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1. Introduction

Mercaptans, one of several significant chemical products, have found comprehensive applications in various fields during the rapid development of the chemical industry.^{1–3} Among these mercaptans, 2-mercaptobenzothiazole (MBT), an important mercaptan, has been widely used in chemical manufacturing, for use in medicines, antidotes, rubber vulcanization, and so forth. Although MBT has many purposes, there is no doubt that MBT has a certain virulence, which irritates the skin and mucous membrane resulting in skin ulcers.⁴ Aside from the abovementioned industrial pollutants, there are some domestic pollutants in water, such as tetracycline (TC) and rhodamine B (RhB). These can cause damage to the functioning organs of the body in high concentrations. Therefore, there is an urgent need to reduce and remove MBT, TC and RhB from water to protect the environment and human health from harm.⁵



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A new Z-scheme MoS_2/Bi_2O_3 heterojunction photocatalyst was successfully prepared using a facile and practical hydrothermal method. The Z-scheme MoS_2/Bi_2O_3 heterojunction exhibits a superior degradation efficiency compared to pure MoS_2 and Bi_2O_3 for removing industrial and domestic pollutants under visible light, such as 2-mercaptobenzothiazole, tetracycline and rhodamine B. The enhancement in the photocatalytic performance mainly stems from the interfacial interaction between the MoS_2 nanosheets and Bi_2O_3 rods, which can increase the specific surface area and accelerate the separation of the photo-induced electron-hole pairs. To explain this interfacial interaction between MoS_2 and Bi_2O_3 in the Z-scheme MoS_2/Bi_2O_3 heterojunction, several characterization techniques were applied. In addition, the photocatalytic mechanism for degrading pollutants was demonstrated using trapping experiments and electron spin resonance. This work could provide a promising approach for the formation of other Z-scheme transition metal compound heterojunctions with outstanding photocatalytic activity.

Recently, photocatalysis has become more and more attractive because it has been described as a potential method to deal with industrial and domestic pollutants.⁶⁻⁸ Thus, a range of single photocatalysts can be applied to remove organic pollutants in order to solve the increasing and devastating environmental problems.^{9,10} Bismuth trioxide (Bi_2O_3), as a metal oxide semiconductor, stands out among the other metal semiconductor materials.^{11,12} Bi₂O₃ has been used in a lot of fields, such as for use in sensors, supercapacitor electrodes, and solid oxide fuel cells.^{14–16} It has a low cost and a suitable band gap of 2.5-2.8 eV.¹³ In addition, unlike other popular semiconductor photocatalysts, such as TiO₂ and SrTiO₃, Bi₂O₃ can be excited by visible light.¹⁷⁻¹⁹ Nevertheless, rapid recombination of charge carriers in pure Bi₂O₃ frequently leads to its poor photocatalytic activity. Thus, a bare Bi2O3 semiconductor photocatalyst cannot meet the demands of daily life.¹³ In order to overcome this drawback, numerous researchers have reported various means to modify Bi₂O₃, including semiconductor compositing, carbon introduction and metal/nonmetal ion doping.²⁰⁻²² However, the above described approaches have several shortcomings such as a high cost, low efficiency and a lack of stability. It is well known that the fabrication of Z-scheme heterojunctions with a suitable band structure has been researched widely and can accelerate charge separation effectively and give the rest of the electrons and holes a higher oxidation-reduction ability.²³⁻²⁶ Until now, a lot of Bi₂O₃ heterojunction photocatalysts have been studied for enhancing the photocatalytic performance, such as



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WO₃/g-C₃N₄/Bi₂O₃, BiOCl/Bi₂O₃, RGO-Cu₂O/Bi₂O₃, and Cs₂O-Bi₂O₃-ZnO.²⁷⁻³⁰ By combining the abovementioned Z-scheme and heterojunction structures, building a Z-scheme heterojunction photocatalyst seems to be an excellent method with great potential to handle the disadvantages of Bi₂O₃. Thus, a semiconductor needs to be found which is well matched with Bi₂O₃ to form a Z-scheme heterojunction to further increase the photocatalytic performance.

