Facile fabrication of Bi₂S₃/SnS₂ heterojunction photocatalysts with efficient photocatalytic activity under visible light

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Abstract

In this work, Bi₂S₃/SnS₂ heterojunction photocatalysts were prepared by combining a hydrothermal technique and a facile in situ growth method. The nanocomposites were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, inductively coupled plasma spectroscopy, X-ray photoelectron spectroscopy, UV-Vis diffusion reflectance spectroscopy and room-temperature photoluminescence spectra. Their photocatalytic performances were evaluated by degrading methyl orange (MO) in aqueous solution (50 mg/L) under visible light ($\lambda > 420$ nm) irradiation. It was found that when the mass percentage of Bi₂S₃ in Bi₂S₃/SnS₂ was 7.95 wt%, the as-prepared Bi₂S₃/SnS₂ nanocomposite showed the best photocatalytic activity for the degradation of MO. The highly improved performance of the Bi₂S₃/SnS₂ nanocomposite was mainly ascribed to the efficient charge separation.

Keywords: photocatalysts $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterojunctions degradation methyl orange visible light

1. Introduction

Global environmental pollution is becoming an increasingly serious issue for human beings to confront in modern society. Many methods have been tried to solve the problem, among which developing new environmental remediation technologies and utilizing new green energies become hot topics in recent years. Photocatalysis, as a clean, economical, environmentally friendly “green” technique, offers great potential for environmental protection because organic pollutants usually can be effectively decomposed by semiconductor-based photocatalysts under light irradiation with the photon energy higher or equal to the band gaps of the photocatalysts [1, 2]. The sun delivers about 4 orders of magnitude larger energy to the earth’s surface per year than the energy annually used by humans all over the world [3]. To better utilize the solar energy to tackle the issues of environmental pollution, it is strongly desirable to explore catalysts with visible-light-driven photocatalytic performance. This has aroused extensive attention of researchers and achieved fruitful results [3, 4].

Organic dyes, especially azo dyes like methyl orange (MO), have been reported to be highly cytotoxic for the mammalian tissues [5]. Such dye molecules are difficult to be decomposed by natural means. Various methods, such as adsorption [6], advanced oxidation processes [7], biological treatment [8], electrocatalysis [9] and photocatalysis [10], have been developed to remove organic dyes. Among them, photocatalytic

degradation of organic pollutants receives increasing interest owing to the absence of secondary pollution and the low cost by using solar light. To date, a large number of photocatalysts have been developed [3, 4].

As the first discovered photo-chemical active semiconductor, TiO_2 has been extensively investigated for the elimination of organic pollutants in the environment [11]. However, the wide band gap of 3.2 eV makes TiO_2 only active under UV light irradiation and not responsive to visible light which accounts for about 46% of the total solar energy. Although some dyes could be degraded over TiO_2 by self-photosensitization under visible light irradiation, the efficiencies are relatively lower than those under UV light irradiation. It is well known that only about 4% of the solar spectra falls in the UV region, thus it is appealing to develop photocatalysts with narrow band gaps so as to be sensitive to visible light in view of the better utilization of solar energy.

Semiconductors of metal sulfide usually have the capability to harvest light in the visible and short-wavelength near-infrared regions, which makes them a class of promising sensitizers for wide band gap semiconductors [12-14] or visible-light-driven photocatalysts [15-17]. Among them, CdS, with a band gap of about 2.4 eV, received significant attention as a visible-light-driven photocatalyst [17]. However, it is well known that CdS is not stable enough during the photocatalytic reaction because photocorrosion is prone to occur. This may not only significantly affect the photocatalytic reaction but also cause additional environmental damage [18]. Alternatively, SnS_2 , with a bandgap of 1.91-2.35 eV is non-poisonous, inexpensive, and has good stability in acid

and neutral aqueous solutions as well as certain oxidative and thermal stability in air [13]. Thus, it is a promising visible light-sensitive photocatalyst. Recently, various morphologies of SnS₂ nanostructures, such as fullerene-like nanoparticles [19], nanobelts [20], nanosheets [21], nanoflakes [22], thin films [23] and modified SnS₂ [10, 13, 24-26], have been synthesized successfully. Although SnS₂ has unique advantages such as relatively lower toxicity and wider spectrum response as compared with CdS, reports on its photodegradation performance are still relatively limited. Therefore, from the viewpoints of both fundamental science and practical applications, more researches should be pursued to explore the properties of SnS₂-based photocatalysts.

In comparison with single semiconductor, the coupling between two different semiconductors has proved to be successful in developing higher performance photocatalysts [27-29]. The improved photocatalytic activity of semiconductor composites is attributed to a large extent to the enhanced separation of photoinduced electrons and holes via interfacial charge transfer [10, 12, 27-29]. Bismuth sulfide (Bi₂S₃) is a semiconductor with a narrow bandgap about 1.3 eV [30]. The narrow band gap and large absorption coefficient make it an ideal candidate for photoresponsive materials [31-33]. More recently, Bi₂S₃ has been acted as a sensitizer due to its ability to absorb visible light with wavelength up to 800 nm [34].

Herein, the Bi₂S₃/SnS₂ heterostructured nanocomposites were synthesized by combining the hydrothermal growth technique and a simple in situ growth method for the first time. Then, these novel heterostructures were applied for the degradation of organic

dye MO under visible light radiation. During the degradation of MO, most of the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ composites exhibited much higher photocatalytic activity than that of pure SnS_2 hexagonal nanosheets, and the highest efficiency was obtained when the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ mass percentage was 7.95 wt%. The enhanced photocatalytic efficiency and stability could be attributed not only to the high light-harvesting capacity of $\text{Bi}_2\text{S}_3/\text{SnS}_2$ nanocomposite, but also to the effective separation of photogenerated carriers driven by the electrostatic field in the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ junction. Furthermore, the catalyst is much easier to be separated from the reaction system than pure SnS_2 after photodegradation reaction, and its catalytic activity does not exhibit a significant decrease after six successive catalytic cycles. Finally, the visible light photocatalytic mechanism was also illustrated based on the band structure of $\text{Bi}_2\text{S}_3/\text{SnS}_2$.

2. Experimental section

2.1 Materials

Stannic chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$), thioacetamide ($\text{C}_2\text{H}_5\text{NS}$), bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), ethylene glycol (EG) were purchased from Tianjin Chemical Reagent Co., Ltd, China. All the reagents were analytical grade and used as received without further purification.

2.2 Preparation of layered SnS_2 nanosheets

SnS_2 nanosheets were prepared by a hydrothermal method [35]. In a typical synthesis, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (3.75 mmol) and thioacetamide (15 mmol) were dissolved in deionized water (60 mL) under vigorously magnetic stirring. The as-obtained transparent solution

was transferred to a Teflon-lined stainless steel autoclave and then heated in an electric oven at 433 K for 12 h. After the hydrothermal synthesis, the resulting yellow SnS_2 powder was washed with distilled water and ethanol, respectively. Finally, the SnS_2 powder was collected by high-speed centrifugation and dried at about 50 °C.

