



# Article Rational Design and Synthesis of ZnWO<sub>4</sub> Nanorods Decorated with SnS Nanodots with Enhanced Visible-Light Photocatalytic Performance

Xiaoyi Shan <sup>1,2</sup>, Tiekun Jia <sup>2,\*</sup> and Fang Fu <sup>2</sup>

- <sup>1</sup> Siping Hongda New Material Technology Co., Ltd., Siping 136000, China; shan@sphdyy.com
- <sup>2</sup> Henan Province International Joint Laboratory of Materials for Solar Energy Conversion and Lithium Sodium Based Battern Lucrence Institute of Spin on and Tarke also and Materials for Solar Energy (2002). China (47,022)
- Based Battery, Luoyang Institute of Science and Technology, Luoyang 471023, China; fufang1@lit.edu.cn \* Correspondence: tiekunjia@126.com or tiekun\_jia@lit.edu.cn; Tel.: +86-379-6592-8196

**Abstract:** Aiming to construct a direct Z-scheme binary heterostructure for efficient degradation of the organic dye Rhodamine B (RhB), ZnWO<sub>4</sub> nanorods decorated with SnS nanodots were rationally designed and prepared via a facile two-step route. Morphological observation and structural study showed that ultra-fine SnS nanodots were anchored on the surface of ZnWO<sub>4</sub> nanorods to form an intimate contact between the two components. Such a special structure provided SnS/ZnWO<sub>4</sub> nanocomposites with significantly enhanced light harvesting capacity, revealed by the results of UV-vis diffuse reflection spectroscopy (DRS). Photoluminescence (PL) analysis in combination with electrochemical measurements demonstrated that the recombination of photoactivated charge carriers was efficiently inhibited and the transfer of photoactivated charge carriers was successfully achieved due to the introduction of SnS. The degradation rate over SnS/ZnWO<sub>4</sub> nanocomposites reached a maximum value at SnS content of 9 wt%. The significantly enhanced light absorption ability and effective photogenerated charge carriers' transfer and separation.

Keywords: ZnWO4; SnS; binary heterostructure; visible-light; photocatalytic degradation

# 1. Introduction

After stepping into the 21st century, a large number of pollutants from industry and aquaculture have been increasingly charged into water. By now, water contamination has become a worsening problem, which is most likely to be evolved as a huge obstacle for the sustainable development of human beings, since water resources are a vital factor to the living of human beings. Additionally, most of the charged pollutants from wastewater are of high stability, and cannot be naturally degraded in the environment. The existence of the above hazardous pollutants will pose an increasingly serious threat to humanity's future. Thus, establishing an alternative environmentally friendly and sustainable approach for the remediation of soluble organic pollutants has become a matter of primary importance. Semiconductor photocatalysis technology is endowed with several notable merits, such as easy control, sufficient degradation, and zero secondary pollution, as well as ecological safety, and is reckoned as one of the most promising solutions to remediate water contamination [1–4].

Previous studies showed that  $ZnWO_4$  (ZWO) belongs to a kind of wide band-gap semi-conductors (3.5 eV) with the appropriate conduction band and valence band positions. Thus, ZWO nanomaterials have drawn substantial interest and been widely investigated in photocatalysis due to their high photosensitivity, excellent chemical stability, and nontoxicity [5,6]. Zhu et al. adopted a hydrothermal route to prepare ZWO nanorods, and initiated an interesting research on the influence of aspect ratio of ZWO nanorods on the photocatalytic degradation of methylene blue under ultraviolet light irradiation [7]. The



