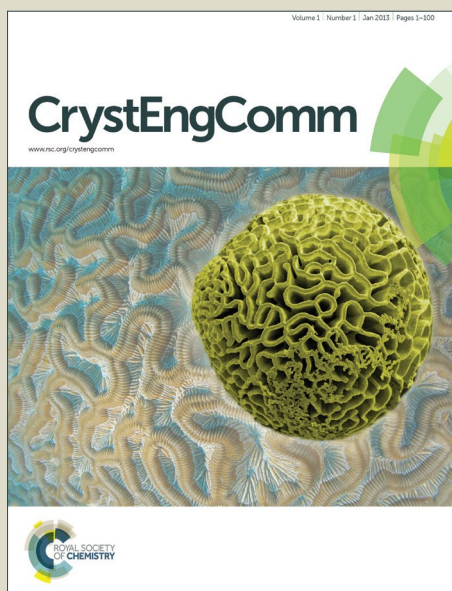


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One-step synthesis of hierarchical Bi₂S₃ nanoflower\In₂S₃ nanosheet composite with efficient visible light photocatalytic activity

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In this study, hierarchical nanoflower superstructures composed of In₂S₃ nanosheets grown on Bi₂S₃ nanoflower backbone (denoted as Bi₂S₃/In₂S₃) are fabricated by a facile one-step solvothermal route based on different growth rate of the two kinds of sulphides. The Bi₂S₃ nanoflowers were first formed due to quick growth rate, which serves as the substrate for the growth of In₂S₃ ultra-thin nanosheets with relatively slow reaction rate to form hierarchical Bi₂S₃/In₂S₃ composite superstructure. The introduction of In₂S₃ nanosheets on the surface of Bi₂S₃ nanoflower can not only increase visible light response, but also remarkably promote the photogenerated charges transport and separation driven by the heterojunction. Because of their marked synergistic effects, the as-prepared hierarchical Bi₂S₃ nanoflower \In₂S₃ nanosheet superstructures exhibit significant visible light photocatalytic activity and stability for degradation of 2, 4-dichlorophenol.

1. Introduction

In recent years, metal sulfides have been widely investigated as highly efficient catalysts for visible light photocatalytic applications.¹⁻³ Among these metal sulfides, Bi₂S₃ and In₂S₃, with bandgaps of ~1.3 eV and 2.2 eV, respectively, have been used as sensitizers due to its ability to absorb a large part of visible light region.⁴⁻⁶ Nevertheless, the widespread application of Bi₂S₃ and In₂S₃ suffers from some limitations related to fast recombination of photoinduced electron-hole pairs during the visible light photocatalytic processes.⁷⁻⁹ Therefore, an enormous amount of effort has been done to lower the recombination rate of electron-hole pairs by designing metal/metal oxide (sulfide) heterostructure nanocatalysts.¹⁰ The formed heterostructures favor charge separation through quick transfer of electrons or holes from one material to the other.

Recently, lots of Bi₂S₃-based visible light photocatalysts were synthesized to improve photoinduced charge separation and visible light photocatalytic activity. For example, Bi₂S₃-TiO₂, Bi₂S₃/Bi₂Sn₂O₇, and Bi₂S₃/BiOBr composites.¹¹⁻¹³ The combination of these metal oxides and Bi₂S₃ is an efficient way for the separation of photoinduced carries, and thus raise photocatalytic efficiency of the composites.^{14,15} Meanwhile, Bi₂S₃ is also coupled with the carbon materials, and Bi₂S₃-reduced graphene oxide composites and Bi₂S₃/g-C₃N₄ composites were prepared and exhibited obviously enhanced visible-light-driven photocatalytic property.¹⁶⁻¹⁸ Recently, coupling Bi₂S₃ with another metal sulfide could effectively accelerate the separation and transfer of photogenerated carriers. Such as, CuS-Bi₂S₃, MoS₂ nanosheet-coated Bi₂S₃, Pd₄S coated Bi₂S₃ nanorods, and Bi₂S₃/CdS composites.¹⁹⁻²² In most cases, the loading processes of metal sulfide are often complicated, general synthesis strategy used to fabricate metal