2.3 Preparation of $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures

The $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures were synthesized via a simple in situ growth method. First, the as-prepared SnS_2 nanosheets (0.1828 g, 1 mmol) were dispersed to 25 mL EG under ultrasonication for 30 min. Then, 12 mL $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}/\text{EG}$ solution (The amounts of Bi salt in solution were 0.04 mmol, 0.06 mmol, 0.08 mmol, 0.20 mmol, respectively) was added to the above suspension. After stirring at room temperature for 10 min, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ dissolved in EG (12 mL) was added dropwise into the reaction vessel slowly to make a mixed solution with the molar ratio of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ to $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ to be 2:3. Stirred for another 20 min at room temperature, the mixture was maintained at 80 °C for 1h with magnetic stirring. Finally, the precipitates of $\text{Bi}_2\text{S}_3/\text{SnS}_2$ with different theoretical molar ratios (0.02:1, 0.03:1, 0.04:1, 0.10:1) of Bi_2S_3 to SnS_2 (denoted as BS-2, BS-3, BS-4, BS-10, respectively) were collected, washed with deionized water and ethanol for several times and then dried at about 50 °C.

For comparison, pure Bi_2S_3 was prepared as follows: 0.2911 g (0.6 mmol) of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 24 mL EG to form a clear solution. Subsequently, 0.9 mmol $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}/\text{EG}$ solution (24 mL) was added dropwise into above solution slowly. After stirring for 20 min, the mixture was maintained at 80 °C for 1 h with magnetic

stirring, and then cooled to room temperature. Finally, the product was separated, washed with deionized water and ethanol for several times, and then dried at about 50 °C.

2.4 Characterization

The crystal structures of the obtained samples were examined using an X-ray diffractometer (BDX3300) with a reference target: Cu K α radiation ($\lambda = 1.54 \text{ \AA}$), voltage: 30 kV and current: 30 mA. The samples were measured from 10° to 80° (2 θ) with steps of 4 °/min. The surface elemental compositions were further determined using X-ray photoelectron spectrometer with a Mg K α anode (PHI1600 ESCA System, PERKIN ELMER, US). The Bi, Sn and S contents were analyzed by inductively coupled plasma spectroscopy (VISTA-MPX CCD Simultaneous ICP-OES, Varian, American) analysis. The morphology of the as-prepared samples was examined by transmission electron microscopy (TEM, Philips Tecnai G2 F20) operated at 200 kV and scanning electron micrography (SEM, JEOL-6700F ESEM, Japan) using a field emission SEM (FE-SEM) instrument. UV-vis diffuse reflectance spectra (DRS) were recorded on a UV-3600 spectrophotometer (Shimadzu Corporation, Japan) using BaSO₄ as reference. The photoluminescence (PL) spectra of photocatalysts were recorded using a Fluorescence Spectrophotometer (Fluorolog3, Japan) at room temperature with an excitation wavelength of 325 nm.

2.5 Photocatalytic activity test

The photocatalytic activities of the as-prepared samples were evaluated by degradation of MO under visible light radiation from a 450 W medium pressure quartz mercury vapor

lamp surrounded by a circulating cooling water quartz jacket. A cutoff filter was equipped to remove UV light with wavelength (λ) below 420 nm. The photochemical reactor is produced by Shanghai BiLon Instrument Co., Ltd, which has been improved slightly before experiments. All reactions were carried out at room temperature in several 8 mL quartz tubes, in which 5 mg photocatalyst was added into 5 mL aqueous solution containing 50 ppm MO to form suspensions. In each experiment, the distance between the lamp and quartz tubes was set to be 5 cm. Before illumination, the suspensions were ultrasound treated for 3-5 min and magnetically stirred in the dark for 30 min to ensure the establishment of adsorption/desorption equilibrium between the photocatalysts and MO. The suspensions were still under constant vigorous stirring with the photoreactor during the degradation and the temperature of the suspensions was maintained at about 25 °C by circulating cooling water in the quartz jacket and two ventilating fans. At given time intervals of illumination, one sample tube was taken out and centrifuged to remove photocatalyst powders from the solution for further analysis.

The concentration of MO was determined by measuring the absorption intensity at its maximum absorbance wavelength (462 nm) using a UV-vis spectrophotometer (TU-1901). The degradation efficiency of MO was calculated by the following equation:

$$\begin{aligned}\text{Degradation rate} &= (C_0 - C_t) / C_0 \times 100\% \\ &= (A_0 - A_t) / A_0 \times 100\% \quad (1)\end{aligned}$$

Where, C_0 is the initial concentration of MO solution before degradation, C_t is the concentration of MO solution after illumination for t min, A_0 and A_t are the absorbance

intensities of MO aqueous solution before ($t = 0$ min) and after illumination for t min, respectively.

In order to determine photostability of the catalyst, the cycle experiments were carried out. The target catalyst was separated and collected by centrifugation. After being washed with water for 3 times and dried in air at 50 °C for 12 h, the catalyst was reused with a fresh MO aqueous solution for subsequent reactions under the same conditions.

To explore the reactive oxygen species during the photocatalytic process, a series of reactive species trapping experiments were performed. The experimental procedure was similar to the former photocatalytic activity test except that the different quenching chemicals were added into the MO solution. The concentration of the scavengers was 1 mM.

3. Results and discussion

3.1 Design and preparation of Bi₂S₃/SnS₂ heterostructures

As is known to all, the selection of coupled semiconductor is crucial, when heterojunction composites are fabricated. As a typical semiconductor material, Bi₂S₃ has prominent photosensitization due to the narrow bandgap of ~1.3 eV. However, primary reason of choosing Bi₂S₃ as a coupling semiconductor to SnS₂ is based on separating mechanism of photoinduced electrons and holes by heterojunction structure. When the Bi₂S₃/SnS₂ heterostructures are irradiated by visible light, Bi₂S₃ and SnS₂ have matching band potentials (the conduction band (CB) potential of SnS₂ is more negative (or energetically higher) than that of Bi₂S₃). This allows the photoinduced electrons transfer

from the CB of SnS_2 to the CB of Bi_2S_3 , which can enhance the separation of photogenerated charge carriers. So, it is reasonable to expect that the photocatalytic efficiency of $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures would be higher than that of pure SnS_2 nanosheets.

The $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures were prepared by combining hydrothermal growth technique and a simple in situ growth method, shown in Scheme 1. In the first step, the SnS_2 nanosheets were prepared by using $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and thioacetamide as precursors. They can serve as the substrates to guide the growth of the Bi_2S_3 nanoparticles. So in the second step, the Bi_2S_3 nanoparticles were assembled onto the as-prepared SnS_2 nanosheets through a simple in situ growth method. Obviously, the process for forming $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures is simple and mild.

Scheme 1 Schematic illustration of the formation of $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures.