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**Copyright:** © 2021 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/). results showed that increasing the aspect ratio of ZWO nanorods elevated the separation rate of photoactivated electron-hole pairs. Saravanakumar et al. prepared ZWO nanoparticles with the aid of different surfactants and investigated the catalytic activity toward the photodegradation of ciprofloxacin drug [8]. Wang and his coauthors reported a simple solvothermal procedure to prepare porous hydrangea-like ZnWO<sub>4</sub> microspheres. The results showed that the hierarchical porous structure contributed to the enhancement of photocatalytic performance under UV light irradiation [9]. A chemical polymerization method was developed by Brijesh and his coauthors to prepare a sponge-like  $PPy/ZnWO_4$ nanocomposite, which showed excellent electrocatalytic activity [10]. Based on above demonstration, the continuously deep insight into the modification of single phase ZnWO<sub>4</sub> has indeed elevated its catalytic activity, however, the key issues hampering the practical application of pure ZWO still exist and can mainly be summarized in two aspects: one is narrow light absorption range, the other is poor quantum efficiency. Undoubtedly, coupling of ZWO with another photocatalyst with suitable band positions is regarded as a promising and valid approach to solve the above key issues [11–13]. Previously, Huo et al. reported the fabrication of ZnWO<sub>4</sub>-CdS heterostructure photocatalysts toward the efficient degradation of ciprofloxacin antibiotics under visible light irradiation [11]. Panneerselvam et al. prepared graphitic carbon nitride decorated ZWO heterojunctions and discussed the effect of the dosage of graphitic carbon nitride on the photocatalytic activity. The results showed that the g-C<sub>3</sub>N<sub>4</sub>-ZnWO<sub>4</sub> hybrid photocatalysts exhibited outstanding visible-light degradation efficiency toward Rhodamine B (RhB) [12]. As for photocatalytic hydrogen evolution,  $ZnWO_4/ZnFe_2O_4$  composites were designed and prepared via a facile coprecipitation approach, and the results showed that the optimal loading amount of ZnFe<sub>2</sub>O<sub>4</sub> is 30% for achieving the largest hydrogen evolution rate [13]. Based on above, the coupler, such as CdS, g-C<sub>3</sub>N<sub>4</sub>, ZnFe<sub>2</sub>O<sub>4</sub>, and so on, not only amplifies the photoresponse range of composite photocatalysts, but also lessens the annihilation rate of photogenerated charge carriers. Thus, pursuing a novel and suitable sensitizer is of great interest to constructing ZWO heterostructured photocatalysts with excellent photocatalytic performance.

Previous studies reported that the morphological and structural characteristics of hybrid materials are strongly related to their photocatalytic activities [14–19]. Among them, the quantum dots (QDs) sensitizer in hybrid systems has drawn great attention, because it can lessen the average diffusion time of photo-activated charge carriers from bulk to surface due to its tiny particle size, resulting in restricting the recombination rate of electrons and holes [18,19]. Besides the above, such a hybrid system can efficiently avoid self-aggregation and become more dispersive and stable owing to the high surface energy and substantial defects of QDs sensitizer. Simultaneously, the tight interaction between the sensitizer and the matrix can facilitate the efficient migration and separation of photo-activated electrons and holes. As for SnS, it has a wide photoresponse range from visible-light to near infrared owing to its narrow band-gap (~1.3 eV) [20]. In our previous work, SnS was proved to be used as an efficient coupler for the synthesis of  $g-C_3N_4/SnS$  with enhanced photocatalytic performance [21]. Inspired by the achievements above, we intended to rationally design ZnWO<sub>4</sub> nanorods decorated with SnS nanodots and investigate the photodegradation performance toward RhB pollutants under visible-light irradiation. It is reasonably anticipated that construction of ZnWO<sub>4</sub> nanorods decorated with SnS nanodots is promisingly effective to achieve excellent visible-light photocatalytic performance.

Herein, we employed a facile two-step route to prepare ZnWO<sub>4</sub> nanorods decorated with SnS nanodots. Firstly, ZnWO<sub>4</sub> nanorods with small diameters were hydrothermally prepared at 160 °C. Subsequently, ultra-fine SnS nanodots were in-situ anchored on the surface of ZnWO<sub>4</sub> nanorods to form hybrid composites. SnS/ZnWO<sub>4</sub> hybrid composites were well characterized by a series of testing techniques, and their photocatalytic activities were investigated through the photodegradation of RhB under visible-light irradiation. The results showed that the loading amount of SnS had an extremely notable effect on the photocatalytic activity. To our knowledge, this work is the first report about the preparation and catalytic activity of SnS nanodots/ZnWO<sub>4</sub> nanorods hybrid photocatalysts.