Among numerous semiconductors, molybdenum disulphide (MoS_2) as a flake transition metal sulfide has been commonly researched for the enhancement of the photocatalytic efficiency.³¹⁻³⁴ It acts as a two dimensional (2D) sheet structure, which is comparable, and even better in some cases, to other multidimensional metal materials in the photocatalytic field.³⁵⁻³⁸ Very recently, MoS₂ as a metal dichalcogenide, has received a large amount of attention for the degradation of organic pollutants owing to its large surface area, high electrical conductivity, and stable chemical properties.³⁹⁻⁴² A variety of studies have reported the ability of MoS₂ heterojunctions for the degradation of organic pollutants, such as MoS₂/g-C₃N₄, MoS₂/Bi₂WO₆ and MoS₂/Mn_{0.2}Cd_{0.8}S/MnS heterojunctions.⁴³⁻⁴⁵ Moreover, the unique 2D layered crystalline structures of MoS₂ can ensure the separation and transportation of the charge carrier.46,47 In addition, the conduction band (CB)/valence band (VB) of MoS₂ is located at -0.38 eV/1.52 eV, which conforms well with Bi2O3 (0.16 eV/2.98 eV) to create a Z-scheme heterojunction. Therefore, it is hoped that preparation of a Z-scheme heterojunction by recombination of MoS₂ with Bi₂O₃ will promote the charge carrier separation for the photocatalytic removal of various pollutants under visible light. Finally, it must be emphasized that there are no reports published to date detailing research on the Z-scheme MoS₂/Bi₂O₃ heterojunction and its application in the photocatalysis field.

In light of the above described considerations, in this paper a Z-scheme MoS_2/Bi_2O_3 heterojunction was achieved by a facile and practical hydrothermal method. In order to evaluate the photocatalytic activity of the Z-scheme MoS_2/Bi_2O_3 heterojunction, a series of MBT, TC and RhB degradation experiments were carried out under visible light. These results all proved that the Z-scheme MoS_2/Bi_2O_3 heterojunctions not only distinctly strengthens the visible-light photocatalytic efficiency compared with pure MoS_2 and Bi_2O_3 , but also possessed outstanding stability and reusability. As expected, the enhanced photocatalytic performance for the degradation of various organic pollutants is on account of the strong interfacial interaction between MoS_2 and Bi_2O_3 and the fast transportation of the electron hole pairs in the interface, which also extends the lifetime of the photogenerated charge carriers.

2. Experimental

The Z-scheme MoS_2/Bi_2O_3 heterojunction photocatalyst was successfully prepared using a facile and practical hydrothermal method. The MoS_2 nanosheets were prepared by combining 1.21 g $Na_2MoO_4.2H_2O$ and 1.56 g $CS(NH_2)_2$ and heating at 180 °C for 24 h. Subsequently, the Bi₂O₃ solid rods were attained using a typical synthesis procedure using 4.8 g of Bi(NO₃)₃·5H₂O. Finally, the Z-scheme MoS₂/Bi₂O₃ heterojunction photocatalyst was prepared *via* a hydrothermal process.

X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and other measurements were used to characterize the samples. Photocatalytic tests, trapping experiments and photoelectrochemical measurements were all carried out to detect the photocatalytic performance of the Z-scheme MoS_2/Bi_2O_3 heterojunction. The details of the experimental process, characterization and measurements are described in the ESI.[†]

Results and discussion

3.1. XRD analysis

The crystalline phase of the different samples was determined using XRD analysis. As shown in Fig. 1a, the as-synthesized Bi₂O₃ solid rods and MoS₂ nanosheet samples present strong diffraction peaks, which suggest a good crystalline phase for these samples. The sharp diffraction peaks of Bi₂O₃ and MoS₂ correspond with the standard spectra (Bi₂O₃ JCPDS No. 41-1449; MoS₂ JCPDS No. 37-1492) respectively, and no other impurity diffraction signals were found. In addition, for the Z-scheme MoS₂/Bi₂O₃ heterojunction all of the diffraction peaks were similar to that of pure MoS₂ and Bi₂O₃, which means that the Z-scheme MoS₂/Bi₂O₃ heterojunction was successfully constructed. It should be noted that the diffraction peaks are consistent with the (002) lattice plane of MoS_2 and the (012) lattice plane of Bi2O3 in the MoS2/Bi2O3 heterojunction and both become weaker compared with those of the single MoS₂ and Bi₂O₃ respectively. This indicates that the intense interaction between MoS₂ and Bi₂O₃ appears in the Z-scheme MoS₂/Bi₂O₃ heterojunction, and this is beneficial to the transport and separation of charge carriers between them, and therefore the photocatalytic activity is enhanced.¹⁴ On the one hand, it is the same as the (012) lattice plane of Bi₂O₃, and the characteristic peaks of (101) and (110) lattice plane of MoS_2 are too weak in the composite. This is mainly because the content of MoS₂ is not



