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# Highly efficient In<sub>2</sub>S<sub>3</sub>/WO<sub>3</sub> photocatalysts: Z-scheme photocatalytic mechanism for enhanced photocatalytic water pollutant degradation under visible light irradiation†

 Qingqing Qiu,<sup>a</sup> Peng Zhu,<sup>a</sup> Yao Liu,<sup>b</sup> Tongxiang Liang,<sup>b</sup> \*a Tengfeng Xie<sup>b</sup> \*c and Yanhong Lin<sup>c</sup>

A Z-scheme system In<sub>2</sub>S<sub>3</sub>/WO<sub>3</sub> heterojunction was fabricated *via* a mild hydrothermal method and further applied for photocatalytic degradation of tetracycline (TCH) and Rhodamine B (Rh B) under visible light irradiation. The morphological structure, chemical composition and optical properties were studied by XRD, SEM, HRTEM and UV-visible absorption spectra. The results revealed that In<sub>2</sub>S<sub>3</sub>/WO<sub>3</sub> hierarchical structures were successfully constructed, and the prepared In<sub>2</sub>S<sub>3</sub>/WO<sub>3</sub> photocatalysts exhibited enhanced visible-light absorption compared to pure WO<sub>3</sub> nanorods, which are essential to improve the photocatalytic performance. The degradation rate of TCH using the In<sub>2</sub>S<sub>3</sub>(40 wt%)/WO<sub>3</sub> heterostructure (WI40) photocatalyst was about 212 times and 22 times as high as that for pure WO<sub>3</sub> and pure In<sub>2</sub>S<sub>3</sub>, respectively. The degradation rate of Rh B with the WI40 photocatalyst was about 56 times the efficiency of pure WO<sub>3</sub> and 7.6 times that of pure In<sub>2</sub>S<sub>3</sub>. The results of the surface photovoltage (SPV), transient photovoltage (TPV) and reactive oxidation species (ROS) scavenger experiments indicated that the Z-scheme system of In<sub>2</sub>S<sub>3</sub>/WO<sub>3</sub> is favorable for photoexcited charge transfer at the contact interface of In<sub>2</sub>S<sub>3</sub> and WO<sub>3</sub>, which benefits the charge separation efficiency and depresses the recombination of photoexcited charge, resulting in favorable photocatalytic pollutant degradation efficiency under visible light irradiation.

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## 1 Introduction

In the past few decades, water pollutants have seriously threatened human health due to rapidly developing industries.<sup>1–5</sup> Various techniques for purifying the environment have been investigated. Among these techniques, photocatalytic degradation technology has captured much attention as a new environment-purifying technique because of its low toxicity, low cost and easy recovery.<sup>6–8</sup> However, the performance of most photocatalysts is seriously restricted by the range of sunlight utilization and the photoexcited charge separation efficiency.<sup>9</sup>

Recent studies suggest that an excellent catalytic system should meet three conditions: the high utilization of sunlight, strong oxidation–reduction properties and high separation efficiency of photoexcited charge.<sup>10–13</sup> Obviously, it is difficult to have high catalytic activity for a mono-component

semiconductor photocatalyst. In this regard, construction of heterojunction structures is an effective method to boost the photocatalytic performance.<sup>14</sup> The traditional type II heterojunction structures can achieve a band structure with adjustable and high separation efficiency of photogenerated charge.<sup>15</sup> However, the type II heterojunction structures lead to photoexcited electron transfer to the conduction band with lower position, then the photoexcited holes transfer to the valence band with a higher position, which is a disadvantage for the photocatalytic oxidation–reduction properties of photoexcited charge.<sup>10,15</sup> Thus, the design and construction of novel heterojunction structures seem inevitable. The design of Z-scheme heterojunction structures instantly became the focus of photocatalytic studies, and is considered to be the most promising strategy to solve the issues above.<sup>15,16</sup>

To date, many studies about Z-scheme heterojunction structures have been reported, such as g-C<sub>3</sub>N<sub>4</sub>/WO<sub>3</sub>, CdS/Au/TO<sub>2</sub>, CdS/Au/WO<sub>3</sub>, Mn<sub>x</sub>Cd<sub>1–x</sub>S/WO<sub>3</sub>, ZnO/Au/SnO<sub>2</sub>, CeO<sub>2</sub>/Ag/AgBr, WO<sub>3</sub>/Au/In<sub>2</sub>S<sub>3</sub>, CdS/Au/BiVO<sub>4</sub> and BiOI/Pt/g-C<sub>3</sub>N<sub>4</sub>.<sup>17–25</sup> In most cases of the Z-scheme heterojunction catalytic system, however, noble metals are used as the electron mediator, such as Pt, Au and Ag, which can increase the cost of preparation and application.<sup>26</sup> Thus, it is necessary to construct direct Z-scheme heterojunction structures.

<sup>a</sup>College of Rare Earths, Jiangxi University of Science and Technology, Ganzhou 341000, P. R. China

<sup>b</sup>Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, P. R. China

<sup>c</sup>College of Chemistry, Jilin University, Changchun 130012, P. R. China

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Indium sulfide ( $\text{In}_2\text{S}_3$ ), with a bandgap of 2.2 eV, is an effective visible-light-driven photocatalyst that has been extensively used in the field of photocatalysis due to its narrow bandgap, good chemical stability and low toxicity.<sup>27–30</sup> Besides these, the energy structure of  $\text{In}_2\text{S}_3$  semiconductor has excellent reduction performance due to its conduction band with a higher position. But the  $\text{In}_2\text{S}_3$  crystal has poor crystallinity and too rapid rate of charge recombination, which leads to undesirable photocatalytic degradation activity.<sup>29,30</sup>  $\text{WO}_3$  semiconductor has high carrier mobility, good crystallinity, good chemical stability, thermal stability and excellent antioxidant properties due to its valence band with lower position compared to other semiconductor materials, but has a wide bandgap and the limitation of visible-light utilization.<sup>31–33</sup> Thus, we exploit a suitable preparation method to prepare  $\text{In}_2\text{S}_3/\text{WO}_3$  composite, which can expand visible light utilization and improve the photoexcited charge separation efficiency. Besides, we also noticed that the Z-scheme system  $\text{WO}_3/\text{Au}/\text{In}_2\text{S}_3$  was used in the photocatalytic reduction of  $\text{CO}_2$ .<sup>24</sup> The report suggested that the Z-scheme  $\text{In}_2\text{S}_3/\text{WO}_3$  heterostructure can form and accelerate the rate of charge carrier separation. However, there are few reports on the application and photocatalytic mechanism of all-solid-state Z-scheme  $\text{In}_2\text{S}_3/\text{WO}_3$  heterostructure in photocatalytic degradation.