sulfide composite structure is to first prepare the substrate material, and then couple other materials with the substrate to form composite structure.²³⁻²⁵ Therefore, constructing metal sulfide composites via a facile route is a significant work. Our recent study showed the combination of In₂S₃ and Bi₂S₃ in a single core@shell composite could significantly improve the overall performance of the core@shell system for the photocatalytic degradation reaction.²⁶ This kind of synthetic method can form effective interfacial contact and strong interaction between two components in the composite and lead to an enhanced photogenerated charge transfer and separation. In core@shell system, if the shell layer is too thick, it can obstruct light utilization of the core material, so influencing the further enhancement of the photocatalytic activity. Recently, ultrathin structures, such as nanosheets, have been used to act as shell to construct hierarchical structure composites basically due to the large specific surface areas and high light utilization and quick photogenerated charge carriers transfer from the interior to the surface of photocatalysts to participate in the photocatalytic reactions.^{27,28} Significant progress has been made in combining these advantages. For instance, Lou et al. Prepared 1D hierarchical structures composed of Ni₃S₂ nanosheets on carbon nanotubes backbone to significantly improve supercapacitors and photocatalytic H₂ production performance.²⁹ Wang and coworkers have prepared helical 1D/2D epitaxial nano-heterostructures between CdS rod and ZnIn₂S₄ nanosheets. The resulting well defined interface induces the delocalized interface states, thus facilitate the charge transfer and enhance the performance in the photoelectrochemical cells.³⁰ In spired by these studies, it is expected to grow In₂S₃ nanosheets on the Bi₂S₃ support to fabricate hierarchical Bi₂S₃/In₂S₃ composites with enhanced visible light photocatalytic activity.

In this study, we reported a facile one-step hydrothermal route for the synthesis of hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composites. In this process, because of significant reaction rate difference, quick reaction rate of thiourea with Bi salt forms Bi_2S_3 nanoflowers firstly, and then the slow reaction rate causes the growth of In_2S_3 nanosheets on the surface of Bi_2S_3 nanoflowers, leading to the formation of hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composites. In this special composite structure, the fluffy In_2S_3 nanosheets on the surface of Bi_2S_3 nanoflowers benefit multiple light reflection and increase light-harvesting. Together with quick photogenerated charge carriers transfer, enhanced photocatalytic efficiency and photostability were obtained from the hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composites for the degradation of 2, 4-dichlorophenol under visible light irradiation.

2. Experimental section

2.1. Synthesis of hierarchical Bi_2S_3 nanoflower/ In_2S_3 nanosheet composite

In a typical experiment, 0.3 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 0.15 g thiourea (Tu), a specified quality of $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ (the molar ratios of Bi^{3+} to In^{3+} is 3:1) and 5 mL glycerol were added into 25 mL ethanol and stirred for 30 min at room temperature. Then, the obtained yellow solution was transferred to a 50 mL Teflon-lined stainless steel autoclave, which was heated to 150 °C and maintained for 10 h. After cooling, the as-synthesized brown products were rinsed with distilled water, absolute ethanol, respectively, and dried at 60 °C overnight. Similarly, $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composites with different mole ratios (4:1, 2:1, and 1:1) of Bi and In were also prepared. For comparison, bare Bi_2S_3 and In_2S_3 were obtained under the same experimental conditions in the absence of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$, respectively.

2.2. Characterization

Structure and morphology of the product was investigated by Scanning electron microscopy (SEM, Hitachi S-4800, Japan), SEM-EDS analyses were carried out with a Hitachi S-4800 SEM equipped with an EDAX energy dispersive X-ray analyzer. Transmission electron microscopy (TEM, JEOL 2100, Japan), and powder X-ray diffraction (XRD, Bruker D8 Advance using $\text{CuK}\alpha$ radiation). Raman spectra were recorded on a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. The UV-visible diffuse reflectance spectra of the samples were obtained from a UV-visible spectrophotometer (Shimadzu UV-2550). The fluorescence spectra of the samples at room temperature were characterized via the fluorescence spectrophotometer (F-7000, Hitachi, Japan). The excitation wavelength was 350 nm induced from a He-Cd laser source to excite the samples.