Fig. 1 (a) XRD patterns for the pure MoS₂ nanosheets, Bi_2O_3 rods and 15% MoS₂/Bi₂O₃ heterojunction; (b) EDX spectrum of 15% MoS₂/Bi₂O₃ heterojunction and the mass and atomic ratios of the 15% MoS₂/Bi₂O₃ heterojunction (inset).

significant in the composite. Therefore, there is no characteristic peak for MoS_2 observed in the Z-scheme MoS_2/Bi_2O_3 heterojunction except for the peak for the (002) lattice plane. Moreover, an elemental composition of 15% for the MoS_2/Bi_2O_3 heterojunction was detected from the EDX. As shown in Fig. 1b, the elements Mo, S, Bi and O were observed in the Z-scheme MoS_2/Bi_2O_3 heterojunction, confirming that the MoS_2 nanosheets were successfully combined with the Bi_2O_3 rods. The aforementioned results further demonstrate that the MoS_2 nanosheets were deposited on the surface of Bi_2O_3 .

3.2. Microstructural analysis

The morphology and microstructure of MoS₂, Bi₂O₃ and the MoS₂/Bi₂O₃ heterojunction were characterized using SEM and TEM analysis. From Fig. 2a, it can be observed that bare Bi₂O₃ possesses high uniform micron-sized rods with a diameter of approximately 0.5 μ m, and that pure MoS₂ presents small irregular nanosheets with a tendency to aggregate, as shown in Fig. 2b. Fig. 2c and d show typical SEM and TEM images of the coupling photocatalytic 15% MoS₂/Bi₂O₃. From the abovementioned images, it can be seen that the MoS₂ nanosheets have been successfully absorbed onto the surface of the Bi₂O₃ micron-sized rods during the hydrothermal process and the formation of MoS₂ has no obvious effect on the Bi₂O₃. The SEM image shown in Fig. 2c demonstrates that the small irregular MoS₂ nanosheets are uniformly distributed on the surface of Bi₂O₃. Meanwhile, the TEM image shown in Fig. 2d also describes the tight connection between the MoS₂ nanosheets and Bi₂O₃ micron-sized rods, which allows the interparticle photo-induced transfer of the carriers. Furthermore, elemental mapping has also been performed on the Z-scheme MoS₂/Bi₂O₃ heterojunction, which also confirms the presence of all elements (Mo, S, Bi and O) in the heterojunction (Fig. 2e). This result is in accordance with the EDX analysis, and reveals that MoS₂ has been successfully combined with Bi₂O₃. In addition, high-resolution TEM (HRTEM) of the heterojunction was also



Fig. 2 SEM images of pure: (a) Bi_2O_3 rods; (b) single MoS_2 nanosheets; (c) $15\% MoS_2/Bi_2O_3$ heterojunction; (d) TEM images of the $15\% MoS_2/Bi_2O_3$ heterojunction; and (e) elemental mapping of the $15\% MoS_2/Bi_2O_3$ heterojunction showing the presence of the constituent elements (Mo, S, Bi and O).

performed and is shown in Fig. S2 (ESI[†]). From this image the lattice fringes of the MoS_2 nanosheets in the MoS_2/Bi_2O_3 heterojunction can be clearly observed and the lattice spacing was measured to be 0.2604 nm, which corresponds with a typical (100) plane for MoS_2 . Meanwhile, the (120) plane of Bi_2O_3 with a lattice spacing of 0.32 nm was also found in the MoS_2/Bi_2O_3 heterojunction nanocomposite. Thus, the results of the HRTEM analysis further prove that the composite structure is a Z-scheme MoS_2/Bi_2O_3 heterojunction.

3.3. XPS analysis

The surface chemical constituent of the Z-scheme MoS₂/Bi₂O₃ heterojunctions and the chemical interactions between MoS₂ and Bi₂O₃ were further examined using XPS. The XPS spectrum of the Z-scheme MoS₂/Bi₂O₃ heterojunction includes the elements Mo, S, Bi and O, and is shown with the XRD, EDX and elemental mapping results in Fig. 3a. The XPS spectrum of Mo 3d can be observed from Fig. 3b, and it reveals two strong peaks at 229.1 and 232.5 eV belonging to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ respectively, which obviously indicates that the valence state of the molybdenum element is 4+ in the MoS₂/Bi₂O₃ heterojunction.⁴⁸ As shown in Fig. 3e, in the high resolution XPS spectrum of Bi 4f, two peaks appearing at 158.6 and 164.2 eV are evident, corresponding to Bi 4f7/2 and Bi 4f5/2 in the sample respectively.^{49,50} Meanwhile, the peaks at 161.8 and 162.9 eV can be ascribed to S $2p_{3/2}$ and S $2p_{1/2}$ because of the spin orbit separation of the S element, which also certifies the emergence of S^{2-} in the final photocatalyst.^{51,52} The O 1s peaks in Fig. 3d can be fitted to the two peaks at 529.9 and 531.3 eV, they belong to the surface hydroxyl groups (Bi-O-H) and Bi-O bond in the sample respectively.⁵³ Fig. 3g displays the XPS pattern of S 2p, there are two distinct peaks at 162.4 and 163.8 eV which are matched with S $2p_{3/2}$ and S $2p_{1/2}$. Finally, it is worth noting that the XPS spectrum of Mo 3d and Bi 4f is evidently shifted to a higher binding energy (Fig. 3c and f) comparing with the pure