# 2. Results and Discussion

## 2.1. Characterization of As-Prepared Catalysts

Morphological observation of the as-prepared ZWO and SnS/ZWO hybrid composites was executed by FESEM. Figure 1 displays FESEM images and elemental mapping images of as-prepared ZWO and SZWO-9 samples. From the panoramic and high magnification image (Figure 1a,b), it can be inferred that pristine ZWO is composed of substantial numbers of nanorods with average length of 100 nm. After the addition of SnS, no obvious change about morphology can be observed for the as-prepared SnS/ZWO hybrid composites from Figure 1c,d. The main reason for inconspicuous morphology variation is probably that the formed SnS nanodots are ultrafine in the in-situ reaction. In efforts to demonstrate the existence of SnS in hybrid composites, EDS analysis was performed and the results are displayed in Figure 1e, from which we can see that both Sn and S elements are homogeneously distributed throughout the product. Clear nanorod-like morphology of ZWO was further observed by high resolution transmission electron microscopy image, as is shown in Figure 2a. The average diameter of ZWO nanorods was about 25 nm. In the marked region, it is obvious that ultrafine SnS nanodots were anchored on the surface of ZWO nanorods. Additionally, SnS nanodots had an irregular sphere-like shape with a size of about 3–5 nm. High-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) image is presented in Figure 2b, from which it can be found that Sn and S elements are uniformly distributed on the surface of ZWO nanorods, leading to the formation of intimate interface between ZWO nanorods and SnS nanodots.



**Figure 1.** (**a**,**b**) Low magnification SEM image and high magnification SEM image of ZWO sample; (**c**,**d**) low magnification SEM image and high magnification SEM image of the SZWO-9 sample; (**e**) elemental mapping of the SZWO-9 sample.



**Figure 2.** (a) HRTEM image of the SZWO-9 sample; (b) HAADF-STEM image and EDS elemental mapping images of the SZWO-9 sample.

The phase structure of the as-prepared ZWO, SnS and SnS/ZWO hybrid composites was determined by X-ray diffraction patterns, as is depicted in Figure 3. For pristine ZWO, all distinguishable diffraction peaks are perfectly in accord with those of monoclinic ZnWO<sub>4</sub> reported in standard JCPDS card (89-7624). Specifically, several main peaks observed at 20 value of 15.45°, 18.87°, 23.77°, 24.48°, 30.65°, 36.3°, 38.28°, 41.25°, 51.62°, 53.88°, 61.66°, and 64.66° were individually indexed (010), (100), (011), (110), (111), (002), (200), (121), (130), (221), (-113) and (-131) planes of ZWO. Moreover, no other peaks related with Zn, W and O elements revealed its high purity, and narrow and sharp diffraction peaks with relatively high intensity demonstrated its good crystallinity. As for pure SnS, all diffraction peaks are in perfect accordance with those of orthorhombic phase SnS reported in JCPDS card (39-0354). Weak and broad diffraction peaks of SnS signified its poor crystallinity. No obvious change occurred to the diffraction patterns of SnS/ZWO hybrid composites, probably due to the fact that the formed SnS nanodots adhering to the surface of ZWO nanorods are in low concentration with inferior crystallinity. Aiming to gain an insight into the interaction between ZWO and SnS, XPS measurement was taken to probe the chemical status of Zn, W, O, Sn and S elements. Figure 4 shows the high resolution XPS spectra of ZWO, SnS and SZWO-9 sample. Based on the results presented in Figure 4, it can be concluded that the SZWO-9 sample is composed of Zn, W, O, Sn and S elements, which is in perfect accord with the observation in XRD patterns. However, it is worth mentioning that the binding energies of Zn 2p, Sn 3d, and O1s for SZWO-9 are different from those of the counterparts for pristine ZWO. Specifically, the high resolution Zn 2p spectrum displayed two contributions positioning at 1045.98 eV and 1022.78 eV core-level spin-orbit of  $Zn^{2+}$  ion oxidation state, individually ascribing to  $Zn 2p_{1/2}$  and  $Zn 2p_{3/2}$ . Both of them exhibited a shift of about 0.6 eV toward high binding energy direction in comparison with those in high resolution Zn 2p spectrum for pristine ZWO. Simultaneously, a similar blue shift was found in W4f and O1s spectra for the SZWO-9 sample; only the value of the blueshift for W 4f and O 1s is different from that for Zn 2p. On the contrary, Sn  $3d_{5/2}$  and Sn  $3d_{3/2}$  peak positioning at 485.58 eV and 494.68 eV for SZWO-9 sample displayed a notable shift toward low binding energies by ca. 0.4 eV compared with those of pristine ZWO. Similarly, a red shift was also observed in S 2p spectrum for the SZWO-9 sample. The blue shift or red shift of binding energies is most possibly correlated with the strong interaction between ZWO nanorods and ultrafine SnS nanodots. Theoretically, charge carriers will migrate from one to the other under the built-in electric field, when two semiconductors combine together. The migration of electrons between two components will result in the variation of electron concentration. According to the demonstration of electron screening effect [21-24], decreased electron concentration makes a valuable contribution to the augment of binding