3.2 Structural and Composition Characterization

The as-prepared $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures were characterized with some analytic methods. Figure 1 shows the X-ray diffraction (XRD) results of the pure Bi_2S_3 , SnS_2 and $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures with different Bi_2S_3 contents. As can be seen from Fig. 1a and f, all of the diffraction peaks can be assigned to the 2T-type hexagonal berndtite SnS_2 (JCPDS, no. 23-0677) or orthorhombic Bi_2S_3 (JCPDS no. 17-0320), respectively. The XRD patterns of the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures show all the diffraction peaks assigned to hexagonal SnS_2 except the 2θ peaks at 23.72° and 24.93° which correspond to (101) and (130) planes of orthorhombic Bi_2S_3 (Fig. 1b-e), indicating the existence of SnS_2 and Bi_2S_3 in the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures. Moreover, the intensities of the corresponding diffraction peaks of Bi_2S_3 strengthened gradually along with the increase of the Bi_2S_3 contents in the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ composites, while those of SnS_2 weakened simultaneously.

Fig. 1 XRD patterns of the as-fabricated products: (a) pure SnS_2 , (b) BS-2,

(c) BS-3, (d) BS-4, (e) BS-10 and (f) pure Bi_2S_3 .

In order to illustrate the morphology of $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures, the detailed structural information was investigated by TEM, high resolution TEM (HRTEM) and electron dispersive spectroscopy (EDS). Figure 2 shows TEM images of the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures with different Bi_2S_3 contents, as well as the pure SnS_2 and Bi_2S_3 samples. In Fig. 2a, a large number of SnS_2 nanosheets with hexagonal morphology in the size range of 30-60 nm are observed. Each hexagonal nanosheet presents relatively neat edge and smooth surface. As shown in Fig. 2b-2e, the introduction of Bi_2S_3 has significant influence on the morphology and microstructure of SnS_2 nanosheets, for instance, the surface and edge of SnS_2 nanosheets become rough and irregular gradually. As the Bi_2S_3 content is low, it mainly exists in the form of nanoparticles on the surface and edge of isolated SnS_2 hexagonal nanosheets. With the increase of its content, many Bi_2S_3 particles may act as bridges to combine SnS_2 nanosheets. When higher concentration of Bi^{3+} ions and S^{2-} ions were used in the preparation, more Bi_2S_3 particles were deposited and they almost completely covered SnS_2 nanosheets, so the surface and edge of SnS_2 nanosheets became difficult to identify. In the end, neat hexagonal phase could not be identified easily. Meanwhile, the dispersibility of these composites was declining, which might be related to their particle sizes and surface energy parameters. As shown in Fig. S3, 8 mg photocatalyst was added to 8 mL aqueous solution and ultrasound treated to form suspensions. After standing for 120 min, BS-3 gradually deposited to the bottom of the container, and the pure SnS_2 suspension was still relatively uniform. Figure 2f reveals

that pure Bi_2S_3 sample is composed of nanorod aggregates. The diameter of the nanorods is about 5-10 nm and the length is up to 40-60 nm. Figure 2g-h gives the HRTEM of the top views of the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures. The fringe interval of 0.275 nm agrees with the interplanar spacing of (101) crystal plane of hexagonal phase SnS_2 , whereas the fringe intervals of 0.287 nm and 0.312 nm correspond to the interplanar spacing of (040) and (211) crystal planes of orthorhombic Bi_2S_3 . The HRTEM images and Fig. S2 clearly demonstrate the formation of $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures and their difference from SnS_2 structures, which will make the interfacial electron transfer spatially available and smooth, and accordingly increase the photocatalytic activity. The EDS (Fig. 2i) indicates the presence of S, Sn, and Bi elements (the C and Cu signals come from the holey carbon TEM grid), further revealing that Bi_2S_3 is successfully combined with SnS_2 . The mass percentages of $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures were determined by ICP analysis. The actual Bi_2S_3 contents are 5.52 wt% for BS-2, 7.95 wt% for BS-3, 9.98 wt% for BS-4 and 21.38 wt% for BS-10, whereas the theoretical Bi_2S_3 contents in BS-2, BS-3, BS-4, BS-10 were targeted at 5.32 wt%, 7.78 wt%, 10.11 wt%, 21.95 wt%. So the actual compositions of the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures are similar to the theoretical ones.

Fig. 2 TEM images of the as-prepared (a) SnS_2 , (b) BS-2, (c) BS-3, (d) BS-4, (e) BS-10, and (f) pure Bi_2S_3 ; HRTEM images (g)-(h) and EDS image (i) of the BS-3 sample.

Figure 3 shows SEM images of SnS_2 , BS-3 and BS-10, respectively. The shape transforms from SnS_2 platelets to $\text{Bi}_2\text{S}_3/\text{SnS}_2$ particles gradually and some morphological changes are also found at the edge and surface of some SnS_2 nanosheets (pointed with

arrow) as they are integrated with Bi_2S_3 . In addition, the particle size of BS-10 is bigger than that of SnS_2 , which is consistent with the result observed by TEM.

Fig. 3 SEM images of the as-fabricated (a) pure SnS_2 , (b) BS-3, and (c) BS-10.

The surface chemical composition and valence state of the BS-3 sample were further analyzed by X-ray photoelectron spectra (XPS). The survey scan spectrum (Fig. 4a) clearly indicates the presence of Sn, Bi and S elements (C and O signals may come from ambient contamination or adsorbed impurities). The high-resolution XPS spectrum of the Sn 3d orbital region (Fig. 4b) shows the binding energies of Sn 3d_{3/2} and Sn 3d_{5/2} peaks at 494.70 and 486.20 eV, respectively. The splitting energy of 8.50 eV between Sn 3d_{3/2} and Sn 3d_{5/2} is a typical value for Sn^{4+} in SnS_2 [13]. Figure 4c shows high-resolution XPS spectra of Bi 4f and S 2p, two peaks at about 163.61 eV and 158.31 eV can be assigned to Bi 4f_{5/2} and Bi 4f_{7/2}, respectively. The peak separation between the Bi 4f_{5/2} and Bi 4f_{7/2} is 5.30 eV, indicating that the valence state of bismuth in the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ sample is +3 [18,

284 [36]. The peak (161.45 eV) found between Bi 4f_{5/2} and Bi 4f_{7/2} could be assigned to S 2p
285 [37]. Meanwhile, the peak at 225.45 eV (Fig. 4d) can be assigned to S 2s [38].
286 Consequently, the XPS results indicate that the BS-3 is consisted of SnS₂ and Bi₂S₃.
287 For comparison, the XPS spectra of pure SnS₂, Bi₂S₃ and BS-3 are shown in Fig. S1. It
288 is clear that the binding energies of Sn 3d_{5/2} (486.20 eV) and Sn 3d_{3/2} (494.70 eV) in
289 BS-3 are higher than those of pure SnS₂ (485.99 eV and 494.49 eV). Meanwhile, the
290 binding energies of Bi 4f_{7/2} and Bi 4f_{5/2} peaks of BS-3 are located at 158.31 eV and
291 163.61 eV, which are slightly lower than those of pure Bi₂S₃ (158.46 eV and 163.71 eV).
292 This could be explained by the fact that different Fermi levels of SnS₂ and Bi₂S₃ prompt
293 the electrons transfer between Sn atoms and Bi atoms, which changes the outer electron
294 cloud densities of Sn and Bi and makes the binding energies of Sn 3d and Bi 4f vary [39].
295 According to relevant report [40], this phenomenon did not happen for the samples
296 prepared by simple physical mixing, suggesting that the BS-3 must be a composite and
297 the interaction between SnS₂ and Bi₂S₃ in the composite is strong.

