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Flower-like Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction superstructures with enhanced visible-light-driven photocatalytic activity

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Abstract: A prerequisite for the development of photocatalytic technology is to obtain efficient visible-light-driven photocatalysts. Herein, we have reported flower-like Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction as a novel and efficient visible-light-driven photocatalyst. Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction has been prepared by a solvothermal method. It consists of flower-like superstructures with diameters ranging from 1 to 3 µm, which are built from Bi$_2$MoO$_6$ nanosheets with a thickness of about 15 nm decorated with Bi$_2$S$_3$ nanoparticles with diameter of ~3.5 nm. Furthermore, the photocatalytic activity of Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction has been evaluated through the degradation of rhodamine B (RhB) dye and colorless parachlorophenol (4-CP) under visible-light irradiation (λ > 400 nm). The results demonstrate that Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction exhibits higher photocatalytic activity in degrading RhB and 4-CP than single Bi$_2$S$_3$ or Bi$_2$MoO$_6$. More importantly, the photocatalytic
activity of Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction is superior to the sum of the activities of two individual photocatalysts (Bi$_2$MoO$_6$ and Bi$_2$S$_3$). The recycling experiment confirms that Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction is essentially stable during the photocatalytic process. Therefore, Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction can be used as an efficient and stable visible-light-driven photocatalyst for the purification of the environments.

Keywords: Bi$_2$S$_3$/Bi$_2$MoO$_6$; superstructures; visible-light-driven; photocatalysis

1. Introduction

Over the past few years, environmental problems, especially associated with harmful organic pollutants in water, are posing severe threats to human health. Among the widespread methods for the purification of the environments, semiconductor photocatalysis, as a “green” and energy saving technology for completely eliminating organic pollutants, has drawn worldwide attention.$^{1-4}$ A prerequisite for the development of photocatalytic technology is to obtain efficient photocatalysts.$^{1-4}$ Up to now, TiO$_2$ is undoubtedly one of the most excellent and widely used photocatalysts due to its abundance, chemical stability, low cost, and nontoxicity.$^{5,6}$ But a major drawback of TiO$_2$ is its large bandgap (~3.2 eV), and thus only UV light (typically $\lambda < 400$ nm; a small fraction of the solar spectrum, ~5%) can be absorbed, which significantly limits the utilization of solar light in the visible region ($400 < \lambda < 700$ nm).$^{5,6}$ To utilize solar energy more effectively, the development of efficient visible-light-driven (VLD) photocatalysts has drawn worldwide attention.

Recently, bismuth(iii)-based semiconductor photocatalysts have been demonstrated to exhibit superior photocatalytic activities under visible-light irradiation ($\lambda > 400$ nm), since Bi
6s and O 2p levels can form a preferable hybridized conduction band (VB) to show strong oxidative ability for degrading organic pollutants.\textsuperscript{7-19} Thus, a series of single-component bismuth(iii)-based photocatalysts have been developed, such as CaBi\textsubscript{2}O\textsubscript{4},\textsuperscript{7} Bi\textsubscript{2}O\textsubscript{3},\textsuperscript{8} BiVO\textsubscript{4},\textsuperscript{9} Bi\textsubscript{2}WO\textsubscript{6}\textsuperscript{10, 11} BiOX (X=Cl, Br, I)\textsuperscript{12} and Bi\textsubscript{2}MoO\textsubscript{6}\textsuperscript{13-19}. Among these bismuth(iii)-based photocatalysts, bismuth molybdate (Bi\textsubscript{2}MoO\textsubscript{6}, band gap ~2.7 eV) possesses excellent photocatalytic performance for water splitting and organic pollutant degradation.\textsuperscript{13-19} For instance, Kudo et al. have reported that Bi\textsubscript{2}MoO\textsubscript{6} shows high photocatalytic activity for O\textsubscript{2} evolution under visible-light irradiation\textsuperscript{15} and several groups have confirmed that Bi\textsubscript{2}MoO\textsubscript{6} exhibits excellent photocatalytic activity for the degradation of rhodamine B dye.\textsuperscript{16-19} However, there are still some drawbacks hindering their practical application, such as the unsatisfactory photo-response range and short photogenerated electron-hole pair lifetime.\textsuperscript{13-19}