Fig. 3 XPS spectra of the 15% MoS_2/Bi_2O_3 heterojunction: (a) survey spectrum; (b) and (c) Mo 3d; (d) O 1s; (e) and (f) Bi 4f; and (g) S 2p.



Fig. 4 (a) UV-vis DRS of different samples; (b) the plots of $(ah\nu)^2$ versus $(h\nu)$ of Bi₂O₃; (c) XPS valence band spectra of MoS₂; and (d) Bi₂O₃.

 MoS_2 and Bi_2O_3 , this may be due to the heterojunction interaction between MoS_2 and Bi_2O_3 .⁵⁴ The above described results prove the existence of a strong interaction between MoS_2 and Bi_2O_3 in the Z-scheme MoS_2/Bi_2O_3 heterojunction, which could promote the migration of an electron-hole pair, and also increase the photocatalytic performance and stability.

3.4. UV-vis adsorption of the as-prepared photocatalysts

Using UV-vis diffusion reflectance spectra is a common method to analyze the light absorption and energy band features of a photocatalyst. Therefore, the UV-vis absorption spectra of the different samples are shown in Fig. 4. As shown in Fig. 4a, the absorption edge of Bi₂O₃ is approaching 440 nm, which exhibits a photo-response to visible light. In comparison, the pure MoS₂ nanosheets present a broad absorption spectra because of their black color, which indicates that they can absorb all of the photons from visible light and this is similar to previously reported results.¹³ Furthermore, after being added to MoS₂, a striking full spectral absorption can be observed in the absorption spectrum of the MoS₂/Bi₂O₃ composite samples, which is due to the transition of MoS₂ and Bi₂O₃. Meanwhile, there are other factors affecting the photocatalytic efficiency achieved, such as the optical range, containment of the charge transfer, specific surface area and the suppression of the recombination of electron-hole pairs of the Z-scheme MoS₂/Bi₂O₃ heterojunction. Moreover, in order to determine the relative band gap and the position of Bi_2O_3 , the band gap energy (E_{α}) of the sample was counted using the following formula based on the differential reflectance spectroscopy (DRS) results:⁵⁵ $\alpha h\nu = A(h\nu (E_g)^{n/2}$. From Fig. 4b, the E_g of Bi₂O₃ counted using a plot of $(ah\nu)^2$ versus $(h\nu)$ was found to be 2.82 eV.

Furthermore, in order to ensure the VB and CB of the edge potential of the semiconductors, samples were analyzed using XPS and previous reports. From Fig. 4c and d, it can be seen that the VB of MoS_2 and Bi_2O_3 were 1.52 and 2.98 eV, as detected using XPS. By combining this with the result of the UV-vis, the band gap of Bi_2O_3 was found to be 2.82 eV. Interestingly, the abovementioned results correspond with previously published reports. Thus, by combining the XPS spectral data and previous reports, it can be determined that the band gap of MoS_2 is 1.9 eV, meanwhile, the conductance bands of MoS_2 and Bi_2O_3 are -0.38 and 0.16 eV respectively.^{13,56} Based on the above described findings, it can be confirmed that MoS_2 and Bi_2O_3 can form a perfect Z-scheme heterojunction.