energies, but increased electron concentration is responsible for the decrescence of binding energies. In this work, we can infer that after ZWO nanorods are in contact with ultrafine SnS nanodots, interfacial charge carrier transfer from ZWO to SnS would occur, then lead to the decrease of electron concentration in ZWO, inducing the binding energies of Zn 2p and W 4f shift toward higher energy direction.



Figure 3. XRD patterns of ZWO, SnS and SnS/ZWO hybrid composites.

Figure 5 presents nitrogen adsorption-desorption isotherms of ZWO, SnS and SZWO-9 samples. From Figure 5a, it is distinct that the above three samples display type IV isotherm combining with typical H3 hysteresis loop in light with Brunauer–Deming–Deming–Teller (BDDT) classification. The features of the above isotherms indicated mesoporous structures of the as-prepared products, arising from the interspaces of the aggregated nanorods or nanoparticles. Referring to the Brunauer–Emmett–Teller (BET) method, the specific surface area (S<sub>BET</sub>) of ZWO was measured to be 26.5 m<sup>2</sup>/g, while the S<sub>BET</sub> value for SZWO-9 increased up to 51.2 m<sup>2</sup>/g after the introduction of SnS. The feature of larger specific areas is capable of providing more active sites and strong adsorption ability for pollutant molecules. From Figure 5b, it can be clearly deduced that tiny pores with the size 2~3 nm were especially dominant in the pore distribution for SZWO-9 sample compared with pristine ZWO, probably accrediting to the stacking of SnS nanodots in the hybrid system.

As is well known, UV-Vis spectrum can reveal the light absorption range and absorbance of a semiconductor under being activated by radiant photon energy. Herein, the light absorption characteristics of pristine ZWO and SnS/ZWO hybrid photocatalysts were examined by UV-vis DRS to pursue the effect of SnS loading an amount on the optical property. Owing to its intrinsic characteristic of large band-gap energy, pristine ZWO displayed a relatively narrow absorption range and strong absorption capacity in the UV light region, as is seen from the curve in Figure 6a. After hybridization of ZWO nanorods with SnS nanodots, a continuous redshift is clearly found in the absorption band of composite photocatalysts with the increase of SnS loading amount. Specifically, not only the light absorption range is substantially broadened access to visible-light, but also the absorbance intensity is continuously enhanced in comparison with pristine ZWO. In order to estimate band gap energies of pristine ZWO and SnS, the plots of photon energy (hv) with respect to ( $\alpha$ hv)<sup>2</sup> are displayed in Figure 6b,c. According to the Tauc plots [25], the band gap energies individually approached 3.9 eV and 1.4 eV for ZWO and SnS. However, the band gap energy for ZWO is a bit larger than that in previous study [8], mainly ascribed to its fine size of nanorods. Based on above, the establishment of binary heterostructure through strong interaction between ZWO nanorods and SnS nanodots is capable of reducing bandwidth with improved light-absorbing ability of hybrid photocatalysts. Thus, more incident visible light can be harvested for augmenting the number of photoactivated charge carriers, which could facilitate the generation of more active radicals.