It is well known that the construction of semiconductor heterojunctions is an efficient method for the improvement of photocatalytic performances, as summarized in our recent review.\textsuperscript{3} To improve the photocatalytic activity of Bi\textsubscript{2}MoO\textsubscript{6}, several kinds of Bi\textsubscript{2}MoO\textsubscript{6}-based heterojunctions have been developed, including Bi\textsubscript{2}MoO\textsubscript{6}-oxide (oxide: TiO\textsubscript{2},\textsuperscript{20} \(\zeta\)-Bi\textsubscript{2}O\textsubscript{3},\textsuperscript{21} CuPc,\textsuperscript{22} BiOCl,\textsuperscript{23} ZnTiO\textsubscript{3},\textsuperscript{24} and Bi\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}\textsuperscript{25}), Bi\textsubscript{2}MoO\textsubscript{6}-metal (metal: Ag\textsuperscript{26} and W\textsuperscript{27}), Bi\textsubscript{2}MoO\textsubscript{6}-carbon (carbon: graphene\textsuperscript{28} and carbon nanofibers\textsuperscript{29}), multicomponent (such as Ag-AgBr-Bi\textsubscript{2}MoO\textsubscript{6}\textsuperscript{30} and Ag-AgCl-Bi\textsubscript{2}MoO\textsubscript{6}\textsuperscript{31}). Compared with pure Bi\textsubscript{2}MoO\textsubscript{6}, these Bi\textsubscript{2}MoO\textsubscript{6}-based heterojunctions exhibit higher photocatalytic activity for the degradation of organic pollutants, hydrogen generation, and/or photocatalytic disinfection.\textsuperscript{20-32} However, to the best of our knowledge, there is little work that reports on the development of Bi\textsubscript{2}MoO\textsubscript{6}-sulfide heterojunction photocatalysts, except for MoS\textsubscript{2}/Bi\textsubscript{2}MoO\textsubscript{6}.\textsuperscript{32}
As a lamellar binary semiconductor, bismuth sulfide (Bi$_2$S$_3$) has significant applications in photovoltaics and photocatalysis. Several kinds of Bi$_2$S$_3$ heterojunctions have been demonstrated to exhibit excellent photocatalytic activity, such as Bi$_2$S$_3$/Bi$_2$WO$_6$ and Bi$_2$S$_3$/BiOX (X=Cl, Br, I). Moreover, the size quantization enables Bi$_2$S$_3$ nanoparticles (1.3 eV for bulk) to show tunable photosensitization and considerable photoactivity in the visible region. Herein, to improve the photocatalytic activity of Bi$_2$MoO$_6$, we designed and constructed Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction as a novel photocatalyst. Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction was prepared via a solvothermal method, and it consisted of flower-like superstructures with diameters ranging from 1 to 3 µm, which were built from Bi$_2$MoO$_6$ nanosheets decorated with Bi$_2$S$_3$ nanoparticles (~3.5 nm). Importantly, under visible-light irradiation, Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction exhibited higher photocatalytic activity in degrading rhodamine B (RhB) dye and colorless parachlorophenol (4-CP) than single Bi$_2$S$_3$ or Bi$_2$MoO$_6$.

2. Experimental Details

2.1 Materials

Bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O), sodium molybdate (Na$_2$MoO$_4$·2H$_2$O), thiourea ((NH$_2$)$_2$CS), absolute ethanol (CH$_3$CH$_2$OH) and ethylene glycol were purchased from Sinopharm Chemical Reagent Co., Ltd (P.R. China). Rhodamine B (RhB) was purchased from Sigma (America) and parachlorophenol (4-CP) was purchased from J&K CHEMICAL Ltd. (P.R. China). All chemicals were of analytical grade and were used as received without further purification.

2.2. Preparation of photocatalysts
Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction was prepared via a solvothermal method. In a typical procedure, Bi(NO$_3$)$_3$·5H$_2$O (2.1 mmol) and Na$_2$MoO$_4$·2H$_2$O (1 mmol) were ultrasonically dissolved in 10 mL ethylene glycol, respectively. Meanwhile, (NH$_2$)$_2$CS (0.15 mmol) was ultrasonically dissolved in 60 mL absolute ethanol. Subsequently, Na$_2$MoO$_4$ solution and (NH$_2$)$_2$CS solution were added in turn to Bi(NO$_3$)$_3$ solution. The resulting precursor solution was agitated for about 10 min, then transferred to a 100 mL autoclave, sealed, and solvothermally treated at 160 °C for 12 h. The system was cooled to room temperature naturally, and the solid sample was collected by filtration, washed thoroughly with water and ethanol and dried at 60 °C for 24 h. For comparison, pure Bi$_2$MoO$_6$ and Bi$_2$S$_3$ sample were also respectively prepared by adopting the same method in the absence of (NH$_2$)$_2$CS or Na$_2$MoO$_4$·2H$_2$O.