2.3. Measurement of photocatalytic activity

The photodegradation experiments were performed in a slurry reactor containing 100 mL of 50 mg/L 2, 4-dichlorophenol and 0.05 g of catalyst. An 150 W xenon lamp (Institute of Electric Light Source, Beijing) was used as the solar-simulated light source, and visible light was achieved by

utilizing a UV cut filter ($\lambda > 420$ nm). Prior to light irradiation, the suspension was kept in the dark under stirring for 30 min to ensure the establishing of an adsorption/desorption equilibrium. Adequate aliquots (5 mL) of the sample were withdrawn after periodic interval of irradiation, and centrifuged at 10000 rpm for 5 min, then filtered through a Milipore filter (pore size: 0.22 μm) to remove the residual catalyst particulates for analysis. The filtrates were analyzed using a UV-vis spectrophotometer (Shimadzu UV-2550).

In order to detect the radical species over the catalyst during the photocatalytic reaction, the electron spin resonance (ESR) technique (with DMPO) was used on a Bruker EMX-8/2.7 spectrometer by accumulating three scans at a microwave frequency of 9.85 GHz and a power of 6.35 mW. Before testing, DMPO was added to the suspension system, and then the system was irradiated by visible light using a halogen tungsten lamp with a UV cutoff filter ($\lambda > 420$ nm). Besides, to detect the active species generated during photocatalytic reactivity, various scavengers were added into 2, 4-dichlorophenol solutions, including 1 mM p-benzoquinone (BQ, a quencher of $\text{O}_2^{\bullet-}$), 1.0 mM isopropanol (IPA, a quencher of $\bullet\text{OH}$), 1 mM triethanolamine (TEOA, a quencher of h^+), and 6 mM AgNO_3 (e^- scavenger), followed by the photocatalytic activity test.

3. Results and discussion

3.1. Characterization of phase structure and morphology

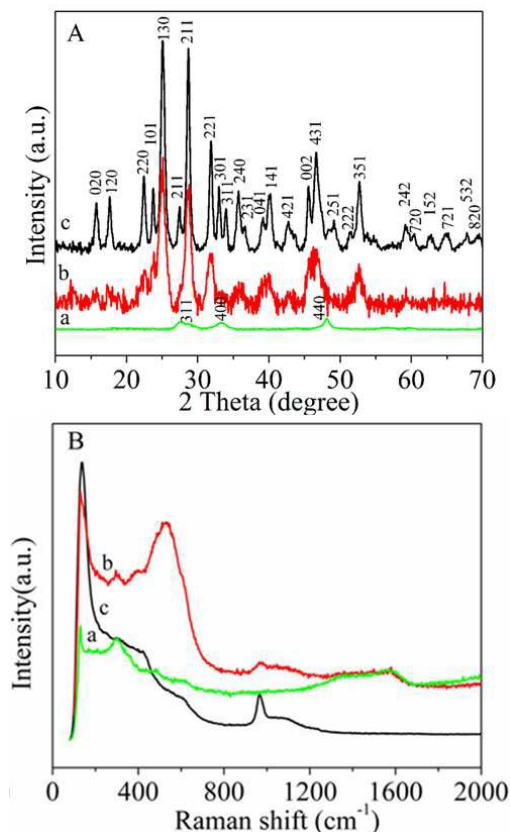


Fig. 1 (A) XRD patterns and the corresponding (B) Raman spectra of In_2S_3 (a), $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ (Bi:In=3:1) (b), and Bi_2S_3 (c).

The phase structures of these samples were determined by XRD measurements (Fig. 1A). The X-ray diffraction spectra of a and c shown in Fig. 1D reveal the presence of pure orthorhombic phase Bi_2S_3 (JCPDS card No.17-0320) and cubic $\beta\text{-In}_2\text{S}_3$ (JCPDS Card No. 32-0456), respectively. For hierarchical composite (Line b in Fig. 1A), diffraction peaks of Bi_2S_3 match with the reflections from the orthorhombic phase Bi_2S_3 lattice planes of (130), (021) and (211), making it easy to reveal the presence of Bi_2S_3 .³¹ In contrast, no diffraction peaks attributed to cubic $\beta\text{-In}_2\text{S}_3$ can be found, which may be due to low crystallinity and the overlap of the diffraction peaks with those of Bi_2S_3 . However, the corresponding Raman spectra of the three samples shown in Fig. 1B proved the existence of cubic $\beta\text{-In}_2\text{S}_3$. All the above results suggest that the ultrathin In_2S_3 nanosheets could *in situ* grow on the surface of Bi_2S_3 nanoflowers.