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Fig. 4 XPS spectra of the BS-3 sample: (a) survey spectrum, (b) Sn 3d, (c) Bi 4f and S 2p, (d) S 2s.

3.3 Optical properties

The UV-vis DRS was measured to investigate the optical absorption property of the samples. Figure 5 shows the UV-Vis absorption spectra of as-fabricated SnS₂ nanosheets, Bi₂S₃/SnS₂ heterostructure (BS-3), and Bi₂S₃ nanorods, which have been converted from

corresponding diffuse reflectance spectra by means of the Kubelka-Munk function [13, 41-43]:

$$F(R) = (1-R)^2/2R = \alpha/S \quad (2)$$

$$R = R_{\text{sample}}/R_{\text{BaSO}_4} \quad (3)$$

Where $F(R)$, R , α and S are the Kubelka-Munk function, reflectance, absorption coefficient and scattering coefficient, respectively. As can be seen from Fig. 5, SnS_2 , BS-3 and pure Bi_2S_3 display optical absorption capabilities nearly in the entire visible light spectrum. However, the intensity of optical absorption of SnS_2 is much weaker than the excellent photoresponse performances of BS-3 and Bi_2S_3 , especially the pure Bi_2S_3 nanorods that show intense absorption over the visible range, even extending to the infrared region. Due to the coupling effect of Bi_2S_3 , photoresponse performance of the as-prepared $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructure has been improved significantly and its absorption band has a significant red-shift. The result demonstrates that the architecture of the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructure could effectively enhance the absorption of visible light and consequently raise the utilization ratio of light energy. The broad and strong spectrum response implies that the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures may be good visible light-sensitive photocatalysts.

According to previous report [44], the band gaps of the SnS_2 nanosheets, BS-3 heterostructure, and Bi_2S_3 nanorods were calculated by the following formula:

$$\alpha h\nu = B(h\nu - E_g)^{n/2} \quad (4)$$

Where, $h\nu$, E_g , and B are the discrete photon energy, band gap, and a constant, respectively. Furthermore, n is a constant depended on the characteristics of the transition in a semiconductor: direct transition ($n = 1$) or indirect transition ($n = 4$). SnS_2 and Bi_2S_3 are direct transition semiconductors [13, 45, 46]. Thus, the values of n are 1 for SnS_2 nanosheets and Bi_2S_3 nanorods. The value of α can be calculated from the diffuse reflectance data using the Kubelka-Munk function. But, for the diffuse reflectance spectra, the Kubelka-Munk function can be used instead of α for estimating the optical absorption edge energy [13, 26, 42]. So, the curves of $(F(R)h\nu)^2$ vs $(h\nu)$ for the samples are plotted in Fig. 6. By extrapolating the linear portion of the curves to $F(R) = 0$, the E_g values of SnS_2 , BS-3, and Bi_2S_3 were evaluated to be 2.20eV, 1.50eV and 1.30eV, respectively. The values for SnS_2 and Bi_2S_3 are close to those in the reports [25, 30, 47, 48].

Fig. 5 UV-Vis absorption spectra of the as-fabricated (a) SnS_2 , (b) BS-3, and (c) pure Bi_2S_3 .

Fig. 6 Plots of $(F(R)hv)^2$ vs (hv) for estimating optical band gaps of (a) SnS_2 ,
(b) BS-3, and (c) pure Bi_2S_3 .

Since PL emission mainly arises from the recombination of free carriers, PL spectroscopy is a facile technique to survey the separation efficiency of photoinduced electron-hole pairs in a semiconductor. The recombination rate of the photo-induced electrons and holes is considered to be an important factor to influence the photocatalytic activity of materials [25]. To investigate the efficiency of charge carrier trapping, immigration, and transfer in the as-prepared SnS_2 and $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructure (BS-3), the PL emission spectra of these samples were measured in the wavelength region of 400-640 nm with an excitation wavelength of 325 nm. As shown in Fig. 7, the pure SnS_2 exhibits a strong emission peak at around 570 nm, which can be ascribed to the typical excitonic band-to-band radiative emission of SnS_2 due to its location near the absorption edge. However, when Bi_2S_3 (7.95 wt%) is attached on the SnS_2 nanosheets, the emission

peak drop significantly, or almost disappear, suggesting that the recombination of photoinduced charge carrier is inhibited greatly by the interfacial charge transfer between Bi_2S_3 and SnS_2 nanosheets. Therefore, in the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ hybrids, the Bi_2S_3 indeed provided efficient charge separation to suppress the electron-hole recombination, which could greatly enhance the overall photocatalytic activity under visible-light irradiation.

Fig. 7 Room-temperature PL spectra of pure SnS_2 and BS-3 ($\lambda_{\text{Ex}} = 325 \text{ nm}$).

3.4 Photocatalytic activity

The photocatalytic activities of the as-prepared $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures were evaluated by measuring the degradation of MO in an aqueous solution under visible light. For each kind of samples, two control experiments were performed under the following conditions: (1) in the presence of the photocatalysts but in the dark and (2) with visible light irradiation but in the absence of photocatalysts. The results revealed that the adsorption-desorption equilibrium of the MO on the photocatalysts could be established

368 within about 30 min in the dark. Besides, in the absence of visible light irradiation or
 369 photocatalysts, there was no appreciable degradation of the MO after 240 min. It
 370 indicates that MO is stable in the test condition and no photocatalytic degradation
 371 happens. The MO concentration after the adsorption-desorption equilibrium was used as
 372 the original concentration (C_0) for the degradation dynamics measurements. In this way,
 373 the influence of MO adsorption on the photocatalysts could be largely neglected during
 374 the photocatalytic process. The time-dependent absorption spectra of MO solutions under
 375 visible light illumination in the presence of pure SnS_2 , Bi_2S_3 and BS-3 are shown in Fig.
 376 8a-c.

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Fig. 8 UV-vis absorption spectra changes of MO aqueous solution in the presence of (a) SnS₂ nanosheets, (b) BS-3 sample, and (c) pure Bi₂S₃; (d) photocatalytic activities of different catalysts; (e) kinetic linear simulation of MO photocatalytic degradation over the different photocatalysts.