2.3. Characterization of photocatalysts

X-ray diffraction (XRD) measurements were recorded on a D/max-2550 PC X-ray diffractometer using Cu Ka radiation (λ = 0.15418 nm). The scanning electron microscope (SEM) characterizations were performed on a Hitachi S-4800 field emission scanning electron microscope. The transmission electron microscope (TEM) analyses were performed by a JEOL JEM-2100 high-resolution transmission electron microscope. The optical diffuse reflectance spectrum were conducted on a UV-VIS-NIR scanning spectrophotometer (Lambda 35, PerkinElmer) using an integrating sphere accessory. The electronic states of elements in the sample were analyzed by using X-ray photoelectron spectroscopy (PHI-5400, PerkinElmer). The Brunauer-Emmett-Teller (BET) surface area was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P$_0$) range of.
A desorption isotherm was used to determine the pore size distribution via the Barret-Joyner-Halender (BJH) method, assuming a cylindrical pore model.

### 2.4. Photocatalytic activity

Photocatalytic activities of as-prepared photocatalysts were evaluated by degrading the aqueous solution of rhodamine B (RhB) dye or colorless parachlorophenol (4-CP) under visible-light irradiation using a 300 W xenon lamp (Beijing Perfect Light Co. Ltd., Beijing) with a cut-off filter (λ > 400 nm) as light source. In each experiment, 30 mg of photocatalyst was added to 50 mL of RhB (10 mg L\(^{-1}\), pH = 6.27) or 4-CP (1 mg L\(^{-1}\), pH = 6.34) solution. Prior to irradiation, the suspension was mildly magnetically stirred in the dark for 30 min to ensure that an adsorption/desorption equilibrium was established between the photocatalysts and the target contaminant (RhB or 4-CP). During visible-light irradiation, 2 mL suspension was collected at given time intervals and then centrifuged to remove the remaining solids for analysis. For the photocatalytic test of RhB, the UV-vis absorption spectra of the solutions were recorded on a U-2910 UV-vis spectrophotometer (Hitachi, Japan), and then RhB concentration was calculated by analyzing the photoabsorption intensity at wavelength of 554 nm. For the photocatalytic test of 4-CP, the 4-CP concentrations in the solutions were analyzed by high-performance liquid chromatography (HPLC) using an Dionex Ultimate 3000 series (USA) equipped with a diode array detector (DAD) with wavelength set at 280 nm directly after filtration through a 0.22 µm hydrofacies syringe filter. The mobile phase was methanol (80%) and water (20%) and the flow rate was 0.5 mL min\(^{-1}\). In the stability and reusability test of the catalyst, four consecutive cycles were tested. The catalysts were washed thoroughly with water and dried after each cycle, and then it was immersed in the same volume (50 mL) of fresh parachlorophenol aqueous solution (1 mg L\(^{-1}\)) again.
Total organic carbon (TOC) analysis was carried out by adding 300 mg Bi$_2$S$_3$/Bi$_2$MoO$_6$ into 100 mL RhB aqueous solution (60 mg L$^{-1}$). Prior to irradiation, the suspension was magnetically stirred for 60 min in the dark to achieve a saturated RhB absorption onto the photocatalyst surface. During visible-light irradiation, 10 mL suspension was collected at given time intervals and filtered by the membrane pore size of 0.45 µm to remove the photocatalyst, and then was detected by a Shimadzu TOC-VCPH total organic carbon analyzer.

3. Results and discussion

3.1 Preparation and characterization of catalysts

Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction was prepared by a one-step solvothermal method. Bi$_2$MoO$_6$ was produced by the reaction of Bi(NO$_3$)$_3$ (2 mmol) and Na$_2$MoO$_4$ (1 mmol) and then crystallized during the solvothermal process. The redundant Bi(NO$_3$)$_3$ (0.1 mmol) molecules were adsorbed on the surface of Bi$_2$MoO$_6$. Sulfur ions were slowly released from (NH$_2$)$_2$CS in the solvothermal process, resulting in the in situ growth of Bi$_2$S$_3$ nanoparticles on Bi$_2$MoO$_6$ superstructures to form Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction (theoretical molar ratio of Bi$_2$S$_3$:Bi$_2$MoO$_6$ was 1:20).