Figure 4. High resolution XPS spectra of the SZWO-9 sample, (a) Zn 2p, (b) W 4f, (c) O 1s, (d) Sn 3d; (e) S 2p.

(b) (a) 0.012 zwo Volume adsorbed (cm<sup>3</sup>/g) SnS SZWO-9 dV/dD(cm<sup>3</sup>/g/nm) 0.009 0.006 szwo-9 0.003 SnS 0.000 zwo 20 5 10 15 25 0.0 0.2 0.6 0.8 1.0 0.4 Relative pressure (P/P<sub>0</sub>) Pore diameter (nm)

**Figure 5.** (a) The Nitrogen adsorption–desorption isotherms and (b) the corresponding pore size and distribution curves of ZWO, SZWO-9 and SnS samples.



**Figure 6.** (a) UV–vis absorbance spectra of ZWO, SnS and SnS/ZWO hybrid composites, (b) the derived plot of  $(\alpha hv)^2$  versus hv from the absorption spectrum for ZWO; (c) the derived plot of  $(\alpha hv)^2$  versus hv from the absorption spectrum for SnS sample.

## 2.2. Photocatalytic Performance

In this research work, RhB was determined as the model pollutant to examine the photodegradation efficiency of ZWO nanorods and SnS/ZWO hybrid catalysts. Figure 7 displays the photodegradation curves of RhB under different conditions. Among them, the concentration of RhB exhibited little change in the absence of catalysts under visible-light irradiation. The concentration of RhB solution over pristine ZWO catalyst gradually dwindled with illumination time prolonging. It took 100 min for the ZWO catalyst to degrade 55.8% of RhB molecules, suggesting the inferior photodegradation efficiency,

which was mainly ascribed to the weak light absorption capacity and high recombination rate of photoinduced electron-hole pairs. However, after the hybridization of ZWO with SnS, the concentration of reacted RhB solution promptly dwindled away. Furthermore, there existed notable discrepancy among photodegradation curves over SnS/ZWO hybrid catalysts with different loading amounts of SnS, that is to say, the loading amount of SnS exerted a remarkable impact on the photodegradation efficiency. Specifically, the photodegradation rate of RhB first increased with the increase of the loading amount of SnS. Thereafter, it decreased with the loading percentage of SnS beyond 9%. The SZWO-9 sample showed the highest photodegradation rate. About 97.5% of RhB molecules were degraded under 80 min of visible light illumination.



**Figure 7.** (**a**) the photodegradation performance of RhB solution, (**b**) the corresponding apparent reaction rate constant, (**c**) cycling performance of the photodegradation of RhB solution over the SZWO-9 sample.

Owing to the fact that the removal of RhB followed the pseudo-first order reaction kinetics of  $-\ln(C/C_0) = kt$ , where k,  $C_0$  and C, respectively, represent reaction rate constant, initial concentration, and concentration at time t of RhB concentration, the kinetic constant (k) values for RhB over different catalysts are shown in Figure 7b. It is clearly observed from Figure 7b that the SZWO-9 had the highest constant value, being approximately 0.046 min<sup>-1</sup>, which was probably 8 times higher than that of pristine ZWO. Moreover, the variation trend of the constant value was similar to that of the photodegradation rate. Considering that the enduring stability and reusability of the catalyst should be addressed in practical application other than photodegradation efficiency, the SZWO-9 sample was taken as the target catalyst to recycle RhB photodegradation for four successive runs under the identical conditions. In each cycling experiment, the recovered catalyst was centrifuged, respectively, washed by D.I. water and alcohol for five times, finally dried at 70 °C for 10 h. The concentration profiles of RhB solution is presented in Figure 7c. As is seen from Figure 7c, the photodegradation rate only decreased a little bit after four successive runs, demonstrating the excellent enduring stability and reusability of the hybrid catalyst.