The absorbance of MO solution in the presence of Bi₂S₃ is hardly changed, which indicates that Bi₂S₃ has lower photocatalytic activity under the experimental conditions. This may be owing to the rapid recombination of photoinduced electrons and holes,

which is consistent with previous report [28]. During the experiment, we found that the Bi_2S_3 nanorods synthesized by the simple precipitation method had obvious adsorption towards MO. This nature gave a reasonable explanation for the phenomenon that $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructures were superior than pure SnS_2 in terms of adsorption to MO. Just as shown in Table S1, when 5 mg catalyst was added to 5 mL MO solution (50ppm) and the system was stirred for 30 min in the dark, the MO concentration of the solution containing composites was significantly lower than that containing SnS_2 , which could be clearly reflected by the different changes of absorbance. As is known to all, the adsorption ability of the photocatalysts to target pollutants is one of the most important factors deciding catalytic activity [25], because increasing adsorption can promote photocatalytic activity of photocatalysts to some extent. The absorbance of MO in both SnS_2 and BS-3 suspensions gradually decrease during the photodegradation process. Obviously, the concentration of MO in BS-3 suspension decrease more quickly.

Figure 8d gives the photocatalytic activities of different photocatalysts in the degradation of MO under visible light irradiation. In the case of pure SnS_2 nanosheets, only 76.68% of MO is decomposed after visible light irradiation for 120 min. However, in the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructure, the photoactivities of SnS_2 nanosheets are remarkably enhanced. The photodegradation efficiencies of MO are about 92.33%, 98.16% and 86.64% for BS-2, BS-3, and BS-4, respectively. The optimal photocatalyst, BS-3, can remove 98.16% of MO after 120 min of visible light irradiation. Generally, the photocatalytic activity of semiconductor photocatalysts is mainly ascribed to their photo

absorption ability in the available light energy region, the ability of photocatalysts to adsorb target molecules, and the separation and transporting rate of the photogenerated electrons and holes in the catalysts [25]. This obvious enhancement of photocatalytic activity of BS-3 should associate with these reasons. With the increase of the amount of coupled Bi₂S₃, the utilization ratio of visible light and separation efficiency of the photoinduced electron-hole were improved gradually. The synergistic effect of SnS₂ and Bi₂S₃ achieved an optimum (BS-3). When excess Bi₂S₃ was coupled in the Bi₂S₃/SnS₂ heterostructures, the surface of SnS₂ was almost completely covered with Bi₂S₃ and the active sites for the degradation of organic dyes via SnS₂ were reduced, meanwhile, excess Bi₂S₃ can become a recombination center for photogenerated electrons and holes, leading to photoactivity fading [49]. That is why the photodegradation efficiency of MO in BS-10 suspension is only 61.21% under the same experimental conditions.

To quantitatively compare the photocatalytic activities of these samples, the corresponding reaction rate constants (k_{app}) were calculated by adopting the pseudo-first-order model as expressed by eq 5, which is generally used for photocatalytic degradation process if the initial concentration of pollutant is low

$$\ln(C_0/C) = k_{app}t \quad (5)$$

Where, C_0 and C are the initial concentration of MO and concentration at t , respectively, t is the irradiation time and k_{app} denotes the apparent reaction rate constant (min⁻¹). The relation between $\ln(C_0/C)$ and irradiation time (t) is plotted and shown in Fig. 8e. The values of k_{app} and the corresponding correlation coefficients R^2 were calculated and

listed in Table1. It is found that the rate constant for BS-3 is $3.17 \times 10^{-2} \text{ min}^{-1}$, which is 2.79 times as large as that of pristine SnS_2 ($1.135 \times 10^{-2} \text{ min}^{-1}$).

Table 1 Pseudo-first-order rate constants of the photocatalytic degradation of MO catalyzed by different catalysts.

Catalysts	SnS_2	BS-2	BS-3	BS-4	BS-10	Bi_2S_3
$k_{\text{app}} \times 100/\text{min}^{-1}$	1.135	2.176	3.170	1.674	0.785	0.097
R^2	0.9743	0.9845	0.9795	0.9866	0.9895	0.9955

3.5 Stability of the $\text{Bi}_2\text{S}_3/\text{SnS}_2$ heterostructure

The capability for reuse is one of the most critical factors for an ideal photocatalyst. Hence, the reusability and stability of the BS-3 were investigated. The sample was collected after each degradation experiment and reused for six times [50]. Figure 9 shows the results of six successive MO degradation runs under the same experimental conditions. It can be seen that the BS-3 does not exhibit a significant loss of photocatalytic activity in the six recycles (for example, after 120 min irradiation, the remaining MO was 1.74% and 2.92% in the first and sixth cycles, respectively). In addition, dissolution of solid photocatalyst may be an important factor which affects its stability during application. According to the report [51], the dissolution of SnS_2 was slight when it was used for degradation of pollutants. Based on this, a preliminary test was carried out for determining the content of metal ions in solution after the photocatalytic reaction. As expected, only 0.138 wt% of the Sn initially present in the solid had been dissolved and the Bi was not detected by our instrument (the Bi content in

the solution might be located below the detection limit, that means the maximum solubility of Bi was 0.006 wt%). The results are consistent with the literature [51]. These confirm that the BS-3 catalyst is rather stable during the photocatalytic decomposition of MO.

Fig. 9 Recycling of the BS-3 for the degradation of MO under visible-light irradiation.

3.6 Reactive species trapping experiments

It is well known that the hydroxyl radical ($\cdot\text{OH}$), hole (h^+) and superoxide radical ($\cdot\text{O}_2^-$) are the major reactive species for the photocatalytic decomposition [3]. In this investigation, ammonium oxalate (AO), 1,4-benzoquinone (BQ) and tert-butyl alcohol (t-BuOH) are used as the h^+ , $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ scavengers, respectively [52, 53]. As shown in Fig. 10, after the addition of t-BuOH, the photocatalytic activity of the BS-3 composite is almost invariable, indicating that $\cdot\text{OH}$ has no obvious effect on the degradation of MO in the current photocatalytic systems. However, once AO or BQ is added, the photocatalytic

efficiency of the BS-3 composite decreases obviously, indicating that h^+ and $\cdot O_2^-$ are main reactive oxygen species during the photodegradation process.

Fig. 10 Effects of various scavengers on the visible light photocatalytic efficiency of BS-3 sample.