The phase of the as-prepared Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction was investigated by XRD pattern (Fig. 1). For comparison, the XRD patterns of pure Bi$_2$MoO$_6$ and Bi$_2$S$_3$ were also recorded. All diffraction peaks from pure Bi$_2$MoO$_6$ can be readily indexed to orthorhombic Bi$_2$MoO$_6$ (JCPDS No. 21-0102), and the diffraction peaks for pure Bi$_2$S$_3$ can be assigned to orthorhombic Bi$_2$S$_3$ (JCPDS No. 17-0320). Bi$_2$S$_3$/Bi$_2$MoO$_6$ sample exhibits a XRD pattern which is similar to that of pure Bi$_2$MoO$_6$; four strong diffraction peaks at 28.3°, 32.6°, 46.7°
and 55.6° can be assigned to (131), (002), (202) and (133) planes of orthorhombic Bi$_2$MoO$_6$.

In addition, no characteristic peaks peculiar to Bi$_2$S$_3$ are observed, which may be attributed to the fact that the content of Bi$_2$S$_3$ in Bi$_2$S$_3$/Bi$_2$MoO$_6$ was too low to be efficiently detected.

![XRD patterns](image)

**Fig. 1.** XRD patterns of Bi$_2$MoO$_6$, Bi$_2$S$_3$, as-prepared Bi$_2$S$_3$/Bi$_2$MoO$_6$ and the used Bi$_2$S$_3$/Bi$_2$MoO$_6$ after photocatalytic test, and standard XRD patterns of Bi$_2$MoO$_6$ (JCPDS 21-0102) and Bi$_2$S$_3$ (JCPDS 17-0320).

![SEM images](image)

**Fig. 2.** SEM images of pure Bi$_2$MoO$_6$ (a) and pure Bi$_2$S$_3$ (b).

Subsequently, the sizes and morphologies of Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction as well as pure Bi$_2$MoO$_6$ and Bi$_2$S$_3$ were further studied by SEM and TEM images (Fig. 2, 3). Obviously, pure Bi$_2$MoO$_6$ sample consists of flower-like microspheres with diameters ranging from 1 to 3 µm (Fig. 2a). The close-up view indicates that Bi$_2$MoO$_6$ flower-like superstructure is in fact
built from nanosheets (inset of Fig. 2a). Meanwhile, pure Bi$_2$S$_3$ sample presents the irregular large-size flake structure (Fig. 2b). In addition, Bi$_2$S$_3$/Bi$_2$MoO$_6$ sample is also composed of flower-like superstructures with diameters ranging from 1 to 3 µm (Fig. 3a), which is similar to that of pure Bi$_2$MoO$_6$ sample. These superstructures are in fact built from two dimensional nanosheets with a thickness of about 15 nm and an average length of about 200 nm (Fig. 3b), which can be vividly demonstrated by the part view (Fig. 3c) at higher magnification. More importantly, more hierarchical nanopores and macro-pores superstructures with bigger diameter sizes in nanosheets are obtained by Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction compared with pure Bi$_2$S$_3$ and pure Bi$_2$MoO$_6$, and these hierarchical porous superstructures may improve the physicochemical properties or serve as transport paths for small molecules, are found among the nanosheets in the spherical superstructures (Fig. 3c).

Fig. 3. SEM (a-c) and TEM (d-f) images of Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction.

Further information about Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction is obtained from TEM image (Fig. 3d), and it confirms that the flower-like superstructure is built from nanosheets. The lattice resolved high-resolution TEM image (Fig. 3e) and its corresponding Fourier transform
(FFT) pattern (inset of Fig. 3e) clearly exhibit the (131) and (111) crystal planes with 0.316 nm and 0.370 nm d-spacings and 50° interfacial angle, further indicating the orthorhombic structure of Bi$_2$MoO$_6$. Importantly, one can find that there are plenty of small nanoparticles with the size of ~3.5 nm anchored on the surface of nanosheets (Fig. 3d), and these small nanoparticles exhibit lattice fringes with an interplane spacing of 0.225 nm, which is corresponding to the (141) crystal plane of orthorhombic Bi$_2$S$_3$ (Fig. 3f). In addition, the EDS (Fig. 4) confirms the presence of Bi, Mo, O and S elements in the Bi$_2$S$_3$/Bi$_2$MoO$_6$ sample.