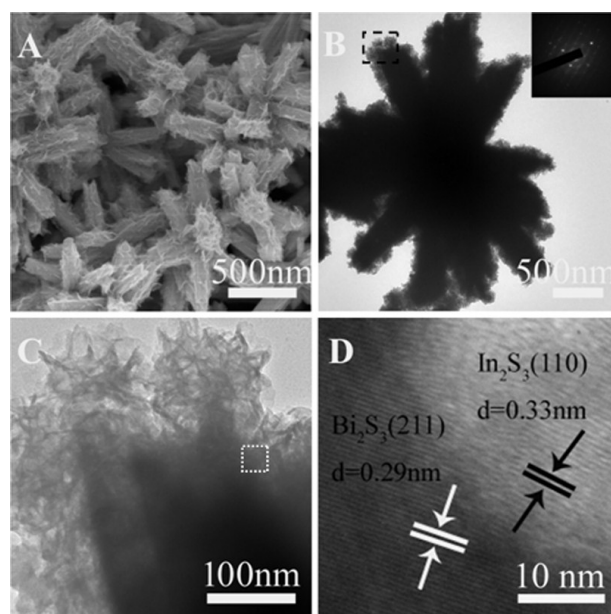


Fig. 2 SEM (A), TEM (B, C), and HRTEM (D) images of the hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ hybrid ($\text{Bi}:\text{In}=3:1$), inset of Fig. C is the selected area electron diffraction pattern.

The morphology of the as-prepared products was characterized by SEM and TEM, Fig. 2A shows the SEM image of the $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite. The uniform flower-like superstructure can be found. The average diameter of these superstructures is about 800 nm. The surface of the Bi_2S_3 nanoflower is covered by In_2S_3 ultrathin nanosheets. From the comparison of the SEM images (Fig. S1A), we could clearly see that bare Bi_2S_3 is composed of nanoflowers with an average diameter of 500-1000 nm. As for pure In_2S_3 , lots of nanosheet aggregates could be obtained (Fig. S1B). Interestingly, this change indicates that In_2S_3 nanosheets may grow along the core of Bi_2S_3 nanoflowers. The more detailed structural information of the hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite was revealed using TEM and HRTEM. As shown in Fig. 2B, ultrathin nanosheets grow uniformly on the surface of nanoflower and the thickness of the nanosheets is estimated to be 3–5 nm measured from the edges (Fig. 2C), which would

contribute to visible light-utilization in the photocatalytic reaction. The HRTEM image in Fig. 2D reveals that the interplanar spacing of 0.29 nm corresponds to the (211) plane of Bi_2S_3 , while the interplanar spacing of 0.33 nm corresponds to the (110) plane of cubic $\beta\text{-In}_2\text{S}_3$, which implying the formation of $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ heterostructure.^{26,32} This suggests that an intimate and coherent interface was formed between In_2S_3 nanosheet with Bi_2S_3 nanoflower core. This is important for improving charge separation and thus photocatalytic activity. The selected area electron diffraction pattern (SAED) shown in the inset of Fig. 2B further proves its mixed-phase nature of single crystal Bi_2S_3 and polycrystalline In_2S_3 .

The element distribution was verified by energy dispersive X-ray (EDX) element mapping. As shown in Fig. 3B–D, the EDS mapping images indicate the coexistence and homogeneous distribution of S, Bi and In elements in the nanoflower composites. It confirms that the In_2S_3 nanosheets are uniformly grown on the surface of the Bi_2S_3 nanoflowers. Moreover, in comparison to the Bi and S elements mapping distribution (Fig. 3B,C), In element content is obvious low (Fig. 3D), which is consistent with other experimental results.

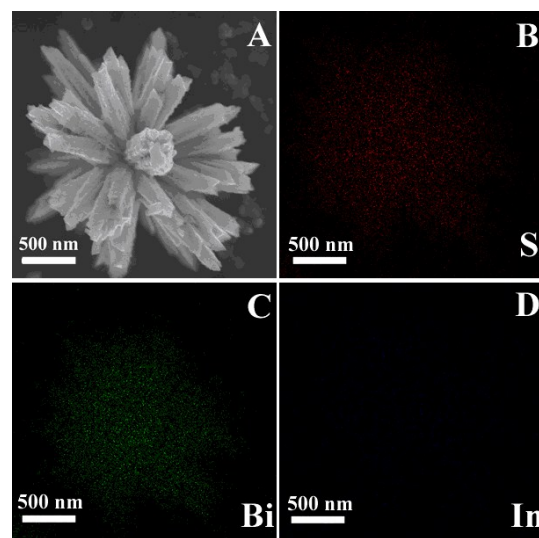


Fig. 3 SEM image (A) of the hierarchical Bi_2S_3 nanoflower/ In_2S_3 nanosheet composite ($\text{Bi}:\text{In}=3:1$) and the corresponding EDS mapping of S (B, red), Bi (C, green) and In (D, blue).