(the ordinate represents the degradation rate of MO in different systems

after visible light irradiation for 120 min)

3.7 Possible mechanism of enhanced photoactivity of the Bi_2S_3/SnS_2 heterostructure

It is interesting to investigate the plausible photocatalytic mechanism for the superior photocatalytic activity of Bi_2S_3/SnS_2 . To illuminate the effect of heterostructure on photocatalytic activity, the energy band structure was investigated. The valence band (VB) and conduction band (CB) potentials of semiconductors at the point of zero charge can be estimated by eq 6 and 7, respectively [54].

$$E_{CB} = \chi - E^e - 0.5E_g \quad (6)$$

$$E_{VB} = E_{CB} + E_g \quad (7)$$

Where E_{CB} is the CB edge potential, E_{VB} is the VB edge potential, χ is the electronegativity of the semiconductor which is the geometric mean of the electronegativity of the constituent atoms (it is worth noting that the electronegativity of an atom is the arithmetic mean of the atomic electron affinity and the first ionization energy), E^e is the energy of free electrons on the hydrogen scale (4.5 eV), and E_g is the band gap energy of the semiconductor. So far, considerable success had been achieved in predicting the relative band edge positions for many oxide and sulfide semiconductors using this method [12, 26, 34]. In our case, the values of these parameters were: $E_{CB}(\text{SnS}_2) = -0.13$ eV, $E_{VB}(\text{SnS}_2) = 2.07$ eV and $E_{CB}(\text{Bi}_2\text{S}_3) = 0.12$ eV, $E_{VB}(\text{Bi}_2\text{S}_3) = 1.42$ eV. Although these data may not be the exact absolute values for the CB and VB potentials of SnS_2 and Bi_2S_3 , they should offer a correct estimation of the relative band edge positions of the two semiconductors. In addition, the present calculations were also consistent with the previous reports [26, 55].

The enhancement of photoactivity of the heterostructures could be explained by some possible mechanisms [56-59]. Since the composite examined here shows better photocatalytic activity than the single components, this may well be due to a better charge separation. This hypothesis based on the experimental observation is illustrated in Scheme S1. When the nanocomposites were irradiated by visible light ($\lambda > 420$ nm, energy less than 2.95 eV), both SnS_2 and Bi_2S_3 semiconductors can be excited because of their suitable band structures. The band alignment according to the estimations may interpret that charge separation is efficient here perhaps because one of the two carriers

photogenerated in SnS₂, electrons and holes, could have much better mobility than the other. By this way, the probability of electron-hole recombination could be lowered which was consistent with the PL results in Fig. 7, and the photocatalytic activity was enhanced greatly.

4. Conclusions

In summary, a series of Bi₂S₃/SnS₂ heterostructures with different compositions have been successfully fabricated via combination of hydrothermal technique and in situ growth method under facile conditions. Compared with the pure SnS₂ nanosheets, the new catalysts not only have more superior catalytic properties, but also are easier to be recycled without a decrease in the photocatalytic activity, which is in line with the requirements of green chemistry. Therefore, it is expected that the Bi₂S₃/SnS₂ heterostructures will greatly promote their industrial application in the treatment of wastewater and environmental cleaning.

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References

- [1] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (1972) 37-38.
- [2] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69-96.

518 [3] S.Y. Dong, J.L. Feng, M.H. Fan, Y.Q. Pi, L.M. Hu, X. Han, M.L. Liu, J.Y. Sun, J.H.
519 Sun, Recent developments in heterogeneous photocatalytic water treatment using visible
520 light responsive photocatalysts: a review, *RSC Adv.* 5 (2015) 14610-14630.

521 [4] C.C. Chen, W.H. Ma, J.C. Zhao, Semiconductor-mediated photodegradation of
522 pollutants under visible-light irradiation, *Chem. Soc. Rev.* 39 (2010) 4206-4219.

523 [5] C.R. Nony, M.C. Bowman, T. Cairns, Metabolism studies of an azo dye and pigment
524 in the hamster based on analysis of the urine for potentially carcinogenic aromatic amine
525 metabolites, *J. Anal. Toxicol.* 4 (1980) 132-140.

526 [6] Y.G. Wang, M.C. Yao, Y.T. Chen, Y.H. Zuo, X.D. Zhang, L.F. Cui, General synthesis
527 of magnetic mesoporous FeNi/graphitic carbon nanocomposites and their application for
528 dye adsorption, *J. Alloy Compd.* 627 (2015) 7-12.

529 [7] A. Thiam, E. Brillas, J.A. Garrido, R.M. Rodríguez, I. Sirés, Routes for the
530 electrochemical degradation of the artificial foodazo-colour Ponceau 4R by advanced
531 oxidation processes, *Appl. Catal. B: Environ.* 180 (2016) 227-236.

532 [8] M. Punzi, A. Anbalagan, R.A. Börner, B.M. Svensson, M. Jonstrup, B. Mattiasson,
533 Degradation of a textile azo dye using biological treatment followed by photo-fenton
534 oxidation: evaluation of toxicity and microbial community structure, *Chem. Eng. J.* 270
535 (2015) 290-299.

536 [9] E. Brillas, C.A. Martínez-Huitleb, Decontamination of wastewaters containing
537 synthetic organic dyes by electrochemical methods. An updated review, *Appl. Catal. B:*
538 *Environ.* 166-167 (2015) 603-643.

539 [10] Z.Y. Zhang, J.D. Huang, M.Y. Zhang, Q. Yuan, B. Dong, Ultrathin hexagonal SnS₂
540 nanosheets coupled with g-C₃N₄ nanosheets as 2D/2D heterojunction photocatalysts
541 toward high photocatalytic activity, Appl. Catal. B: Environ. 163 (2015) 298-305.

542 [11] K. Nakata, A. Fujishima, TiO₂ photocatalysis: design and applications, J. Photoch.
543 Photobio. C. 13 (2012) 169-189.

544 [12] S. Khanchandani, P.K. Srivastava, S. Kumar, S. Ghosh, A.K. Ganguli, Band gap
545 engineering of ZnO using core/shell morphology with environmentally benign Ag₂S
546 sensitizer for efficient light harvesting and enhanced visible-light photocatalysis, Inorg.
547 Chem. 53 (2014) 8902-8912.

548 [13] Z.Y. Zhang, C.L. Shao, X.H. Li, Y.Y. Sun, M.Y. Zhang, J.B. Mu, P. Zhang, Z.C. Guo,
549 Y.C. Liu, Hierarchical assembly of ultrathin hexagonal SnS₂ nanosheets onto electrospun
550 TiO₂ nanofibers: enhanced photocatalytic activity based on photoinduced interfacial
551 charge transfer, Nanoscale 5 (2013) 606-618.

552 [14] L.P. Wu, J. Li, S.H. Zhang, L.Z. Long, X.J. Li, C.P. Cen, Effect of ordered TiO₂
553 nanotube array substrate on photocatalytic performance of CdS-sensitized ZnO nanorod
554 arrays, J. Phys. Chem. C 117 (2013) 22591-22597.

555 [15] J. Yu, C.Y. Xu, F.X. Ma, S.P. Hu, Y.W. Zhang, L. Zhen, Monodisperse SnS₂
556 nanosheets for high-performance photocatalytic hydrogen generation, ACS Appl. Mater.
557 Inter. 6 (2014) 22370-22377.

558 [16] P. Chandran, P. Kumari, S.S. Khan, Photocatalytic activation of CdS NPs under
559 visible light for environmental cleanup and disinfection, Sol. Energy 105 (2014) 542-547.