![Fig. 4 EDS pattern of Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction.](image)

Furthermore, the elemental composition and chemical status of Bi$_2$S$_3$/Bi$_2$MoO$_6$ sample was investigated by X-ray photoelectron spectroscopy (XPS). The survey spectrum in Fig. 5a clearly demonstrates that the sample is mainly composed of Bi, Mo, O and S elements. The binding energies (Fig. 5b) of 158.3 eV for Bi 4f$_{7/2}$ and 163.6 eV for Bi 4f$_{5/2}$ indicate a trivalent oxidation state for bismuth. Fig. 5c shows that the binding energies of Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$ peaks in sample are respectively located at 234.5 and 231.4 eV, suggesting that Mo$^{6+}$ exists in the Bi$_2$S$_3$/Bi$_2$MoO$_6$ sample. Meanwhile, Fig. 5d gives the binding energies of S
2p_{1/2} and S 2p_{3/2} peaks in sample, which are respectively located in 158.3 and 163.6 eV, indicating that S^{2-} exists in Bi_{2}S_{3}/Bi_{2}MoO_{6} sample. These results support the formation of Bi_{2}S_{3} and Bi_{2}MoO_{6} in the sample.

Based on the above XRD, TEM, EDS and XPS results, one can conclude that there are Bi_{2}S_{3} and Bi_{2}MoO_{6} species in the Bi_{2}S_{3}/Bi_{2}MoO_{6} sample, and the nanojunction in Bi_{2}S_{3}/Bi_{2}MoO_{6} system is well constructed. Subsequently, the nitrogen adsorption/desorption isotherms of Bi_{2}MoO_{6} and Bi_{2}S_{3}/Bi_{2}MoO_{6} heterojunction were investigated (Fig. 6a). The Brunauer-Emmett-Teller (BET) surface area of Bi_{2}MoO_{6} is calculated to be 65.7 m^{2} g^{-1}. Interestingly, Bi_{2}S_{3}/Bi_{2}MoO_{6} heterojunction exhibits a slight increase of BET surface area (74.9 m^{2} g^{-1}). Usually, an increase of the surface area leads to an improvement of the photocatalytic activity. Moreover, the pore size distributions, which are calculated from the desorption branches, reveal the existence of nano-pores in both Bi_{2}MoO_{6} and Bi_{2}S_{3}/Bi_{2}MoO_{6}
heterojunction (the inset of Fig. 6a). The nanopores in Bi$_2$MoO$_6$ have the diameter of about 15.4 nm, while those in Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction have the diameter of about 14.4 nm, which agrees with that revealed by the SEM and TEM images (Fig. 2a and Fig. 3a-c). The presence of nanopores may greatly improve the physicochemical properties and/or serve as transport paths for small molecules.

Fig. 6 (a) Nitrogen adsorption–desorption isotherms of pure Bi$_2$MoO$_6$ and Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction; (b) Uv-vis diffuse reflectance spectra of pure Bi$_2$MoO$_6$, bulk Bi$_2$S$_3$ and Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction.

The optical absorption of Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction was measured by an UV-vis spectrometer (Fig. 6b). For comparison, the optical absorption spectra of pure Bi$_2$MoO$_6$ and bulk Bi$_2$S$_3$ were also recorded. Pure Bi$_2$MoO$_6$ exhibits strong photoabsorption from the UV to visible-light region with an absorption edge around 470 nm (band gap: 2.7 eV). In addition, bulk Bi$_2$S$_3$ shows intense absorption over the visible-light range, even extending to the infrared region. The fitted direct band gap of Bi$_2$S$_3$ is determined to be 1.30 eV, which is equal to its bulk value. Interestingly, Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction displays strong photoabsorption from the UV to visible-light region with an absorption edge around 480 nm, which is similar to that of pure Bi$_2$MoO$_6$. Obviously, the presence of Bi$_2$S$_3$ nanoparticles (NPs) in Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction has no obvious effect on its optical absorption, which should result from the small size and is similar to the previous study. On the basis of the effective
mass approximation model, the blue shift of Bi$_2$S$_3$ NPs relative to the bulk is dominated by
the confinement of electrons and holes, as described by the following equation:\textsuperscript{37, 38}

$$\Delta E_g(R) = \frac{\hbar^2}{8m_0^*R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right)$$

where $\Delta E_g(R)$ is the band gap shift for the crystal radius $R$, $h$ is the Planck’s constant, $m_0$ is
the electron mass, while $m_e^*$ and $m_h^*$ are the effective masses of electrons and holes,
respectively. Since Bi$_2$S$_3$ NPs exhibit the average diameter of ~3.5 nm (Fig. 3d. f), the
calculated band gap should be 2.9 eV which is close to that of (2.7 eV) Bi$_2$MoO$_6$.