### 2.3. Possible Enhancement Mechanism

As demonstrated above, the hybridization of ZWO nanorods with SnS nanodots led to the enhancement of light absorption capacity and the augment of specific surface area. Thus, more photoactivated electron-hole pairs and active sites were likely to be generated in SnS/ZWO hybrid catalysts than those in pristine ZWO, which would make a great contribution to the enhancement of photodegradation efficiency. Besides above, the variation of the charge carrier separation before and after contact of ZWO nanorods and SnS nanodots imposed a prevailing influence on the improvement of photodegradation efficiency. To ascertain the variation of the charge carrier recombination rate before and after contact, PL spectra measurement was performed and the results are displayed in Figure 8a. It is clear that pristine ZWO exhibited the highest intensity of emission peak among all tested samples, owing to its high photoactivated charge carrier's recombination rate. After hybridization, the PL intensity of SnS/ZWO composites decreased continuously until the concentration of SnS was up to 9%, thereafter, the PL intensity of SnS/ZWO composites increased with the increase of SnS concentration. The above result could reflect the variation of the photoinduced charge carrier recombination rate, which was in good accordance with the observation of RhB photodegradation. In order to further examine the process of charge carrier migration, the electrochemical measurement was performed and the results are presented in Figure 8b,c. Generally, the stronger photocurrent intensity is intimately associated with the higher separation efficiency of photogenerated electrons and holes. From Figure 8b, the SZWO-9 sample possesses the largest photocurrent, manifesting its fast separation rate of charge carriers. As is well known, electrochemical impedance spectra (EIS) is capable of reflecting the interfacial barrier for the flow and transfer of charge carriers. Moreover, the smaller the arc radius in a Nyquist plot is, the faster separation rate and higher transfer efficiency of interfacial charge carriers are. In Figure 8c, the Nyquist plot of the SZWO-9 sample displays a smaller semicircle than the other two samples, being well indicative of its lowest charge transfer resistance. The above result could demonstrate that the fastest interfacial charge transfer and most efficient separation rate have been successfully achieved in the SZWO-9 sample, agreeing well with that of photocatalytic activity.



**Figure 8.** (a) PL spectra of ZWO and SnS/ZWO hybrid composites, (b) transient photocurrents and (c) electrochemical impedance spectra of ZWO, SZWO-9 and SnS electrodes under visible light irradiation; (d) effect of various scavengers on the visible light photocatalytic performance of the SZWO-9 sample.

Herein, benzoquinone (BQ 1 mmol L<sup>-1</sup>), tert-butyl-alcohol (t-BuOH 1 mmol L<sup>-1</sup>), and EDTA disodium (EDTA-2Na 1 mmol L<sup>-1</sup>) were, respectively, used as scavengers to capture  $O_2^-$ , •OH, and h<sup>+</sup> radicals for better understanding the effect of the active radicals on the photodegradation of RhB solution. The results of a radical scavenging experiment are shown in Figure 8d, from which a neglectable change in photodegradation rate of RhB was noticed after the addition of BQ, signifying that  $O_2^-$  posed a limited effect on the RhB decomposition process. However, the addition of t-BuOH or EDTA-2Na into the reaction system profoundly suppressed RhB decomposition, demonstrating that •OH or h<sup>+</sup> was the major radical dominating the photodegradation reaction process.

According to Mulliken's electronegativity theory [26], the flat-band potentials of ZWO and SnS can be estimated by typical equations as follows.

$$E_{CB} = X - E^e - 0.5E_g$$
 (1)