560 [17] Y. Kim, H.B. Kim, D.J. Jang, Facile microwave fabrication of CdS nanobubbles with
 561 highly efficient photocatalytic performances, *J. Mater. Chem. A* 2 (2014) 5791-5799.

562 [18] Y.H. Yan, Z.X. Zhou, W.Q. Li, Y.J. Zhu, Y. Cheng, F.Y. Zhao, J.G. Zhou, Facile
 563 ion-exchange synthesis of urchin-shaped CdS/Bi₂S₃ heterostructures with enhanced
 564 photostability and visible light photocatalytic activity, *RSC Adv.* 4 (2014) 38558-38567.

565 [19] A. Yella, E. Mugnaioli, H.A. Therese, M. Panthöfer, U. Kolb, W. Tremel, Synthesis
 566 of fullerene- and nanotube-like SnS₂ nanoparticles and Sn/S/carbon nanocomposites,
 567 *Chem. Mater.* 21(2009) 2474-2481.

568 [20] J. Wang, J. Liu, H.B. Xu, S.M. Ji, J.B. Wang, Y.C. Zhou, P. Hodgson, Y.C. Li,
 569 Gram-scale and template-free synthesis of ultralong tin disulfide nanobelts and their
 570 lithium ion storage performances, *J. Mater. Chem. A* 1 (2013) 1117-1122.

571 [21] R.J. Wei, J.C. Hua, T.F. Zhou, X.L. Zhou, J.X. Liu, J.L. Li, Ultrathin SnS₂
 572 nanosheets with exposed {001} facets and enhanced photocatalytic properties, *Acta*
 573 *Mater.* 66 (2014) 163-171.

574 [22] A. Umar, M.S. Akhtar, G.N. Dar, M. Abaker, A. Al-Hajry, S. Baskoutas,
 575 Visible-light-driven photocatalytic and chemical sensing properties of SnS₂ nanoflakes,
 576 *Talanta* 114 (2013) 183-190.

577 [23] P. Nørby, S. Johnsen, B.B. Iversen, Fine tunable aqueous solution synthesis of
 578 textured flexible SnS₂ thin films and nanosheets, *Phys. Chem. Chem. Phys.* 17(2015)
 579 9282-9287.

580 [24] X.Q. An, J.C. Yu, J.W. Tang, Biomolecule-assisted fabrication of copper doped SnS₂
 581 nanosheet-reduced graphene oxide junctions with enhanced visible-light photocatalytic
 582 activity, J. Mater. Chem. A 2 (2014) 1000-1005.

583 [25] P. Chen, Y. Su, H. Liu, Y. Wang, Interconnected tin disulfide nanosheets grown on
 584 graphene for Li-ion storage and photocatalytic applications, ACS Appl. Mater. Inter. 5
 585 (2013) 12073-12082.

586 [26] Y.C. Zhang, Z.N. Du, K.W. Li, M. Zhang, and D.D. Dionysiou, High-performance
 587 visible-light-driven SnS₂/SnO₂ nanocomposite photocatalyst prepared via in situ
 588 hydrothermal oxidation of SnS₂ nanoparticles, ACS Appl. Mater. Inter. 3 (2011)
 589 1528-1537.

590 [27] Q.Q. Xu, J.T. Feng, L.C. Li, Q.S. Xiao, J. Wang, Hollow ZnFe₂O₄/TiO₂ composites:
 591 High-performance and recyclable visible-light photocatalyst, J. Alloy Compd. 641 (2015)
 592 110-118.

593 [28] L.L. Long, A.Y. Zhang, Y.X. Huang, X. Zhang, H.Q. Yu, A robust cocatalyst Pd₄S
 594 uniformly anchored onto Bi₂S₃ nanorods for enhanced visible light photocatalysis, J.
 595 Mater. Chem. A 3 (2015) 4301-4306.

596 [29] Y. Xu, W.D. Zhang, CdS/g-C₃N₄ Hybrids with improved photostability and visible
 597 light photocatalytic activity. Eur. J. Inorg. Chem. 2015 1744-1751.

598 [30] G. Manna, R. Bose, N. Pradhan, Photocatalytic Au-Bi₂S₃ heteronanostructures,
 599 Angew. Chem. Int. Ed. 53 (2014) 6743-6746.

600 [31] G.H. Chen, Y.Q. Yu , K. Zheng, T. Ding, W.L. Wang, Y. Jiang, Q. Yang, Fabrication
 601 of ultrathin Bi₂S₃ nanosheets for high performance, flexible, visible-NIR photodetectors,
 602 Small 11 (2015) 2848-2855.

603 [32] C.J. Tang, Y.S. Zhang, J.F. Su, C.Q. Wang, R.R. Sun, J. Zhang, G.H. Li, Synthesis
 604 and photocatalytic properties of vertically aligned Bi₂S₃ platelets, Solid State Sci. 51
 605 (2016) 24-29.

606 [33] S. Vadivel, A. Nirmalesh Naveen, V.P. Kamalakannan, P. Cao, N. Balasubramanian,
 607 Facile large scale synthesis of Bi₂S₃ nano rods-graphene composite for photocatalytic
 608 photoelectrochemical and supercapacitor application, Appl. Surf. Sci. 351 (2015)
 609 635-645.

610 [34] N. Liang, J.T. Zai, M. Xu, Q. Zhu, X. Wei, X.F. Qian, Novel Bi₂S₃/Bi₂O₂CO₃
 611 heterojunction photocatalysts with enhanced visible light responsive activity and
 612 wastewater treatment, J. Mater. Chem. A 2 (2014) 4208-4216.

613 [35] Y. Bai, X. Zong, H. Yu, Z.G. Chen, L.Z. Wang, Scalable low-cost SnS₂ nanosheets as
 614 counter electrode building blocks for dye-sensitized solar cells, Chem. Eur. J. 20 (2014)
 615 8670-8676.

616 [36] B. Weng, X. Zhang, N. Zhang, Z.R. Tang, Y.J. Xu, Two-dimensional MoS₂
 617 nanosheet-coated Bi₂S₃ discoids: Synthesis, formation mechanism, and photocatalytic
 618 application, Langmuir 31 (2015) 4314-4322.

619 [37] K.L. Ai, Y.L. Liu, J.H. Liu, Q.H. Yuan, Y.Y. He, L.H. Lu, Large-scale synthesis of
 620 Bi₂S₃ nanodots as a contrast agent for in vivo x-ray computed tomography imaging, Adv.
 621 Mater. 23 (2011) 4886-4891.

622 [38] W.C. Xu, J.Z. Fang, Y.F. Chen, S.Y. Lu, G.Y. Zhou, X.M. Zhu, Z.Q. Fang, Novel
 623 heterostructured Bi₂S₃/Bi₂Sn₂O₇ with highly visible light photocatalytic activity for the
 624 removal of rhodamine B, Mater. Chem. Phys. 154 (2015) 30-37.