Based on the above discussion, we focus on the construction of a direct Z-scheme  $\text{In}_2\text{S}_3/\text{WO}_3$  heterostructure through a simple and facile method. The degradation efficiency of the all-solid-state  $\text{In}_2\text{S}_3/\text{WO}_3$  photocatalyst was much higher than that of the pristine  $\text{In}_2\text{S}_3$  and  $\text{WO}_3$ . The photoexcited charge behavior of the Z-scheme  $\text{In}_2\text{S}_3/\text{WO}_3$  heterostructure was studied using the SPV and TPV techniques. Furthermore, reactive oxidation species (ROS) scavenger experiments confirmed that the Z-scheme  $\text{In}_2\text{S}_3/\text{WO}_3$  structure induces electrons in  $\text{In}_2\text{S}_3$  and holes in  $\text{WO}_3$  with an unobstructed charge transfer route, effectively improving the separation efficiency of photoexcited charge.

## 2 Experimental details

### 2.1. Preparation of $\text{WO}_3$ nanorods

The  $\text{WO}_3$  nanorods were prepared using a simple hydrothermal method according to the previous reports.<sup>26,31</sup> In a typical experiment, 2.0 g of sodium tungstate hydrate and 0.6 g of sodium chloride in 60 mL distilled water was stirred for 6 h at room temperature. Afterwards, concentrated hydrochloric acid was added dropwise until the pH of solution reached 2.0, and the solution was kept stirring for 3 h. The resulting solution was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. Finally, the obtained  $\text{WO}_3$  nanorods were centrifuged and washed with distilled water and ethanol, and then the precipitates were dried at 50 °C for 12 h under vacuum condition.

### 2.2. Preparation of the Z-scheme $\text{In}_2\text{S}_3/\text{WO}_3$ photocatalyst

The Z-scheme  $\text{In}_2\text{S}_3/\text{WO}_3$  photocatalyst was prepared by a simple and facile hydrothermal method. First, 0.3 g of  $\text{WO}_3$

was ultrasonically dispersed in 30 mL distilled water. A certain amount of indium trichloride hydrate was dissolved in the  $\text{WO}_3$  suspension, then a certain amount of sodium sulfide hydrate was added dropwise. After vigorous stirring for 5 h, the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. Finally, the obtained precipitate was centrifuged and washed with distilled water and ethanol, and the precipitates were dried at 50 °C for 12 h under vacuum condition. The mass ratios of  $\text{In}_2\text{S}_3$  to  $\text{WO}_3$  were  $R = 0, 20, 30, 40$  and  $50$ , which were marked as WI0, WI20, WI30, WI40 and WI50, respectively. The pure  $\text{In}_2\text{S}_3$  powder sample was prepared under the same conditions without  $\text{WO}_3$  powder.

### 2.3. Characterization and measurements

The surface morphology of the obtained powder samples was examined by the MLA 650F field emission scanning electron microscope (SEM, Navo NanoSEM FEI). X-ray diffraction (XRD) was carried out to study the crystal structure of the samples using an X-ray diffractometer with Cu K $\alpha$  radiation (Empyrean, PANalytical B.V.;  $\lambda = 1.54 \text{ \AA}$ ) in the range of 10–70° ( $2\theta$ ). The absorption spectra were measured with a UV-vis spectrophotometer (UV3600, Shimadzu).

Surface photovoltage (SPV) spectra were obtained using a lock-in-based surface photovoltage (SPV) measurement system with a grating monochromator (Omni- $\lambda$ 5007, Zolix), a lock-in amplifier (model SR830-DSP), and an optical chopper (model SR540) running at a frequency of 24 Hz.<sup>34</sup> Transient photovoltage (TPV) measurements were carried out using a self-assembled instrument with a Nd:YAG laser (Q-smart 450, Quantl, Inc.).<sup>34,35</sup> The intensity of the pulse was regulated with a neutral gray filter and a Joule meter (Starlite, Ophir, Inc.). The transient signal was recorded using a 500 MHz digital phosphor oscilloscope (TDS 5054, Tektronix). Both the SPV and TPV measurements were performed in ambient air.

### 2.4. Photocatalytic degradation experiments

In a typical photocatalytic degradation experiment, 50 mg of photocatalyst was mixed with 100 mL of tetracycline hydrochloride aqueous solution (TCH, 30 mg L<sup>-1</sup>) (pH = 4.5) or Rhodamine B aqueous solution (Rh B, 35 mg L<sup>-1</sup>) (pH = 6.0), then ultrasonically dispersed for 5 min. The obtained mixed solution was vigorously stirred for 30 min in the dark to achieve the absorption-desorption equilibrium. In order to investigate the water pollutant degradation efficiency, 1 mL of the mixture was taken out after a given time interval and centrifuged for 10 min to achieve the purpose of solid-liquid separation after visible light irradiation ( $\lambda > 420 \text{ nm}$ ). The concentration of TCH and Rh B was measured with the absorption wavelength of 357 nm and 554 nm, respectively, using a UV-vis spectrometer (UV 2400).

Scavenger tests for reactive oxidation species (ROSS) were carried out under the same experimental conditions except for the addition of scavengers for the degradation process. Potassium bromate ( $\text{KBrO}_3$ , 10 mM), sodium oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ , 10 mM), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL, 10 mM) and isopropanol (10 mM) were used as  $\text{e}^-$ ,  $\text{h}^+$ ,  $\text{O}_2^-$  and  $\text{OH}$  scavengers, respectively.