$$E_{VB} = E_{CB} + E_g \tag{2}$$

Here, X represents the absolute electronegativity dominated by the geometric mean of the componential atoms electronegativity. For ZnWO<sub>4</sub> and SnS, the X values are individually 6.59 eV and 5.13 eV.  $E_e$  is corresponding to the energy of free electrons with the value of about 4.5 eV. The Eg of  $ZnWO_4$  and SnS were individually determined to be 3.9 eV and 1.4 eV on the basis of DRS results. By calculation, the  $E_{CB}$  of ZnWO<sub>4</sub> and SnS were, respectively, designated as 0.14 eV and -0.07 eV, while the  $E_{VB}$  of ZnWO<sub>4</sub> and SnS as 4.04 eV and 1.33 eV. Based on the above results, a plausible schematic mechanism is depicted in Figure 9 to illustrate the remarkable improvement of photocatalytic behavior for SnS/ZWO hybrid catalysts. As previously reported, pristine ZWO exhibited visible-light driven photocatalytic activity, indicating that ZWO could be excited under visible-light illumination, mainly ascribed to the existence of its defect energy level. Upon visible-light illumination, the electrons from VB position of SnS are readily excited, then migrate to CB position due to its narrow band-gap energy. Assuming that the formed SnS/ZWO system obeys the typical II heterojunction electron-transfer mechanism, the photogenerated electrons on the CB of SnS would flow to that of ZnWO<sub>4</sub>. Accordingly, this photogenerated electron flow would result in the increase of electron concentration in ZWO, which is contradictory to the result of XPS measurements. For this purpose, we think that the formed SnS/ZWO system should be subordinated to the Z-scheme heterojunction electron-transfer mechanism based on the results of scavenging experiments and XPS measurements. The photogenerated electrons in the CB of ZnWO<sub>4</sub> flow toward the VB position of SnS and experience recombination with holes eventually. The remained holes in the VB of ZnWO<sub>4</sub> are positive enough to oxidize OH<sup>-</sup> to form  $\cdot$ OH active species (E<sup>0</sup> OH<sup>-</sup>/ $\bullet$ OH (1.99 eV) vs. NHE) [27–30], which could involve the photocatalytic reaction and effectively degrade RhB molecules. The above demonstration was in good accordance with the result of the scavenging experiment. These novel findings demonstrate that the construction of Z-scheme binary ZnWO<sub>4</sub> nanorods/SnS nanodots composites can efficiently improve the charge-transfer process and the separation of photoinduced charge carriers, which contributes to the remarkable enhancement of RhB photodegradation.



**Figure 9.** Schematic diagram of proposed transfer and separation pathway of photogenerated carriers over SnS/ZWO hybrid system under visible-light irradiation, (**a**) for separate phases and (**b**) after the formation of binary heterostructure.

## 3. Materials and Methods

## 3.1. Materials

The chemicals used in this work, including sodium tungstate dihydrate ( $Na_2WO_4.2H_2O$ ), tin dichloride dihydrate ( $SnCl_2.2H_2O$ ), zinc acetate dihydrate ( $Zn(CH_3COO)_2.2H_2O$ ), sodium sulfide nonahydrate ( $Na_2S.9H_2O$ ), Rhodamine B (RhB), and ethanol were purchased from Sinopharm Chemical Reagent CO., Ltd., Shanghai, China.

### 3.2. Synthesis of SnS/ZnWO<sub>4</sub> Composite

Consulting previous study [6,7], ZnWO<sub>4</sub> (ZWO) nanorods were prepared via an improved hydrothermal route. Briefly, 2 mmol of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and 2 mmol of Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O were separately dissolved into the mixed solvents containing 30 mL deionized water (DIW) and 10 mL ethanol under vigorous magnetic stirring (about 600 r/min). After forming a transparent and homogenous solution, the Na<sub>2</sub>WO<sub>4</sub> solution was added into the Zn(CH<sub>3</sub>COO)<sub>2</sub> solution drop by drop under continuously vigorous stirring for 40 min. Subsequently, the above mixture was poured into a Teflon-lined autoclave (100 mL), then heated to 160 °C and kept for 15 h. After that, the autoclave was naturally cooled down to room temperature. The resulting precipitate was collected through centrifuging, washing with DI.W and ethanol, and drying at 70 °C for 8 h.