3.5. Photocatalytic tests

The photocatalytic ability of Z-scheme MoS₂/Bi₂O₃ heterojunction photocatalysts depend on the content of MoS₂, therefore different MoS₂ contents in MoS₂/Bi₂O₃ heterojunction photocatalysts must be studied for degrading MBT under the visible light. As shown in Fig. 5a, it was noted that the bare MoS₂ and Bi₂O₃ display a poor photocatalytic performance, and only 13.5% and 37.0% of MBT is removed respectively. Moreover, the photocatalytic degradation efficiency of MBT was 57.6%, 81.2%, 89.6%, 71.2% and 66.2% for the 5% MoS₂/Bi₂O₃, 10% MoS₂/Bi₂O₃, 15% MoS₂/Bi₂O₃, 20% MoS₂/Bi₂O₃ and 25% MoS₂/ Bi₂O₃ heterojunction after irradiation for 120 min. As expected, the Z-scheme MoS₂/Bi₂O₃ heterojunction photocatalysts exhibit a better photocatalytic performance compared to simple MoS₂ and Bi₂O₃, which can also obviously enhance the photocatalytic performance. More interestingly, when the content of MoS_2 is 15 wt% (0.02 g), the highest degradation rate achieved is 89.6%. However, when the content of MoS₂ grows to 25%, the degradation rate is only 66.2%. This is mainly due to the higher content of MoS₂ on the Bi₂O₃ rods which may restrain the absorption of visible light and the light transmission capacity, after that, it will cause a negative influence on the photocatalytic process. On the contrary, with a lower content of MoS₂, there is not enough MoS₂ nanosheets inserted into the Bi₂O₃ rods to create the Z-scheme heterojunction, which will reduce the degradation rate and refraction effect of the visible light. Thus, the reduced photons migrating onto the surface of the photocatalysts may



Fig. 5 (a) Photocatalytic degradation of MBT in the presence of the as-prepared samples under visible light irradiation; (b) absorption spectra of MBT over the 15% MoS_2/Bi_2O_3 heterojunction; (c) the pseudo-first-order reaction kinetics; and (d) values of reaction rate constants over the as-prepared samples.

cause a relatively low removal efficiency. From Fig. 5b, it can be observed that the absorbance peak intensity of the MBT solution over the 15% MoS₂/Bi₂O₃ composite gradually decreased during the degradation process. Furthermore, the reaction kinetics of MBT degradation over the Z-scheme heterojunction photocatalysts were investigated using the model of $\ln(C_0/C) = kt$, in which the slope k is the apparent reaction rate constant (Fig. 5c and d). Evidently, the Z-scheme MoS₂/Bi₂O₃ heterojunctions show a higher k value compared with pure MoS₂ and Bi₂O₃, and the 15% MoS_2/Bi_2O_3 (0.01936 min⁻¹) was about 15.6 and 5.1 times as high as that of MoS_2 (0.00124 min⁻¹) and Bi_2O_3 (0.00382 min⁻¹) respectively. To further confirm the adsorption of the catalysts, adsorption tests for MBT were also carried out and the results are presented in Fig. S1 (ESI[†]). The above described results all demonstrate that the 15% Z-scheme MoS₂/Bi₂O₃ heterojunction distinctly promotes the separation efficiency of the charge carriers and mineralization of the MBT molecules can be achieved.

It is important for the photocatalyst to be reusable and stable to allow its practical application. Thus, to evaluate the reusability and stability of the Z-scheme MoS₂/Bi₂O₃ heterojunction, the 15% MoS₂/Bi₂O₃ heterojunction was assessed via the degradation of MBT under visible light irradiation. It can be seen in Fig. 6a that there is no distinct inactivation in the photocatalyst, which indicates that the 15% Z-scheme $MoS_2/$ Bi₂O₃ heterojunction possesses a high stability. Furthermore, in order to carefully detect the reusability and stability of the photocatalysts, XRD characterization was performed before and after the degradation process, the results are shown in Fig. 6b. As expected, the catalyst does not show any obvious change in the intensity after the degradation process, this means that the 15% Z-scheme MoS₂/Bi₂O₃ heterojunction possesses an outstanding photocatalytic recyclability and stability in practical applications.

Moreover, it is well known that TC, as a universal antibiotic drug, has greatly harmed the environment and food sources owing to its excessive use in human and animals. Therefore, we also evaluated the photocatalytic performance of the as prepared samples *via* the degradation of TC under visible light. Fig. 7a shows the visible-light photocatalytic degradation curves of TC over pure MoS₂, Bi₂O₃ rods and the 15% MoS₂/Bi₂O₃



Fig. 7 (a) Photocatalytic reduction curves for TC over the as-prepared different samples; (b) absorption spectra of TC over the 15% MoS_2/Bi_2O_3 composite; (c) photocatalytic degradation curves; and (d) absorbance variations of RhB solution over the as-prepared different samples under visible light.