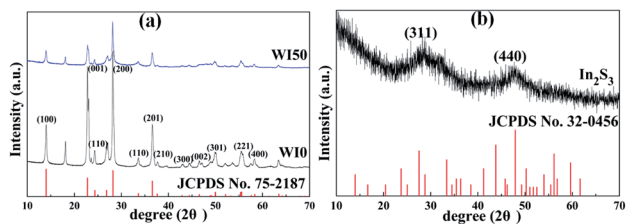


Fig. 1 XRD patterns of (a) W10, WI50 and (b)  $\text{In}_2\text{S}_3$ .

## 3 Results and discussion

### 3.1. Structural characterization of photocatalysts

Fig. 1 shows the X-ray diffraction (XRD) patterns of W10, WI50 and  $\text{In}_2\text{S}_3$  samples. The crystal structure of pure  $\text{WO}_3$  is hexagonal phase (JCPDS card no. 75-2187), as shown in Fig. 1(a).<sup>26–31</sup> The crystal structure of pure  $\text{In}_2\text{S}_3$  is cubic phase (JCPDS card no. 32-0456), as shown in Fig. 1(b).<sup>7,28</sup> Fig. 1(a) shows that only the hexagonal structure  $\text{WO}_3$  is observed, and no obvious diffraction peak is observed for the WI50 sample. This may be attributed to the diffraction peak of  $\text{In}_2\text{S}_3$  sample being too weak compared to the diffraction peak of  $\text{WO}_3$ . In addition, the intensity of diffraction peak for the W120, W130, W140 and WI50 samples is weakened compared to that for the pure  $\text{WO}_3$ , which shows that the preparation of  $\text{In}_2\text{S}_3/\text{WO}_3$  composites makes the crystallinity poorer (see Fig. S1†). With the increase of  $\text{In}_2\text{S}_3$  loading, the intensity of diffraction peak becomes slightly weaker due to the reduced  $\text{WO}_3$  content.

The morphology of pure  $\text{WO}_3$ ,  $\text{In}_2\text{S}_3$ ,  $\text{In}_2\text{S}_3$  (20 wt%)/ $\text{WO}_3$  and  $\text{In}_2\text{S}_3$  (40 wt%)/ $\text{WO}_3$  samples was determined by FESEM (Fig. 2). It can be seen from Fig. 2(a) that the pure  $\text{WO}_3$  consists of nanorods and bulk nanomaterials. The length of nanomaterials is about 0.1–1.1  $\mu\text{m}$ , and the width is about 100–350 nm. Tiny

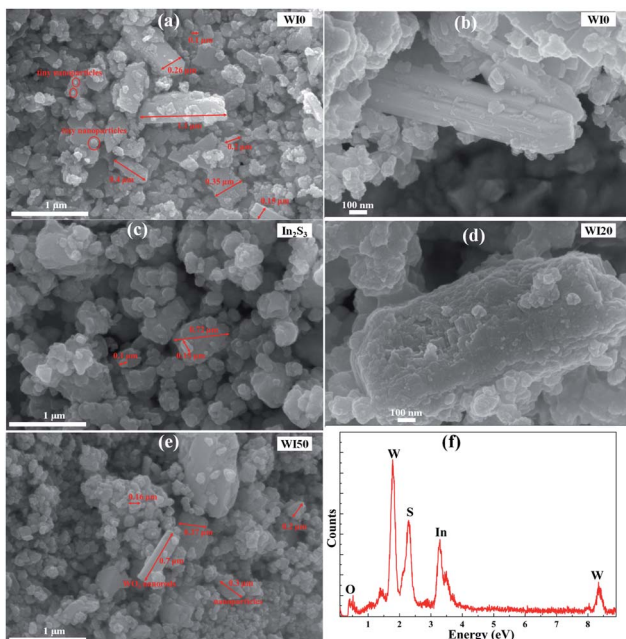


Fig. 2 FESEM images of (a and b) W10, (c)  $\text{In}_2\text{S}_3$ , (d) W120, (e) WI50; (f) energy-dispersive X-ray spectroscopy (EDX) of W140.

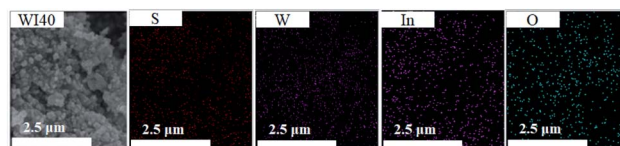


Fig. 3 EDX mappings of W140.

nanoparticles with diameters of 10–110 nm can be observed on the surface of nanorods and bulk nanomaterials. The surface of the nanorods is smooth for pure  $\text{WO}_3$  (see Fig. 2(b)). As shown in Fig. 2(c),  $\text{In}_2\text{S}_3$  nanoparticles with diameters of 100–720 nm were obtained. However, the surface of the nanorods becomes rough with the loading of  $\text{In}_2\text{S}_3$  (see Fig. 2(d)). Fig. 2(e) shows that the nanoparticles increase significantly for W140 composite, which proves that the  $\text{In}_2\text{S}_3$  nanoparticles are loaded on the  $\text{WO}_3$  nanorods and bulk nanomaterials. In Fig. 2(f), the EDX of W140 illustrates that the W140 composite consists of O, W, S and In atoms. Therefore, the above analyses indicate the  $\text{In}_2\text{S}_3$  is deposited on the  $\text{WO}_3$  successfully. The EDX mapping images obtained using TEM-EDX spectroscopy are shown in Fig. S2, S3† and 3. Fig. S2 and S3† show that only the elements W and O for pure  $\text{WO}_3$ , and the elements In and S for pure  $\text{In}_2\text{S}_3$  are detected. Fig. 3 shows the presence of W, O, In and S for W140. The results illustrate all the elements are well distributed.

