, the ESR spectra of the ZnS, PI, and 3PI/ZnS composite samples under dark conditions showed no characteristic peaks. As shown in Figure 11b, the ESR spin capture images of the ZnS, PI, and 3PI/ZnS composite samples under illumination have obvious characteristic peaks, indicating that $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ are induced by light. Clearly, each sample shows a completely different signal intensity under light irradiation. The ZnS sample has a strong $\cdot\text{O}_2^-$ and a relatively weak $\cdot\text{OH}$ signal. Because of its higher CB position, it can well reduce O_2 to obtain more $\cdot\text{O}_2^-$, but has almost no $\text{H}_2\text{O}/\text{OH}^-$

oxidation ability. PI showed a weak $\cdot\text{O}_2^-$ signal, and almost no $\cdot\text{OH}$ was detected. This result may be due to the presence of some electron–hole pairs in the counter center, leading to their recombination. Interestingly, the $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ signals of the 3PI/ZnS composite are weaker than those of ZnS under illumination, which means that the combination of PI and ZnS conforms to the traditional type II heterojunction structure.

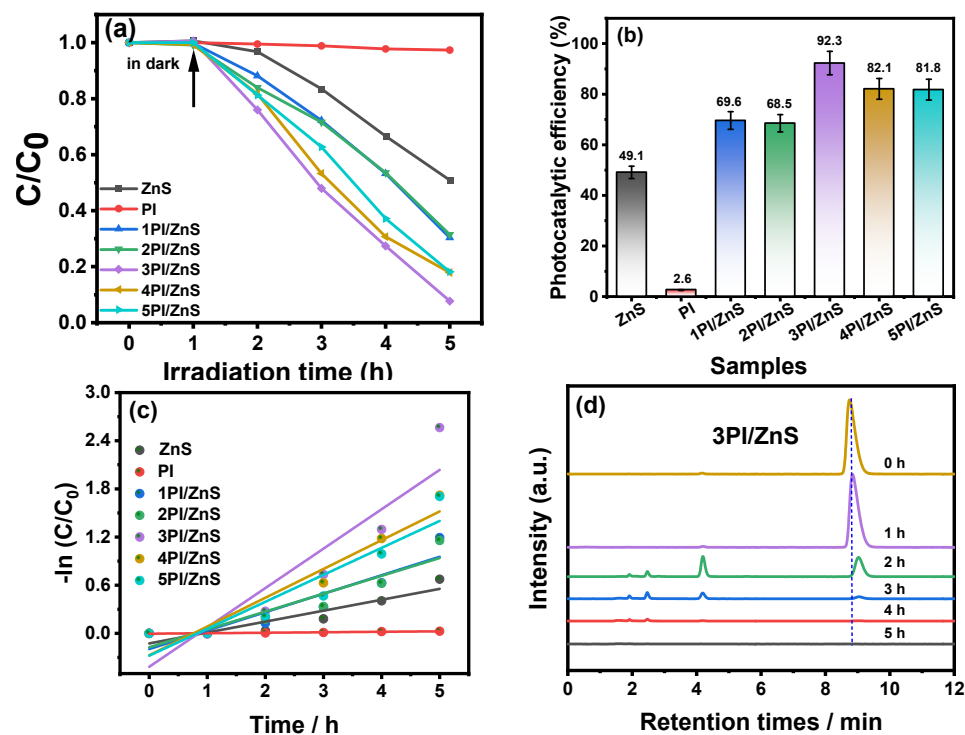
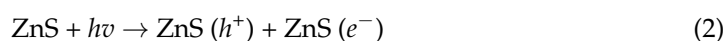


Figure 10. (a) Comparison of photocatalytic degradation rates, (b) photocatalytic degradation efficiency and (c) kinetics of MO by ZnS, PI and PI/ZnS composite under illumination ($\lambda > 420$ nm); (d) high-performance liquid chromatography (HPLC) spectra of MO on 3PI/ZnS after different light irradiation times.

As shown in Figure 12, the PI/ZnS composite exhibits the typical band arrangement characteristics of a type II heterojunction. Based on the analysis of band positions, the bandgap widths of PI and ZnS are 2.76 eV and 3.30 eV, respectively. After their combination, a traditional type II heterojunction structure can be formed. According to the ESR results, the change in $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ signal intensity produced by PI/ZnS composites is consistent with the traditional type II heterojunction charge transfer. According to the carrier transport mechanism of the traditional type II heterojunction, the photogenerated electrons on the PI conduction band (CB) are transferred to the ZnS conduction band (CB), while the photogenerated holes in the ZnS VB will migrate to the PI VB. Therefore, the electrons obtained on the CB of ZnS will easily generate $\cdot\text{O}_2^-$ through O_2 , and the holes absorbed by the PI VB will also oxidize H_2O to form $\cdot\text{OH}$. The ESR spectroscopy results indicate that the conventional type II heterojunction formed at the PI/ZnS interface is the main electron transfer channel in this system and plays a dominant role in the migration of photogenerated carriers, which is also consistent with the results obtained for other aspects, such as band structure, photocatalytic performance, and other test results. Consequently, the photocatalytic mechanism proceeds as follows:



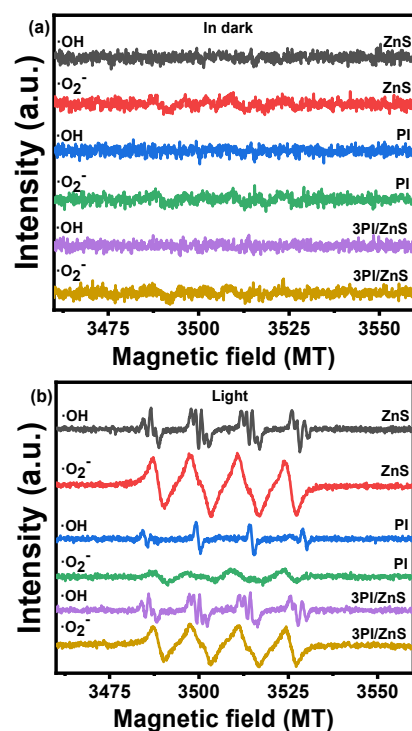
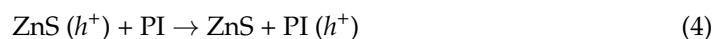
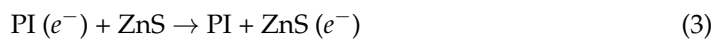


Figure 11. ESR spin-lattice spectra of ZnS, PI and 3PI/ZnS composite under different light conditions: (a) dark reaction condition; (b) light reaction condition.

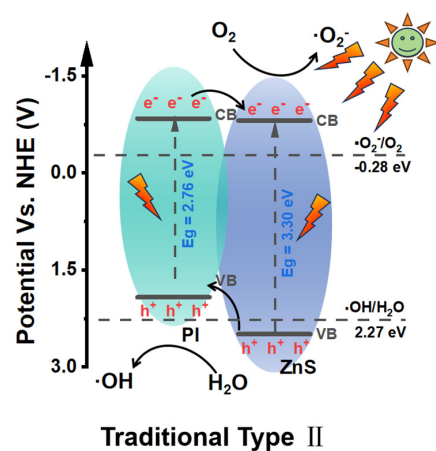


Figure 12. Schematic diagram of PI/ZnS traditional type II heterojunction.

4. Conclusions

In summary, an efficient traditional type II heterojunction PI/ZnS composite photocatalyst was constructed in this work. Through the test of energy band structure and ESR, it is

confirmed that the electrons migrate from PI to the CB of ZnS, and the holes migrate from ZnS to the VB of PI, which indicates that the PI/ZnS composite has formed a traditional type II heterojunction. Moreover, such carrier migration can expand the absorption range of light, which is beneficial to promote the separation of carriers and prolong their lifetime. The maximum photocatalytic H₂ generation rate of 1PI/ZnS material is 587.7 µmol/h/g, which is 1.2 times that of ZnS and 34.6 times that of PI. In terms of organic pollution degradation, 3PI/ZnS has the highest photocatalytic activity, reaching 92.3% degradation efficiency, which is 35.5 and 1.9 times higher than that of PI and ZnS, respectively. The improvement in photocatalytic activity of the PI/ZnS composite may be attributed to the formation of a type II heterojunction at the interface between PI and ZnS. This not only effectively hinders the recombination of photogenerated carriers but also ensures that there are enough photogenerated carriers for the redox reaction, which greatly enhances photocatalytic performance under light irradiation. This work presents a simple synthesis method for preparing a PI/ZnS composite, which is a highly promising photocatalyst for environmental purification and energy conversion applications.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/surfaces9030062/s1>, Catalyst characterization. Figure S1: FT-IR patterns of ZnS, PI, and PI/ZnS composite. Figure S2: Cyclic experiment of 3PI/ZnS under full-amplitude light irradiation. Figure S3: XRD patterns of 3PI/ZnS composite before and after 4 cycles of photoreaction. Table S1: Peak intensity and full width at half maximum of ZnS and a series of PI/ZnS materials. Table S2: Average pore size of PI, ZnS, and 3PI/ZnS. Table S3: The degradation kinetics of PI, ZnS, and a series of PI/ZnS samples were fitted by the K value. Table S4: Comparison of PI/ZnS photocatalysts with other systems.

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