heterojunction. As expected, the 15% Z-scheme MoS_2/Bi_2O_3 heterojunction exhibits the highest efficiency and a reduction of 79.3% is achieved, which is a factor of 4.65 and 1.94 times higher than that of simple MoS_2 (18.6%) and Bi_2O_3 (40.8%) after 120 min respectively. Meanwhile, as can be seen from Fig. 7b, the characteristic absorption peak intensity of TC increasingly declines and there is no shift of the maximum absorption wavelength position at 357 nm. Furthermore, the reaction kinetics of TC over different samples are shown in Fig. S3a and b (ESI†). The rate constant for the 15% MoS_2/Bi_2O_3 heterojunction is higher than that observed for pure MoS_2 and Bi_2O_3 . Thus, these results all prove that the Z-scheme $MoS_2/$ Bi_2O_3 heterojunctions have the ability to accelerate the separation efficiency of the charge carriers and improve the photocatalytic performance compared to pure MoS_2 and Bi_2O_3 .

In addition, RhB was chosen as a representative dye and model pollutant to determine the universal effect of the Z-scheme MoS_2/Bi_2O_3 heterojunctions. As shown in Fig. 7c, 90% of RhB can be removed by the 15% MoS_2/Bi_2O_3 heterojunction under visible light within 120 min and the degradation rate is higher than that



Fig. 6 (a) Five cycle degradation kinetic curves of MBT; (b) XRD patterns of 15% MoS₂/Bi₂O₃ heterojunction after five reaction cycles.

of pure MoS_2 and Bi_2O_3 . The inset in Fig. 7c shows the color changes occurring every 20 min, it can be observed that the color of the solutions changes gradually from pink to colorless. Moreover, Fig. 7d reveals the absorbance variation of the RhB solutions over the 15% Z-scheme MoS_2/Bi_2O_3 heterojunction. It is noted that the characteristic absorption peak intensity of RhB (553 nm) distinctly decreases with each time interval. As with the degradation of TC, the reaction kinetics of RhB over different samples is shown in Fig. S3c and d (ESI†). As expected, the rate constant for the 15% MoS_2/Bi_2O_3 heterojunction is the highest among all of the samples. Finally, the above described degradation experiments demonstrate that the Z-scheme heterojunctions can greatly improve the photocatalytic performance for the degradation of industrial and domestic pollutants under visible light.

Fig. 8 shows the N₂ adsorption–desorption isotherms for the prepared samples. It is well known that the surface area significantly affects the photocatalytic activity of photocatalysts, and it was found that the adsorption–desorption isotherms exhibited a classical type IV with a hysteresis loop. From Fig. 8a, the Brunauer–Emmett–Teller (BET) surface area (S_{BET}) of pure Bi₂O₃ was found to be 8.5 m² g⁻¹, clearly revealing that pure Bi₂O₃ has a low surface area. Compared with the pristine Bi₂O₃, the S_{BET} of the as-prepared 15% Z-scheme MoS₂/Bi₂O₃ heterojunction photocatalyst was found to be 18.5 m² g⁻¹, and this was larger than that found for the simple Bi₂O₃ (Fig. 8b). This obviously indicates that the adsorption activity of 15% MoS₂/Bi₂O₃ and Bi₂O₃ conform well to the surface area. Therefore, the

photocatalytic activity of the 15% Z-scheme MoS_2/Bi_2O_3 heterojunction is much higher than that of pure Bi_2O_3 . This result also indicates that the surface area of the photocatalysts is an important factor that affects the photocatalytic activity.

3.6. Photocurrents and electrochemical impedance spectral analyses

In order to further understand the transfer behavior of the charge carriers in the heterojunctions, photocurrent experiments were carried out. The photocurrent responses of the pure MoS_{2} , Bi₂O₃ and 15% Z-scheme MoS₂/Bi₂O₃ heterojunction are shown in Fig. 9a. Evidently, the 15% MoS₂/Bi₂O₃ heterojunction gives the best photocurrent response, which is 6.47 and 2.21 times that of pristine MoS₂ and Bi₂O₃. This result confirms that the Z-scheme MoS₂/Bi₂O₃ heterojunction has a lower recombination rate for the charge carriers, which means the photocatalytic performance was greatly enhanced. Moreover, after several cycles, the steady and reproducible photocurrent response suggests that the 15% Z-scheme MoS₂/Bi₂O₃ heterojunction possesses a good photophysical stability. In order to further research the interfacial charge transfer abilities of the photocatalysts, EIS tests were performed. As shown in Fig. 9b, the radius of the 15% MoS₂/Bi₂O₃ heterojunction was the smallest compared to that of pure MoS₂ and Bi₂O₃, and it exhibits a faster interfacial charge transfer rate in the Z-scheme MoS₂/Bi₂O₃ heterojunctions. Thus, the photocurrent and EIS results indicate that the 15% Z-scheme MoS₂/Bi₂O₃ heterojunction can efficiently control the recombination of the electron-hole pairs and the Z-scheme heterojunction



Fig. 8 N_2 adsorption-desorption isotherms of the as-prepared samples.