Fig. 4 shows the transition electron microscopy (TEM) and high-magnification transition electron microscopy (HRTEM) images of  $\text{WO}_3$ ,  $\text{In}_2\text{S}_3$  and W140. Fig. 4(a) shows that the pure  $\text{WO}_3$  is made up of nanorods, bulk nanomaterials and tiny

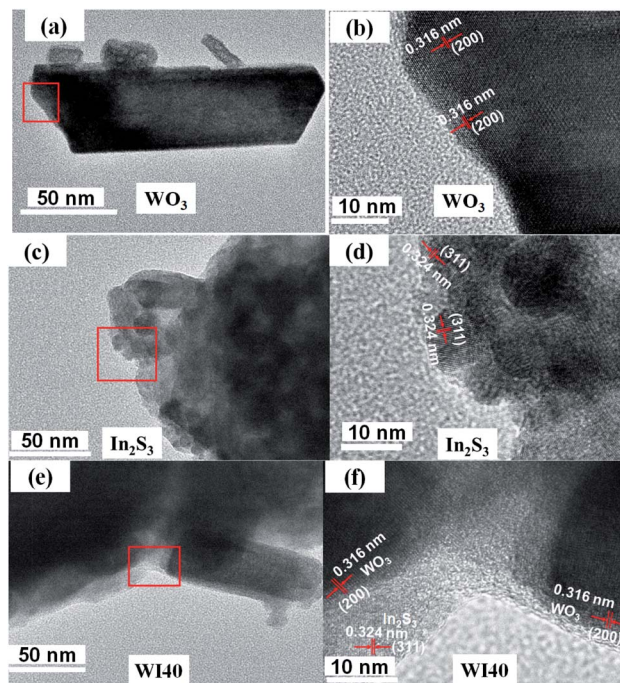


Fig. 4 (a) TEM image of  $\text{WO}_3$  and (b) HRTEM image of  $\text{WO}_3$ ; (c) TEM image of  $\text{In}_2\text{S}_3$  and (d) HRTEM image of  $\text{In}_2\text{S}_3$ ; (e) TEM image of W140 and (f) HRTEM image of  $\text{WO}_3$  and  $\text{In}_2\text{S}_3$ .

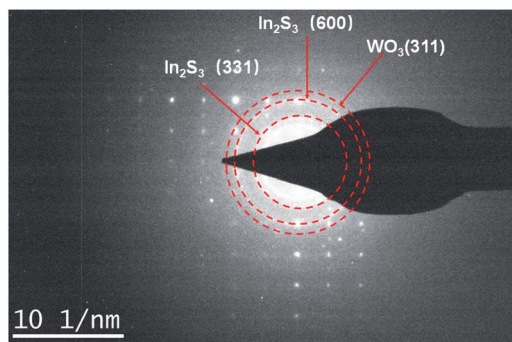


Fig. 5 SAED pattern of WI40.

nanoparticles, corresponding to the SEM images of  $\text{WO}_3$ . The lattice spacing of  $\text{WO}_3$  in the (200) plane is 0.316 nm (see Fig. 4(b)). Fig. 4(c) shows that pure  $\text{In}_2\text{S}_3$  is made up of nanoparticles, and the lattice spacing of  $\text{In}_2\text{S}_3$  in the (311) plane is 0.324 nm (see Fig. 4(d)). As shown in Fig. 4(e), the  $\text{In}_2\text{S}_3$  nanoparticles closely connect with  $\text{WO}_3$  nanomaterials. The HRTEM in Fig. 4(f) shows the  $\text{In}_2\text{S}_3/\text{WO}_3$  heterojunction is formed between  $\text{In}_2\text{S}_3$  and  $\text{WO}_3$ . One can see in Fig. 4(f) that the lattice spacing of 0.316 nm is ascribed to the (200) plane of  $\text{WO}_3$ , while the lattice spacing of 0.324 nm is ascribed to the (211) plane of  $\text{In}_2\text{S}_3$ . The results confirm that  $\text{WO}_3$  and  $\text{In}_2\text{S}_3$  are in close contact with each other, clearly indicating growth of the  $\text{In}_2\text{S}_3/\text{WO}_3$  hierarchical structures.

In addition, we then performed the selected area electron diffraction (SAED) pattern of WI40 to examine the  $\text{In}_2\text{S}_3/\text{WO}_3$  hierarchical structures for more detailed information. Fig. 5 indicates that the lattice spacing of 0.247 nm and 0.179 nm correspond to the values of the (311) lattice plane of hexagonal phase  $\text{WO}_3$  (JCPDS card no. 75-2187), and the observed 0.247 nm and 0.179 nm lattice spacing can be assigned to the (600) and (311) planes of cubic phase  $\text{In}_2\text{S}_3$  (JCPDS card no. 32-0456). The results further indicate that the  $\text{In}_2\text{S}_3/\text{WO}_3$  hierarchical structures were successfully constructed.

The absorption spectra of WI0, WI40 and  $\text{In}_2\text{S}_3$  samples are shown in Fig. 6. The absorption band edge of pure  $\text{WO}_3$  is about 435 nm, and that of pure  $\text{In}_2\text{S}_3$  is about 540 nm. In addition, the absorption band edge of  $\text{In}_2\text{S}_3/\text{WO}_3$  composites exhibits a red shift with the increase of  $\text{In}_2\text{S}_3$  loading. The bandgap energy of the semiconductor is calculated by the following formula:<sup>31</sup>

$$(\alpha h\nu) = A(h\nu - E_g)^{n/2},$$

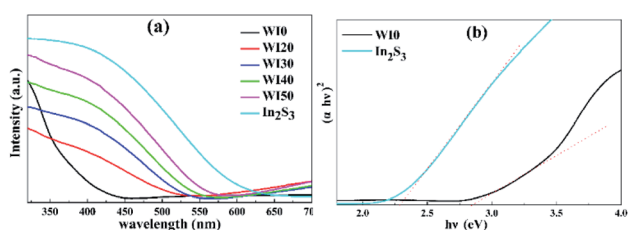


Fig. 6 (a) UV-visible absorption spectra of WI0, WI20, WI30, WI40, WI50 and  $\text{In}_2\text{S}_3$ . (b) Plots of the  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ) for  $\text{In}_2\text{S}_3$  and WI0.