The band edge positions of Bi$_2$MoO$_6$ (2.64 eV), bulk Bi$_2$S$_3$ (1.3 eV) and Bi$_2$S$_3$ NPs (2.9
eV) can be evaluated by the following empirical equation:\textsuperscript{39}

$$E_{VB} = X - E_0 + 0.5E_g \quad (1) \quad E_{CB} = E_{VB} - E_g \quad (2),$$

where $E_{VB}$ is the valence band (VB) edge
potential, $X$ is the electronegativity of the semiconductor, which is the geometric mean of the
electronegativity of the constituent atoms. The $X$ values for Bi$_2$MoO$_6$ and Bi$_2$S$_3$ are calculated
as 5.50 eV \textsuperscript{40} and 5.95 eV \textsuperscript{33}, respectively. $E_0$ is the energy of free electrons on the hydrogen
scale (about 4.5 eV), and $E_g$ is the band gap energy of the semiconductor. According to the
Eqs. (1) and (2), $E_{VB}$ and $E_{CB}$ values of Bi$_2$MoO$_6$ are determined to be 2.32 eV and -0.32 eV,
those of bulk Bi$_2$S$_3$ are 2.1 eV and 0.8 eV, and those of Bi$_2$S$_3$ NPs (~3.5 nm) are 2.90 eV and 0
eV. The VB of Bi$_2$S$_3$ shifts to more positive potentials to produce the larger VB energy
difference ($\Delta E_g$) between Bi$_2$MoO$_6$ and Bi$_2$S$_3$, which further favors the electrons transfer and
strong oxidization ability of holes.

\textbf{3.2 Photocatalytic performances under visible-light irradiation}

Rhodamine B (RhB), a common dye widely used in dyeing cellulose, nylon, silk and
wool, was firstly chosen as a representative pollutant to evaluate the photocatalytic
performance of Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction (Fig. 7). For comparison, RhB degradation without photocatalyst (blank test) and with pure Bi$_2$MoO$_6$ or pure Bi$_2$S$_3$, was also performed under the other identical conditions, respectively. When dissolved in distilled water, RhB displays a major absorption band centered at 554 nm that is used to monitor the photocatalytic degradation. Clearly, Bi$_2$MoO$_6$, Bi$_2$S$_3$ and Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction can reach the absorption equilibrium within 30 min in the dark and Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction can adsorb RhB molecules more efficiently (44.3%) than pure Bi$_2$MoO$_6$ (0.021%) and pure Bi$_2$S$_3$ (0.005%) due to the larger surface area.

Subsequently, the photocatalytic reaction was carried out for another 60 min under visible-light irradiation (Fig. 7). The blank test indicates that the degradation of RhB is extremely slow without photocatalyst under visible-light irradiation. By using the bulk Bi$_2$S$_3$ as the VLD photocatalyst, the degradation of RhB is also slow, and only 14% RhB can be removed after 60 min of reaction. When pure Bi$_2$MoO$_6$ is used as the VLD photocatalyst, the photodegradation efficiency of RhB can just approach 29% after 60 min, indicating low photocatalytic activity. Importantly, when Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction is used as the VLD photocatalyst, 100% RhB can be removed after 60 min of visible-light irradiation, indicating the highest photocatalytic activity. Furthermore, the photocatalytic degradation rate was calculated by the apparent pseudo-first-order model (the inset of Fig. 7). The rate from Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction was determined to be 0.0643 min$^{-1}$ which is greatly higher than that from the pure Bi$_2$S$_3$ (0.000195 min$^{-1}$) and pure Bi$_2$MoO$_6$ (0.000493 min$^{-1}$). These facts indicate that the construction of Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction improve greatly the photocatalytic performances, which is similar to the previous reports on heterojunction
photocatalysts such as Alpha-beta-Ga$_2$O$_3$ junction,$^{41,42}$ Sr$_2$TiO$_4$/SrTiO$_3$ (La,Cr) heterojunction$^{43}$ and Ga$_2$O$_3$/ZnGa$_2$O$_4$ heterojunction$^{44}$.

**Fig. 7** The adsorption and degradation efficiency of RhB in aqueous solution (10 mg L$^{-1}$, 50 mL, pH = 6.27) versus the exposure time under visible-light irradiation ($\lambda > 400$ nm), in the absence of photocatalyst and in the presence of as-prepared samples (30 mg).