Fig. 9 (a) Transient photocurrent response; and (b) electrochemical impedance spectroscopy of the as-prepared samples.



Fig. 10 m/z of degrading MBT over the 15% MoS₂/Bi₂O₃ heterojunction: (a) degradation during 30 min; (b) degradation in 1 h; (c) degradation in 2 h; and (d) possible intermediate products of degradation of MBT over the 15% MoS₂/Bi₂O₃ heterojunction.

structure can remarkably accelerate the charge transfer *via* intimate contact between the MoS_2 and Bi_2O_3 , which also increases the photocatalytic performance of the MoS_2/Bi_2O_3 heterojunctions.

3.7. Intermediates and mineralization ability tests

The intermediates during the degradation of MBT were detected using high performance liquid chromatography mass spectrometry (HPLC-MS) experiments. From Fig. 10a-c, it can be seen that the peak at m/z = 167 of MBT reduces during the degradation reaction and had almost disappeared after two hours. All of the results indicate that MBT was degraded into small molecules, such as CO₂ and H₂O. Taking into account the deep analysis of the photodegradation process, the possible intermediate products were tested by the change in the measured mass, which is shown in Fig. 10d. As can be observed in Fig. 10d, the MBT A (m/z = 167) is fragmented into B (m/z = 187) by the addition reaction. Then C (m/z = 169) is formed by losing the -OH group by the elimination reaction. In the proceeding reaction, D (m/z = 152) is fragmented by losing $-NH_2$. After that, D is further resolved to E (m/z = 110) by an addition reaction. Next, F and G are created by wiping out -SH and by an addition reaction. In the end, these small intermediate products may be further degraded into H₂O and CO₂.

3.8. Trapping experiments and ESR

To gain a better understanding of the process mechanism of the Z-scheme MoS_2/Bi_2O_3 heterojunction, radical trapping tests were carried out by adding the different trapping agents of TEOA, IPA and Vc to catch holes (h⁺), hydroxyl radicals (•OH) and the superoxide radical (•O₂⁻) respectively. As shown in Fig. 11a and b, when Vc and TEOA were added to the MBT solution, the photodegradation rate greatly reduced to 16.3% and 25.7% when compared with the addition of no radical scavengers, indicating that the •O₂⁻ and h⁺ are major active species in the process of removing MBT. Upon the addition of IPA into the MBT solution, the degradation rate was 50.8%, which decreased by almost 39% compared with no radical



Fig. 11 (a and b) Photocatalytic degradation ratios of MBT using different radical scavengers over the 15% MoS_2/Bi_2O_3 heterojunction under visible light irradiation. DMPO spin-trapping ESR spectra of MBT solutions after visible light irradiation: (c) 15% MoS_2/Bi_2O_3 -CH₃OH/DMPO; and (d) 15% MoS_2/Bi_2O_3 -H₂O/DMPO.

scavengers being added. This implies that [•]OH is not the main radical involved in the degradation of MBT. In order to further confirm the emergence of the abovementioned active species, the ESR technique was used to explain the appearance of the ${}^{\bullet}O_2^{-}$ and ${}^{\bullet}OH$ radicals within the photocatalytic processes.^{57,58}

Fig. 11c exhibits the DMPO-•O2⁻ characteristic peaks of MoS₂, Bi₂O₃ and the 15% Z-scheme MoS₂/Bi₂O₃ heterojunction under visible light irradiation. It is worth noting that there are no evident characteristic signals of DMPO- ${}^{\bullet}O_2^{-}$ in Bi₂O₃, which suggests that pure Bi₂O₃ cannot form •O₂⁻ radicals. In contrast to the simple MoS₂ and Bi₂O₃, the 15% MoS₂/Bi₂O₃ heterojunction shows the strongest intensity, which indicates more •O₂⁻ can be generated in the photocatalytic degradation reaction. Similarly, it was also observed that pristine Bi_2O_3 and 15% $MoS_2/$ Bi₂O₃ heterojunction can create DMPO-•OH. There are four characteristic peaks of DMPO-•OH (1:2:2:1 quartet pattern) found in the ESR spectra (Fig. 11d). Obviously, the intensity of all signals for the bare Bi₂O₃ are largely weaker than those of the 15% MoS₂/Bi₂O₃ heterojunction, which means that the 15% Zscheme MoS₂/Bi₂O₃ heterojunction can create more •OH active species compared to the single Bi₂O₃. In summary, these results demonstrate that all three active species play a significant role in the removal reaction, and the degree of their effect on the MBT degradation process is in the order ${}^{\bullet}O_2^- > h^+ > {}^{\bullet}OH$.