where  $\nu$ ,  $\alpha$ ,  $A$ , and  $E_g$  are light frequency, absorption index, constant value, and bandgap energy of the semiconductor, respectively.<sup>28,31</sup> In addition, the value of  $n$  depends on the transition type of the semiconductor ( $n = 1$  for direct transition semiconductor,  $n = 4$  for indirect transition semiconductor). The values of  $n$  for  $\text{In}_2\text{S}_3$  and  $\text{WO}_3$  are 1 and 4, respectively.<sup>28,31</sup> As shown in Fig. 6(b), the  $E_g$  of  $\text{WO}_3$  is calculated to be 2.85 eV, and the  $E_g$  of  $\text{In}_2\text{S}_3$  is about 2.3 eV. With the increase of  $\text{In}_2\text{S}_3$  loading, the  $E_g$  of  $\text{In}_2\text{S}_3/\text{WO}_3$  composites is closer to that of  $\text{In}_2\text{S}_3$ , which indicates the loading of  $\text{In}_2\text{S}_3$  leads to the improvement of visible light utilization.

### 3.2. Photocatalytic performance of photocatalysts

The degradation of Rhodamine B (Rh B) under visible light irradiation ( $\lambda > 420$  nm) was investigated in order to estimate the photocatalytic performance of the prepared photocatalysts. As shown in Fig. 7(a), the Rh B degradation efficiency of 11% was obtained for pure  $\text{WO}_3$  after 20 min of irradiation with visible light, and the Rh B degradation efficiency of 56.54% was obtained for pure  $\text{In}_2\text{S}_3$  under the same condition. However, Fig. 7(a) shows that the  $\text{In}_2\text{S}_3/\text{WO}_3$  composites display apparently superior Rh B degradation activity. The degradation efficiencies of Rh B are 82.2%, 96.0%, 97.8%, and 96.9% for WI20, WI30, WI40, and WI50 composites, respectively, after 20 min of irradiation. Fig. S4(a)† shows the UV-visible absorption spectra of Rh B solutions before and after photocatalytic degradation reaction in the presence of WI40. The WI40 photocatalyst shows an obvious and significant degradation effect, and Rh B is almost completely degraded after 20 min of irradiation with visible light.

In order to quantitatively evaluate the reaction kinetics of Rh B degradation, the experimental data in Fig. 7(a) could be fitted by the Langmuir–Hinshelwood model and expressed by the following equation:<sup>36</sup>

$$\ln(C_0/C) = k_{\text{app}}t,$$

where  $C_0$  and  $C$  are the concentrations of Rh B at irradiation time of  $t_0$  and  $t$ , respectively, and  $k_{\text{app}}$  is the pseudo-first-order rate constant of Rh B photodegradation ( $\text{min}^{-1}$ ). According to the experimental data in Fig. 7(a), the linear fitting curves of  $\ln(C_0/C)$  versus irradiation time  $t$  was obtained, as shown in Fig. 7(b). The Rh B degradation rate constant  $k$  was calculated to

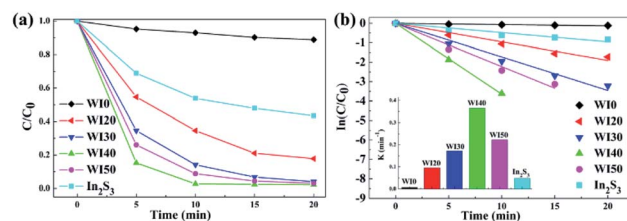


Fig. 7 (a) Photocatalytic degradation performance of WI0, WI20, WI30, WI40, WI50 and  $\text{In}_2\text{S}_3$  for Rh B under visible light irradiation; (b) corresponding plots of  $\ln(C_0/C)$  versus irradiation time  $t$  and the calculated rate constant  $k$ .

Table 1 Comparison of Rh B photocatalytic activity with other photocatalysts

Catalyst	Rh B Concentration (mg L <sup>-1</sup> )	Catalyst Concentration (g L <sup>-1</sup> )	<i>k</i> (min <sup>-1</sup> )	Reference
In <sub>2</sub> S <sub>3</sub> /WO <sub>3</sub>	35	0.50	0.365	This work
Mn <sub>3</sub> O <sub>4</sub> /CeO <sub>2</sub>	10	0.67	0.015	39
Carbon/g-C <sub>3</sub> N <sub>4</sub>	5	0.05	0.008	40
TiO <sub>2</sub> /C	5	0.1	0.080	41
C <sub>3</sub> N <sub>4</sub> /B-C-dots	10	0.5	0.036	42
WO <sub>3</sub> /Cu(II)	10	0.33	0.010	43

be 0.0065, 0.0953, 0.1728, 0.3646, 0.2226 and 0.0477 min<sup>-1</sup> for WI0, WI20, WI30, WI40, WI50 and In<sub>2</sub>S<sub>3</sub>. The results illustrate that the maximum Rh B degradation rate (0.3646 min<sup>-1</sup>) was acquired using the WI40 composites, 56 times as high as pure WO<sub>3</sub> and 7.6 times as high as pure In<sub>2</sub>S<sub>3</sub> when exposed to 20 min of visible light. This may be attributed to the synergistic reaction of WO<sub>3</sub> and In<sub>2</sub>S<sub>3</sub> in the all-solid-state composite photocatalyst, and the interaction is beneficial to the improvement of photocatalytic degradation efficiency. Yet as the amount for In<sub>2</sub>S<sub>3</sub> loading continuously increases, the degradation efficiency of WI50 exhibits a slight decrease compared to that of WI40, and two reasons could explain this decrease of degradation efficiency. On the one hand, the high content of In<sub>2</sub>S<sub>3</sub> could block the WO<sub>3</sub> from absorbing light, which is unfavorable for the interaction between WO<sub>3</sub> and In<sub>2</sub>S<sub>3</sub>. On the other hand, the excess amount of In<sub>2</sub>S<sub>3</sub> can serve as the recombination center of photoexcited charges, which would decrease the activity of the composite photocatalyst.<sup>37,38</sup> Furthermore, the WI40 also exhibits outstanding photocatalytic performance for Rh B degradation compared with the latest works (Table 1).