**Fig. 8** The adsorption and degradation efficiency of 4-CP in aqueous solution (1 mg L$^{-1}$, 50 mL, pH = 6.34), versus the exposure time under visible-light irradiation ($\lambda > 400$ nm), in the absence of photocatalyst and in the presence of as-prepared samples (30 mg).

To further illustrate the fact that the real photocatalytic performance of Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction results from the excitation of the photocatalyst rather than the sensitization mechanism, colorless parachlorophenol (4-CP) was used as the model of pollutants (Fig. 8). Obviously, no 4-CP can be absorbed by all these photocatalysts for 30 min of dark reaction,
which should be attributed to the nature of the electrically neutral of 4-CP. In the subsequent
photocatalytic reaction process, the degradation of 4-CP without photocatalyst and with bulk
Bi$_2$S$_3$, is extremely slow and nearly no 4-CP is removed after 150 min of visible-light
irradiation. By using pure Bi$_2$MoO$_6$ as the VLD photocatalyst, 4-CP degradation is also very
slow and only 13% 4-CP is photocatalytically degraded after 150 min of visible-light
irradiation. Surprisingly, when Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction is used as the VLD
photocatalyst, 4-CP in the solution is rapidly photocatalytically decomposed during 60 min of
visible-light irradiation, and the photodegradation efficiency reaches up to 98.7% at 60 min.
When the illumination time lasts to 90 min, 100% 4-CP has been removed, indicating the
highest photocatalytic activity of Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction among these
above-mentioned photocatalysts.

In order to further confirm the role of the nanojunction in Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction,
the removal efficiencies of RhB and 4-CP were compared (Fig. 9). When pure Bi$_2$MoO$_6$ is
used as the VLD photocatalyst, 29% RhB is removed after 60 min, and the removal efficiency
of 4-CP can reach 13% after 150 min. By using pure Bi$_2$S$_3$ as the VLD photocatalyst, only
14% RhB is removed after 60 min, and nearly no 4-CP is degraded after 150 min. Thus, the
total degradation efficiencies by two individual photocatalysts (Bi$_2$MoO$_6$ and Bi$_2$S$_3$) are 42%
(29% + 13%) for RhB after 60 min, or 14% (14% + 0) for 4-CP after 150 min. More
importantly, Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction can remove 100% RhB after 60 min or 100%
4-CP after 90 min, which are both higher than the total removal efficiencies (42% and 14%)
by pure Bi$_2$MoO$_6$ and Bi$_2$S$_3$ for RhB and 4-CP removal. These results strongly reveal that
there is a synergic effect in Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction, which is similar to the
phenomenon in our previous study.$^{45,46}$
Fig. 9 The comparison of removal efficiencies of RhB after 60 min and 4-CP after 150 min, by Bi$_2$MoO$_6$, Bi$_2$S$_3$ and Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction.

Fig. 10 TOC removal during RhB (60 mg L$^{-1}$, 100 mL) photocatalytic degradation process by Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction (300 mg).

It is well known that the mineralization is the ultimate goal in pollutant treatment, and total organic carbon (TOC) value is usually used as an important index for the mineralization degree of organic species. Herein, the mineralization of RhB was investigated by immersing 300 mg Bi$_2$S$_3$/Bi$_2$MoO$_6$ in 100 mL RhB aqueous solution (60 mg L$^{-1}$) under visible-light irradiation, and TOC value was recorded during the photocatalytic process (Fig. 10). Obviously, with the increase of irradiation time, the TOC concentration continuously decreases, indicating that RhB is steadily mineralized. After six hours, the TOC concentration
decreases from 40.85 mg L\(^{-1}\) at 0 h to 9.791 mg L\(^{-1}\) at 6 h, reaching a high mineralization ratio of 76%. This fact demonstrates that Bi\(_2\)S\(_3\)/Bi\(_2\)MoO\(_6\) heterojunction superstructures can efficiently degrade and mineralize organic pollutants under visible-light irradiation.