SnS nanodots/ZnWO<sub>4</sub> nanorods hybrid composites were prepared with above ZnWO<sub>4</sub> nanorods via a simple in situ deposition route according to our previous study [31]. 0.3 mmol of SnCl<sub>2</sub>·2H<sub>2</sub>O was added into the mixed solvents, composed of 20 mL DI.W and 5 mL HCl (0.1 M). After ultra-sonication for 15 min, a designated amount of ZnWO<sub>4</sub> nanorods was dispersed into the SnCl<sub>2</sub> solution under vigorous stirring (about 600 r/min). At the same time, the equal amount of Na<sub>2</sub>S·9H<sub>2</sub>O (0.3 mmol) was dissolved into 25 mL DI.W under continuous stirring to form a homogeneous solution, which was added dropwise into the mixture containing ZnWO<sub>4</sub> nanorods and SnCl<sub>2</sub> in the subsequent procedure. Afterwards, the resulting mixture was treated in a water bath at 50 °C for 2 h to promote the crystallization of SnS. Finally, SnS nanodots/ZnWO<sub>4</sub> nanorods with different weight ratio of 3%, 6%, 9%, and 12%, was prepared and, respectively, labeled as SZWO-3, SZWO-6, SZWO-9, and SZWO-12 for convenience.

#### 3.3. Characterization

The X-ray diffraction patterns (XRD) of ZWO, SZWO and SnS samples were recorded on an X-ray diffractometer (D8 Advance, Bruker, Billerica, MA, USA) with Cu-K $\alpha$  irradiation (1.5406Å). The morphological features and microstructure of the as-prepared catalysts were probed on a field emission electron scanning microscope (Hitachi S-4800, Tokyo, Japan) in combination with a transmission electron microscope (JEM-2100F, JEOL Ltd., Tokyo, Japan). The surface components and chemical status were examined by X-ray photoelectron spectroscopy (XPS) measurement with an X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi, Thermo Fisher Scientific cooperation), using C1s (284.6 eV) as the criterion for correcting binding energies of other elements. Based on the method of nitrogen adsorption and desorption, the determination of specific surface area together with pore structure was realized on a NOVA 2000e sorption analyzer. Taking BaSO<sub>4</sub> as the standard reference sample, UV-vis diffuse reflectance spectra (DRS) of ZWO, SnS and SnS/ZWO composites were recorded on a UV-vis spectrophotometer (TU 1901, Puxi, China). Photoluminescence (PL) spectra of ZWO, SnS and SnS/ZWO composites were taken on a LS55 fluorescence spectrophotometer (LS55, PE cooperation) by the utilization of an exciting wavelength of 310 nm.

#### 3.4. Photoelectrochemical Measurements

The measurement of electrochemical property was performed on a CHI660E electrochemical workstation, containing a standard three-electrode system, where the saturated Ag/AgCl, Pt wire and as-obtained photocatalysts were, respectively, used as reference electrode, counter electrode and working electrode. The details about measurement were already addressed in our previously reported research [31].

#### 3.5. Photocatalytic Experiments

Photodegradation experiments of RhB solution  $(1.0 \times 10^{-5} \text{ mol L}^{-1})$  were executed in homemade equipment, which was previously demonstrated in our recent study [15–17,32]. Three daylight lamps (30 W for each,  $\lambda \ge 400 \text{ nm}$ ) were designated as the visible light source for triggering the photodegradation reaction. The light intensity was about 450 mW/cm<sup>2</sup>. In each run, we used 60 mL RhB aqueous solution  $(1.0 \times 10^{-5} \text{ mol L}^{-1})$  together with 100 mg of catalysts. Under a regular time of visible-light illumination, the concentration of reacted solution was measured on a UV-vis spectrophotometer by recording variant absorbance intensities of the characteristic peak (554 nm).

#### 4. Conclusions

In summary, the construction of Z-scheme binary SnS/ZnWO<sub>4</sub> composites was easily achieved via a simple two-step route. The experimental results revealed that light harvesting capacity was substantially enhanced and separation rate of photo-activated charge carriers was significantly elevated after ZWO hybridization with SnS forming Z-scheme binary heterostructure. Thus, the synergistic effect of improved visible-light absorption capacity in combination with enhanced separation rate of photoinduced charge carriers contributed to rapid photodegradation toward RhB solution. This work offers a prospective strategy for developing novel ZnWO<sub>4</sub>-based photocatalysts toward efficient and tunable pollutant removal in waste water.

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