625 [39]. T.T. Wang, H. Meng, X. Yu, Y.Z. Liu, H.B. Chen, Y. Zhu, J.P. Tang, Y.X. Tong, Y.M.
 626 Zhang, p-BiOI/n-SnS₂ heterojunction flowerlike structure with enhanced visible-light
 627 photocatalytic performance, RSC Adv., 5 (2015) 15469-15478.

628 [40]. Y.C. Zhang, J. Li, H.Y. Xu, One-step in situ solvothermal synthesis of SnS₂/TiO₂
 629 nanocomposites with high performance in visible light-driven photocatalytic reduction of
 630 aqueous Cr(VI), Appl. Catal. B: Environ. 123-124 (2012) 18-26.

631 [41] F. Spadavecchia, G. Cappelletti, S. Ardizzone, C.L. Bianchi, S. Cappelli, C. Oliva, P.
 632 Scardi, M. Leoni, P. Fermo, Solar photoactivity of nano-N-TiO₂ from tertiary amine: role
 633 of defects and paramagnetic species, Appl. Catal. B: Environ. 96 (2010) 314-322.

634 [42] B.M. Pirzada, N.A. Mir1, N. Qutub, O. Mehraj, S. Sabir, M. Muneer, Synthesis,
 635 characterization and optimization of photocatalytic activity of TiO₂/ZrO₂ nanocomposite
 636 heterostructures, Mater. Sci. Eng. B-Adv. 193 (2015) 137-145.

637 [43] T.T. Li, L.H. Zhao, Y.M. He, J. Cai, M.F. Luo, J.J. Lin, Synthesis of g-C₃N₄/SmVO₄
 638 composite photocatalyst with improved visible light photocatalytic activities in RhB
 639 degradation, Appl. Catal. B: Environ. 129 (2013) 255-263.

640 [44] M.A. Butler, Photoelectrolysis and physical properties of the semiconducting
641 electrode WO_3 , J. Appl. Phys. 48 (1977) 1914-1920.

642 [45] Z.D. Wu, L.L. Chen, C.S. Xing, D.L. Jiang, J.M. Xie, M. Chen, Controlled synthesis
643 of $\text{Bi}_2\text{S}_3/\text{ZnS}$ microspheres by an in situ ion-exchange process with enhanced visible light
644 photocatalytic activity, Dalton Trans. 42 (2013) 12980-12988.

645 [46] F.Z. Liu, X. Shao, S.Y. Yang, $\text{Bi}_2\text{S}_3\text{-ZnS/graphene}$ complexes: Synthesis,
646 characterization, and photoactivity for the decolorization of dyes under visible light, Mat.
647 Sci. in Semicon. Proc. 34(2015)104-108.

648 [47] Y.C. Zhang, J. Li, M. Zhang, D.D. Dionysiou, Size-tunable hydrothermal synthesis
649 of SnS_2 nanocrystals with high performance in visible light-driven photocatalytic
650 reduction of aqueous Cr(VI) , Environ. Sci. Technol. 45 (2011) 9324-9331.

651 [48] Y.M. Cui, Q.F. Jia, H.Q. Li, J.Y. Han, L.J. Zhu, S.G. Li, Y. Zou, J. Yang,
652 Photocatalytic activities of $\text{Bi}_2\text{S}_3/\text{BiOBr}$ nanocomposites synthesized by a facile
653 hydrothermal process, Appl. Surf. Sci. 290 (2014) 233-239.

654 [49] X.G. Li, Y.L. Li, J.F. Shen, M.X. Ye, A controlled anion exchange strategy to
655 synthesize Bi_2S_3 nanoparticles/plate-like Bi_2WO_6 heterostructures with enhanced visible
656 light photocatalytic activities for Rhodamine B, Ceram. Int. 42 (2016) 3154-3162.

657 [50] Y.C. Zhang, Z.N. Du, S.Y. Li, M. Zhang, Novel synthesis and high visible light
658 photocatalytic activity of SnS_2 nanoflakes from $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and S powders, Appl. Catal.
659 B: Environ. 95 (2010) 153-159.

660 [51] R. Lucena, F. Fresno, J.C. Conesa, Hydrothermally synthesized nanocrystalline tin
 661 disulphide as visible light-active photocatalyst: Spectral response and stability, Appl.
 662 Catal. A-Gen. 415-416 (2012) 111-117.

663 [52] D.N. Xiong, G.F. Huang, B.X. Zhou, Q. Yan, A.L. Pan, W.Q. Huang, Facile
 664 ion-exchange synthesis of mesoporous Bi₂S₃/ZnS nanoplate with high adsorption
 665 capability and photocatalytic activity, J. Colloid Interf. Sci. 464 (2016) 103-109.

666 [53] Y.M. Zhu, D.D. Xu, M. Meng, Ultrasonic-assisted synthesis of amorphous Bi₂S₃
 667 coupled (BiO)₂CO₃ catalyst with improved visible light-responsive photocatalytic activity,
 668 J Mater Sci 50 (2015) 1594-1604.

669 [54] T.T. Zhu, Y.H. Song, H.Y. Ji, Y.G. Xu, Y.X. Song, J.X. Xia, S. Yin, Y.P. Li, H. Xu, Q.
 670 Zhang, H.M. Li, Synthesis of g-C₃N₄/Ag₃VO₄ composites with enhanced photocatalytic
 671 activity under visible light irradiation, Chem. Eng. J. 271 (2015) 96-105.

672 [55] Z.J. Zhang, W.Z. Wang, L. Wang, S.M. Sun, Enhancement of visible-light
 673 photocatalysis by coupling with narrow-band-gap semiconductor: a case study on
 674 Bi₂S₃/Bi₂WO₆, ACS Appl. Mater. Inter. 4 (2012) 593-597.

675 [56] X.T. Wang, R. Lv, K. Wang, Synthesis of ZnO@ZnS-Bi₂S₃ core-shell nanorod
 676 grown on reduced graphene oxide sheets and its enhanced photocatalytic performance, J.
 677 Mater. Chem. A 2 (2014) 8304-8313.

678 [57] J.S. Chen, S.Y. Qin, G.X. Song, T.Y. Xiang, F. Xin, X.H. Yin, Shape-controlled
 679 solvothermal synthesis of Bi₂S₃ for photocatalytic reduction of CO₂ to methyl formate in
 680 methanol, Dalton Trans 42 (2013) 15133-15138.

681 [58] S.J.A. Moniz, S.A. Shevlin, D.J. Martin, Z.X. Guo, J.W. Tang, Visible-light driven
682 heterojunction photocatalysts for water splitting-a critical review, *Energy Environ. Sci.* 8
683 (2015) 731-759.

684 [59] H.X. Zhong, G.Z. Yang, H.W. Song, Q.Y. Liao, H. Cui, P.K. Shen, C.X. Wang,
685 Vertically Aligned Graphene-Like SnS₂ Ultrathin Nanosheet Arrays: Excellent Energy
686 Storage, Catalysis, Photoconduction, and Field-Emitting Performances, *J. Phys. Chem. C*
687 116 (2012) 9319-9326.

Graphical Abstract