![Cycling runs in photocatalytic degradation of 4-CP over Bi\(_2\)S\(_3\)/Bi\(_2\)MoO\(_6\) heterojunction.](image)

The stability of Bi\(_2\)S\(_3\)/Bi\(_2\)MoO\(_6\) heterojunction was also studied through the degradation of 4-CP under visible-light irradiation (Fig. 11). It should be noted that the Bi\(_2\)S\(_3\)/Bi\(_2\)MoO\(_6\) heterojunction is easily recycled by simple filtration without any treatment in these experiments. After four cycles of the photodegradation process of 4-CP, the Bi\(_2\)S\(_3\)/Bi\(_2\)MoO\(_6\) heterojunction does not exhibit any significant loss of activity, as shown in Fig. 11, confirming that the components of the Bi\(_2\)S\(_3\)/Bi\(_2\)MoO\(_6\) heterojunction is not corroded by light and that the heterojunction structure is stable during the photocatalytic process. This fact can be further supported by XRD patterns, which reveal that Bi\(_2\)S\(_3\)/Bi\(_2\)MoO\(_6\) heterojunction after the photocatalytic reaction exhibits the similar diffraction peaks compared with that of the as-prepared Bi\(_2\)S\(_3\)/Bi\(_2\)MoO\(_6\) heterojunction (Fig. 1). Therefore, the as-prepared Bi\(_2\)S\(_3\)/Bi\(_2\)MoO\(_6\) heterojunction is an effective and stable VLD photocatalyst.
Based on the above results, one can conclude that Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction exhibits higher photocatalytic activity than the pure Bi$_2$MoO$_6$ and pure Bi$_2$S$_3$ (Fig. 7, 8), and even higher than the sum of two individual photocatalysts (Bi$_2$MoO$_6$ and Bi$_2$S$_3$) for the photocatalytic degradation of RhB or 4-CP (Fig. 9). The possible reasons for the higher photocatalytic activity of Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction are analyzed, and we believe that there are chiefly two reasons. One reason is the hierarchical nanopores of Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction compared with Bi$_2$MoO$_6$ and Bi$_2$S$_3$ as shown in Fig. 3a-c and Fig. 2a, b. Undoubtedly, these hierarchical porous superstructures can improve the physicochemical properties and be served as transport paths for small molecules, further facilitating the absorption and photodegradation of RhB and 4-CP. The other reason should be due to the efficient separation of photogenerated electron-hole pairs. Obviously, more matching band gaps are thus obtained due to the presence of Bi$_2$S$_3$ nanoparticles (NPs) in Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction, further facilitating the separation of photogenerated electrons and holes. The energy band diagram and photocatalytic process of Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction can be proposed, as shown in Fig. 12. Under visible-light irradiation, the photocatalytic reaction is initiated by the absorption of visible-light photons with energy equal or higher than the band-gap in either Bi$_2$S$_3$ or Bi$_2$MoO$_6$ semiconductors, which results in the creation of photogenerated holes in its VB and electrons in its conduction band (CB). Since the CB and VB of Bi$_2$MoO$_6$ lie above those of Bi$_2$S$_3$ NPs, the photogenerated electrons easily migrate from the CB of Bi$_2$MoO$_6$ to that of Bi$_2$S$_3$ NPs; and the photogenerated holes can also be easily transferred from the VB of Bi$_2$S$_3$ NPs to that of Bi$_2$MoO$_6$. As a result, less of a barrier exists due to the promoted separation and migration of photogenerated carriers by the internal field. So the probability of electron-hole recombination can be decreased. Larger numbers of
electrons stored on the Bi$_2$S$_3$ NPs surface and holes stored on the Bi$_2$MoO$_6$ surface can, respectively, participate in photoredox reactions to degrade organic pollution directly or indirectly, which can enhance the photocatalytic reaction greatly.

![Image](Image1.png)

**Fig. 12** The proposed possible mechanism for the improvement of photocatalytic activity.

### 4. Conclusions

In summary, Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction has been prepared by a simple solvothermal synthesis method. It consists of flower-like superstructures with diameters ranging from 1 to 3 µm, which are built from Bi$_2$MoO$_6$ nanosheets with a thickness of about 15 nm decorated with Bi$_2$S$_3$ nanoparticles with diameter of ~3.5 nm. The Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction displays higher efficient visible-light-driven photocatalytic activity in degradation of RhB and 4-CP, even higher than the sum of the activities of two individual photocatalysts (Bi$_2$MoO$_6$ and Bi$_2$S$_3$). Moreover, Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction can efficiently mineralize organic pollutants and be re-used due to excellent stability. Therefore, Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction has great potential as an efficient and stable visible-light-driven photocatalyst for water environmental purification and remediation application.
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Flower-like Bi$_2$S$_3$/Bi$_2$MoO$_6$ heterojunction has been prepared via a solvothermal method and it exhibits stable and remarkable enhanced photocatalytic activity.