3.2. Growth process of the hierarchical Bi_2S_3 nanoflower/ In_2S_3 nanosheet composite

To investigate the formation process of the hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite, time-dependent experiments were carried out. Fig. 4A–D presents a series of SEM images of the products obtained at different reaction times. As shown in Fig. 4A, at the early reaction stage (30 min), the Bi_2S_3 nanoflowers with smooth nanorod surface were fastly formed with a diameter of about 1.5 μm (Fig. 4B). As the reaction proceeded (Fig. 4C), In^{3+} and S^{2-} could get enough energy to crystallize into In_2S_3 nanosheets on the surface of Bi_2S_3 nanoflower. As the reaction proceed, more In_2S_3 nanosheets (Fig. 4C) grew onto the surface of Bi_2S_3 nanoflowers after the reaction was carried out for 4 h. Ultimately, hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite (Fig. 4D) were formed. The corresponding EDS spectra for the samples prepared from different reaction time

also proved this formation process (Fig. S2A). There only exists Bi and S elements for the product prepared at the initial reaction stage (30 min), indicating the fast formation of Bi_2S_3 nanoflowers. As the reaction proceeded, the presence of In element (Fig. S2B) also proved the appearance of In_2S_3 in the composite. Furthermore, the content of In element increased along with the extension of reaction time according to the EDS results (Fig. S2C, D).

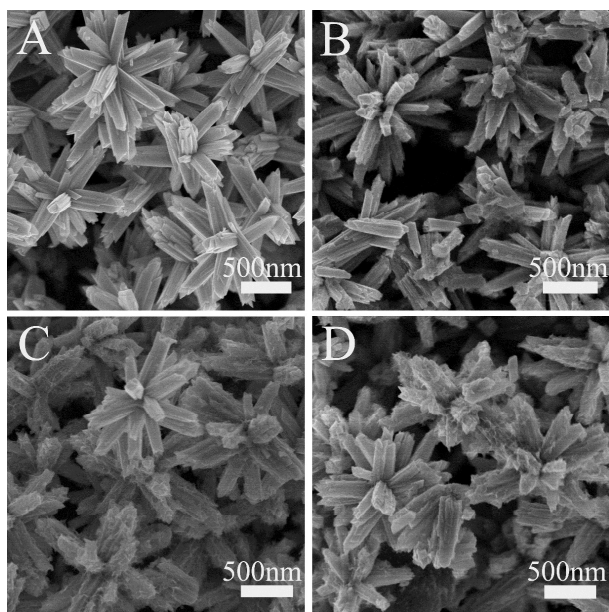
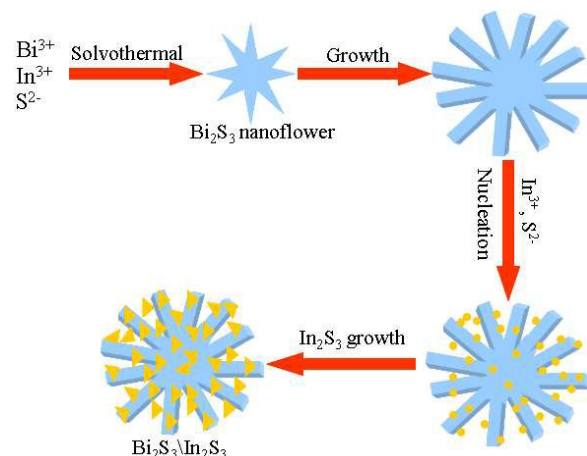


Fig. 4 SEM images of the products obtained from the different reaction times, (a) 30 min, (b) 1 h, (c) 4 h, (d) 10 h.