The degradation efficiency of tetracycline hydrochloride (TCH) under visible light irradiation was studied to further investigate the effect of the interaction between WO<sub>3</sub> and In<sub>2</sub>S<sub>3</sub>. As shown in Fig. 8(a), the degradation efficiencies of TCH for pure WO<sub>3</sub> and In<sub>2</sub>S<sub>3</sub> are 7.1% and 56.6%, respectively, after 150 min of irradiation. However, the degradation efficiencies of TCH are 51.6%, 62.5%, 84.7%, and 81.4% for WI20, WI30, WI40, and WI50 composites after 150 min of irradiation. The corresponding curves of ln(C<sub>0</sub>/C) versus irradiation time *t* and the degradation rate constant *k* were also calculated, as shown in Fig. 8(b). The degradation rate constants (*k*) of TCH are

0.0004, 0.0036, 0.0039, 0.0085, 0.0074 and 0.0038 min<sup>-1</sup> for WI0, WI20, WI30, WI40, WI50 and In<sub>2</sub>S<sub>3</sub>, respectively. The TCH degradation rate constants for WI40 are about 212 times and 22 times as high as that for pure WO<sub>3</sub> and pure In<sub>2</sub>S<sub>3</sub>, respectively, illustrating that the WI40 composite photocatalyst is apparently superior to pure WO<sub>3</sub> and In<sub>2</sub>S<sub>3</sub>. Moreover, the UV-visible absorption spectra of TCH solutions before and after photocatalytic degradation reaction in the presence of WI40 was recorded, as shown in Fig. S4(b).<sup>†</sup> Significantly, the WI40 photocatalyst exhibits effective degradation of the TCH pollutant, and the degradation efficiency for TCH is close to 90% under visible light irradiation. However, WI40 shows relatively low photocatalytic performance for TCH degradation compared with the latest works (Table 2), which suggests that the prepared photocatalyst is more suitable for Rh B degradation. The above results indicate that the synergistic effect between WO<sub>3</sub> and In<sub>2</sub>S<sub>3</sub> plays a crucial role for the degradation of these water pollutants.

The degradation of Rh B and TCH might be affected under different solution pH conditions.<sup>17</sup> The degradation experiments were carried out at different pH values, as shown in Fig. S5.<sup>†</sup> The result indicates that the alkaline solution has remarkable impact on the degradation efficiency of Rh B, where neutral and acidic solutions only have a mild effect on the degradation efficiency; 97.89%, 96.79%, 98.23% and 90.57% of Rh B were removed at pH values of 2, 4, 7 and 10, respectively. However, the initial pH only has slight impact on the photoactivity for TCH degradation, and 82.28%, 84.94%, 86.47% and 85.23% of TCH were removed at pH values of 2, 5, 7 and 9. This gives evidence that the In<sub>2</sub>S<sub>3</sub>/WO<sub>3</sub> photocatalyst maintains a relatively high photocatalytic performance over a wide pH range. To investigate further, a physical mixture of pure WO<sub>3</sub> and In<sub>2</sub>S<sub>3</sub> with the same mass ratio (40%) was used as the control during photocatalytic degradation, as shown in Fig. S6.<sup>†</sup> Obviously, the degradation performance of WI40 is better, compared to that of the physical mixture of In<sub>2</sub>S<sub>3</sub>(40 wt%)/WO<sub>3</sub> for Rh B and TCH degradation under visible light irradiation.

Stability tests of the WI40 photocatalyst for photocatalytic degradation of Rh B and TCH were conducted, as illustrated in Fig. 9. The Rh B degradation efficiency varies from 97.8 to 98.9% after 20 min of irradiation with visible light, and the TCH degradation efficiency varies from 84.7 to 87.9% after 150 min of irradiation under the same condition. There is no significant decline of photocatalytic degradation activity toward Rh B and TCH after four cycles, indicating that the WI40 photocatalyst

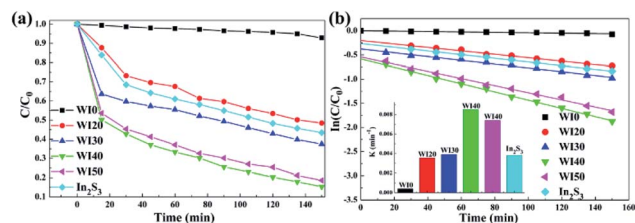


Fig. 8 (a) Photocatalytic degradation performance of WI0, WI20, WI30, WI40, WI50 and In<sub>2</sub>S<sub>3</sub> for TCH under visible light irradiation; (b) corresponding plots of ln(C<sub>0</sub>/C) versus irradiation time *t* and the calculated rate constant *k*.

Table 2 Comparison of TCH photocatalytic activity with other photocatalysts

Catalyst	TCH concentration (mg L <sup>-1</sup> )	Catalyst concentration (g L <sup>-1</sup> )	<i>k</i> (min <sup>-1</sup> )	Reference
In <sub>2</sub> S <sub>3</sub> /WO <sub>3</sub>	30	0.5	0.009	This work
C <sub>3</sub> N <sub>4</sub> /B-C-dots	10	0.5	0.023	42
Ag <sub>2</sub> CO <sub>3</sub> /Ag/WO <sub>3</sub>	10	0.5	0.018	44
Ag <sub>3</sub> PO <sub>4</sub> /BiVO <sub>4</sub>	5	0.5	0.013	45
BiOBr/Ag <sub>3</sub> PO <sub>4</sub>	20	0.5	0.078	46
TiO <sub>2</sub> /CdS	50	0.6	0.030	47

has good stability. Moreover, the physical structure of the fresh and recycled In<sub>2</sub>S<sub>3</sub>/WO<sub>3</sub> composites was characterized by XRD technique (Fig. S7†). No obvious changes can be observed between the fresh and recycled photocatalyst. The results further confirm that the prepared In<sub>2</sub>S<sub>3</sub>/WO<sub>3</sub> photocatalyst has outstanding stability after repeated recycling.