3.9. Possible photocatalytic reaction mechanism

In order to further comprehend the transfer method of the photo-induced charges, a possible photocatalytic mechanism of the Z-scheme MoS_2/Bi_2O_3 heterojunction was proposed. Hypothetically, as shown in Fig. 12, when the MoS_2/Bi_2O_3 heterojunction is excited by visible light, the electrons move from the CB of the MoS_2 nanosheets to the CB of the Bi_2O_3 rods. Meanwhile, the holes will transfer from the VB of the Bi_2O_3 to the VB of the MoS_2 . However, in theory, the photo-induced



Fig. 12 Schematic illustration of the band structure diagram and photoinduced carrier transfer for the Z-scheme MoS_2/Bi_2O_3 heterojunction for the degradation of various organic pollutants under visible-light irradiation.

electrons in the CB of Bi₂O₃ (0.16 eV vs. NHE) cannot react with O_2 to produce $O_2^-(O_2^-, -0.046 \text{ eV } \nu s. \text{ NHE})$ and the holes in the VB of MoS_2 cannot oxidize OH^- to yield $^{\bullet}OH$ ($OH^{-/^{\bullet}}OH$, 2.38 eV vs. NHE),^{59,60} the above described hypothesis goes against the results of the electron spin resonance (ESR) technology and active species trapping experiments. Therefore, the Z-scheme electron-hole pairs transfer methods are illustrated in Fig. 12. On account of the fact that the Z-scheme MoS₂/Bi₂O₃ heterojunction can be irradiated using visible light to generate photo-induced electron-hole pairs, at the same time, the electrons in the CB of Bi₂O₃ have a tendency to transfer and unite with the holes in the VB of MoS₂. Then, the more electrons that are concentrated on the CB of MoS₂ the more will further react with O_2 to generate more O_2^- and the photo-induced holes in the VB of Bi₂O₃ can react with OH⁻ to form more •OH. In other words, the possible photocatalytic degradation is demonstrated below in eqn (1)-(5):

$$MoS_2 + h\nu \rightarrow MoS_2 (e^-) + MoS_2 (h^+)$$
 (1)

$$\operatorname{Bi}_{2}\operatorname{O}_{3} + h\nu \to \operatorname{Bi}_{2}\operatorname{O}_{3}(e^{-}) + \operatorname{Bi}_{2}\operatorname{O}_{3}(h^{+})$$

$$(2)$$

$$MoS_2 + e^- + O_2 \rightarrow {}^{\bullet}O_2^-$$
(3)

$$Bi_2O_3 + h^+ + OH^- \rightarrow {}^{\bullet}OH \tag{4}$$

 ${}^{\bullet}\text{O}_2^- + \text{h}^+ + \text{OH}^- + \text{MBT/TC/RhB} \rightarrow \text{degraded products}$ (5)

4. Conclusions

A novel Z-scheme MOS_2/Bi_2O_3 heterojunction with MOS_2 nanosheets on the surface of Bi_2O_3 rods was prepared for the first time using a facile and practical hydrothermal method. The outstanding sample of the 15% Z-scheme MOS_2/Bi_2O_3 heterojunction gave the best photocatalytic performance, which was almost 6.63 and 2.43 times higher than that of pure MOS_2 and Bi_2O_3 for the degradation of MBT and 4.26 and 1.94 times higher for the removal of TC. Furthermore, the 15% Z-scheme MOS_2/Bi_2O_3 heterojunction exhibited the highest photocatalytic activity for the reduction of RhB, which can attain a 90% removal efficiency within 120 min. In addition, the increase in the photocatalytic efficiency could be attributed to the combination of Bi_2O_3 and MoS_2 extending the light absorption and the formation of Z-scheme MoS_2/Bi_2O_3 heterojunction by the tight face-to-face connection with a good energy band match between the MoS_2 and Bi_2O_3 . The interfacial interaction between MoS_2 and Bi_2O_3 can accelerate the separation of the photo-induced carriers and amplify the specific surface area. Finally, this work provides a novel design and preparation method for use with other high performance Z-scheme heterojunctions for degrading various industrial and domestic pollutants in water.

Conflicts of interest

There are no conflicts to declare.

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