### 3.3. Assessment of the separation efficiency of photoexcited charge carriers

SPV technique was employed to explore the process of photoexcited charge carrier separation and transport in the surface and interface of the photocatalyst samples. The schematic diagram of the SPV test configuration is shown in Fig. 10. For the pure WO<sub>3</sub>, the SPV response is at the wavelength of 300–450 nm, which corresponds to the band-to-band transitions of WO<sub>3</sub>. For the pure In<sub>2</sub>S<sub>3</sub>, the SPV response is around the wavelength of 300–620 nm, which corresponds to the band-to-band transitions of In<sub>2</sub>S<sub>3</sub>. However, the SPV response of WI40 expands to about 620 nm due to the loading of In<sub>2</sub>S<sub>3</sub>, and the SPV intensity of WI40 is significantly stronger compared to that of pure WO<sub>3</sub> and In<sub>2</sub>S<sub>3</sub>. It is generally accepted that for a similar composition of semiconductors, the higher the SPV response intensity, the higher the separation efficiency of the photoexcited charge, indicating interfacial interaction in the all-solid-state composite photocatalyst is in favor of the separation and transport of photoexcited charge carriers and photocatalytic degradation efficiency.<sup>48</sup> This is credible evidence for the crucial role of the construction of the Z-scheme In<sub>2</sub>S<sub>3</sub>/WO<sub>3</sub> heterostructure.<sup>25,31</sup>

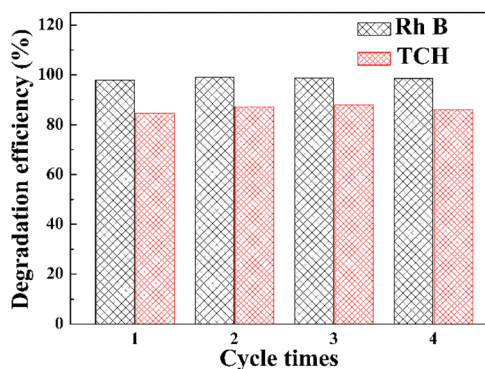


Fig. 9 Stability testing of the WI40 photocatalyst toward the photocatalytic degradation of Rh B and TCH under visible light irradiation.

Furthermore, the transient photovoltage (TPV) technique was applied to investigate the dynamic properties of the photoexcited charge separation and transfer process of WI0, WI40 and In<sub>2</sub>S<sub>3</sub>. Fig. 11 illustrates the TPV results of prepared photocatalysts under 355 nm and 532 nm pulse laser irradiation on a normal timescale. The schematic diagram of the TPV test configuration is presented as well as that of the SPV test configuration, as seen in the inset of Fig. 10. Obviously, a negative TPV signal is observed for all the prepared photocatalysts, which implies the photoexcited electrons transfer to the top electrode. Moreover, a weak positive TPV signal is observed for all the prepared photocatalysts due to the existence of surface state.<sup>49,50</sup> As shown in Fig. 11(a), only a weak signal is observed for the pure WO<sub>3</sub> and In<sub>2</sub>S<sub>3</sub> due to the poor separation efficiency of the pure WO<sub>3</sub> and In<sub>2</sub>S<sub>3</sub>. Similarly, the TPV response intensity of WI40 is significantly stronger compared to that of pure WO<sub>3</sub> and In<sub>2</sub>S<sub>3</sub>, which reveals that the synergistic reaction of WO<sub>3</sub> and In<sub>2</sub>S<sub>3</sub> is beneficial to the separation and transport of photoexcited charge carriers. The TPV response of the prepared photocatalysts shows the same results under 532 nm pulse laser irradiation, as shown in Fig. 11(b). That is to say, WI40 shows a higher photocatalytic water pollutant degradation efficiency, which is reasonable due to the synergistic reaction of WO<sub>3</sub> and In<sub>2</sub>S<sub>3</sub>.

### 3.4. Exploration of photocatalytic degradation mechanism

In order to further understand the photocatalytic degradation mechanism of In<sub>2</sub>S<sub>3</sub>/WO<sub>3</sub> heterostructure, scavenger experiments for WI0 (Fig. 12(a)) and WI40 (Fig. 12(b)) were carried out

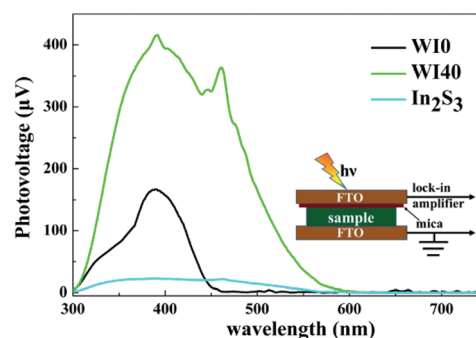


Fig. 10 Surface photovoltage spectra of WI0, WI40 and In<sub>2</sub>S<sub>3</sub>.

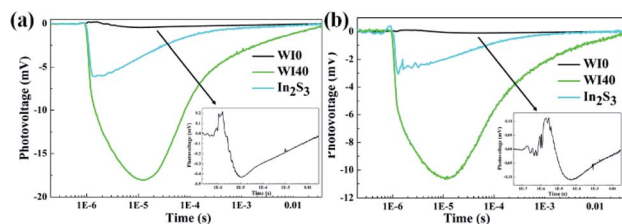


Fig. 11 Transient photovoltage response of W10, WI40 and  $\text{In}_2\text{S}_3$ . (a) The wavelength and the intensity of the laser are 355 nm and 100  $\mu\text{J}$ , respectively. (b) The wavelength and the intensity of the laser are 532 nm and 100  $\mu\text{J}$ , respectively.

to investigate the reactive oxidation species (ROSs) in the degradation process. It is worth noting that the degradation efficiencies decrease obviously both in the presence of potassium bromate and sodium oxalate in the W10 photocatalytic degradation system, indicating that  $e^-$  and  $h^+$  are the main ROS in the degradation process of W10, while  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$  rarely exist. In contrast, all four types of ROS exist in the WI40 photocatalytic degradation system. The degradation efficiency decreases sharply in the presence of TEMPOL, indicating that  $\cdot\text{O}_2^-$  is the major ROS in the degradation process of WI40. However, the degradation efficiencies decrease weakly both in the presence of potassium bromate and isopropanol, which means that  $h^+$  and  $\cdot\text{OH}$  are the minor ROS. Besides, the degradation efficiency decreases with the addition of sodium oxalate, indicating that holes also take part in the oxidation reaction of pollutants. It should be noted that the concentration of  $e^-$  and  $h^+$  reduce sharply in the WI40 system; this may be due to the fact that the photoexcited charges transfer rapidly to form  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$ . In fact, previous reports suggest that the CB position of  $\text{In}_2\text{S}_3$  is at around  $-0.7$  eV,<sup>23</sup> and the redox potential of  $\text{O}_2/\cdot\text{O}_2^-$  ( $-0.33$  eV vs. NHE) is more negative than the CB of the  $\text{In}_2\text{S}_3$ ; thus, the electrons in the CB of  $\text{In}_2\text{S}_3$  could react with  $\text{O}_2$  to produce  $\cdot\text{O}_2^-$ . This is consistent with the results of the scavenger experiments. Similarly, the VB position of  $\text{WO}_3$  (3.2 eV vs. NHE) is more positive than the redox potential of  $\cdot\text{OH}/\text{OH}^-$  (2.4 eV vs. NHE), and  $\cdot\text{OH}$  could be generated through the reaction between holes in the VB and  $\text{OH}^-$ .<sup>25,26</sup> Therefore, the all-solid-state Z-scheme  $\text{In}_2\text{S}_3/\text{WO}_3$  heterostructure is proposed.

Based on the above analysis of experimental results, the possible photocatalytic degradation mechanism with the all-solid-state Z-scheme  $\text{In}_2\text{S}_3/\text{WO}_3$  heterostructure is shown in Fig. 13. Previous reports confirmed that the energy band

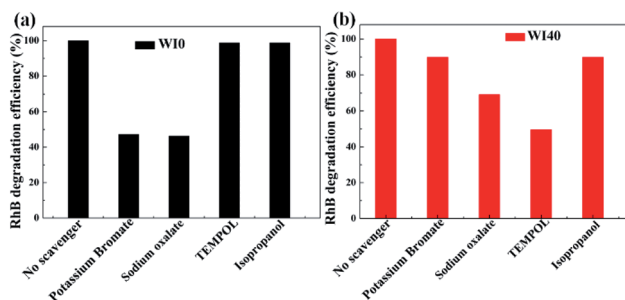


Fig. 12 ROS scavenger experiments during the photodegradation of Rh B over (a) W10 and (b) WI40 under visible light irradiation.

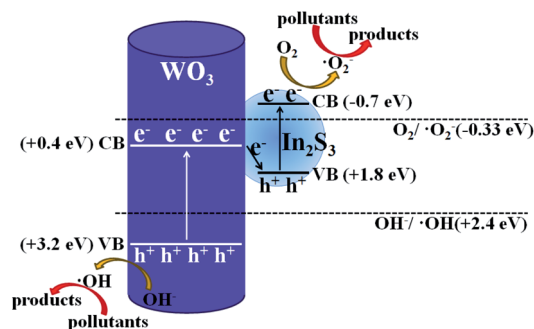


Fig. 13 Possible photocatalytic pollutant degradation mechanism for the all-solid-state Z-scheme  $\text{In}_2\text{S}_3/\text{WO}_3$  photocatalyst.

structures of  $\text{WO}_3$  and  $\text{In}_2\text{S}_3$  are beneficial to the transfer of photoexcited electrons from the CB of  $\text{WO}_3$  to the VB of  $\text{In}_2\text{S}_3$ .<sup>23</sup> Therefore, the charge recombination of electrons in  $\text{WO}_3$  and holes in  $\text{In}_2\text{S}_3$  occurs at the contact interface between  $\text{WO}_3$  and  $\text{In}_2\text{S}_3$ ; this leaves the electrons in the CB of  $\text{In}_2\text{S}_3$  and holes in the VB of  $\text{WO}_3$  to take part in the photocatalytic degradation reaction directly, or generate the  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$ . In this way, the  $\cdot\text{O}_2^-$  with stronger oxidation ability will participate in the oxidation reaction of pollutants and improve the photocatalytic degradation efficiency, as shown in Fig. 13. The above discussion confirms that the designed all-solid-state Z-scheme photocatalyst could promote photocatalytic water pollutant degradation efficiency and enhance the redox ability of the photocatalytic system distinctly.

## 4 Conclusions

In summary, an all-solid-state Z-scheme  $\text{In}_2\text{S}_3/\text{WO}_3$  photocatalyst was successfully designed and synthesized *via* a facile method. The degradation efficiency of the  $\text{In}_2\text{S}_3/\text{WO}_3$  photocatalyst exhibits a significant improvement compared with the pure  $\text{In}_2\text{S}_3$  and  $\text{WO}_3$ . The results suggest that the all-solid-state Z-scheme  $\text{In}_2\text{S}_3/\text{WO}_3$  heterostructure is more beneficial to the photoexcited charge transfer at the contact interface with an unobstructed Z-scheme route, and thus the separation efficiency shows a clear improvement. In this way, the obtained  $\text{In}_2\text{S}_3/\text{WO}_3$  photocatalyst exhibits a significantly improved photocatalytic degradation performance toward Rh B and TCH, eventually. This work demonstrates that the all-solid-state Z-scheme photocatalyst could be accurately designed and prepared *via* a simple hydrothermal method, and it exhibits outstanding photocatalytic performance, presenting a novel route for the design of a highly efficient photocatalyst in the photocatalytic field.

## Conflicts of interest

There are no conflicts to declare.

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