Based on the above experimental results and analysis, the probable morphology evolution process of the hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite nanoflowers is shown in scheme 1. In this study, thiourea was used as sulfide source to supply S^{2-} in solution during the solvothermal process. At elevated reaction temperature, thiourea hydrolyzed to release H_2S with the assistance of a trace amount of the mixture of ethanol and glycerol. According to the K_{sp} of Bi_2S_3 (1.0×10^{-97}) and In_2S_3 (5.7×10^{-73}),²⁶ it is expected that Bi_2S_3 will preferentially deposit and form sea-urchin shaped nanoflowers (crystal seeds) inside the autoclave before In_2S_3 , Bi^{2+} and glycerol first to form flower-like ligand. However, in the reaction system, the positively charged ions, such as In^{3+} and so forth, could weaken the activation energy of the surface of the Bi_2S_3 nanoflowers, which would provide many high energy sites for further growth and promote their desorption from the surface of nanoflowers,³³ so leading to the following growth of In_2S_3 nanosheets. When Bi^{3+} was depleted, the nucleation process of In_2S_3 was initialized. With the extension of reaction time, a larger number of In^{3+} ions in the solution could get enough energy to nucleation onto the surface of the Bi_2S_3 nanoflowers, and ultrathin In_2S_3 nanosheets are uniformly coated on the surface of the Bi_2S_3 nanoflowers. Finally, hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composites were formed. Compared to the conventional two-step synthetic process, this one-spot synthetic route is easy to achieve uniform surface coating due

to compatibility issues between Bi_2S_3 nanoflower and In_2S_3 nanosheet. Furthermore, In_2S_3 nanosheet content can be easily controlled by altering the mole ratio of Bi salt and In salt. When the mole ratio of Bi salt and In salt is large, the In_2S_3 nanosheets on the surface of the nanoflowers are not obvious (Fig. S3A). If the mole ratio of Bi salt and In salt is too low, the additional In_2S_3 would separate from the nanoflowers (Fig. S3C) due to the increased supersaturation of the precursors.



Scheme 1 Illustration of the morphological evolution process of the hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite.

3.3. UV-visible absorption and photoluminescence spectra analysis

The UV-visible absorption spectra of the products are shown in the Fig. 5. A wide absorption across UV-visible light spectrum can be observed for all three samples. Obviously, compared with bare Bi_2S_3 and In_2S_3 , the light absorption ability of the $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite existed some enhancement, which can be attributed to the synergistic affect of the two components in the composite, and the fluffy In_2S_3 nanosheets on the surface of Bi_2S_3 would benefit multiple light reflection and increase light-harvesting. Taking into account the efficient use of visible light, it is believed that this composite may have enhanced visible-light photocatalytic activity.

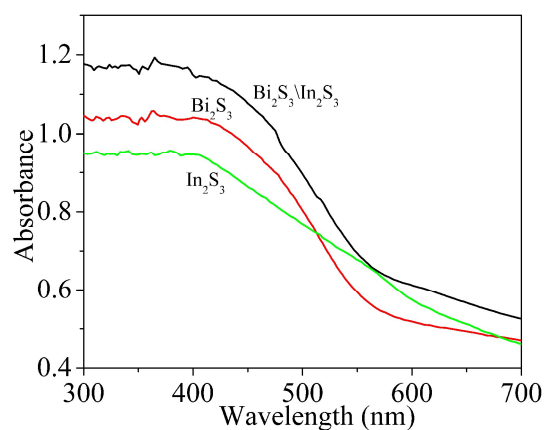


Fig. 5 UV-visible absorption spectra of the different samples: Bi_2S_3 , In_2S_3 and $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$.

It is known that photoluminescence (PL) spectra can give information about the photoexcited energy/electron transfer and recombination processes, and it has been widely used to study the fate of electron-hole pairs.³⁴ Fig. 6 shows the PL spectra of In_2S_3 , Bi_2S_3 , and $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ samples. The broad emission peaks of the Bi_2S_3 and In_2S_3 centered at 535 nm and 537 nm, respectively, are related to the presence of surface defects.^{6,34} Generally, photoluminescence emission originates from the radiative recombination of photogenerated holes and electrons in semiconductor materials. An obvious decrease of the photoluminescence of the $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ heterostructure can be observed as compared with that of Bi_2S_3 nanoflower or In_2S_3 nanosheets alone, indicating that the photogenerated electrons in $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite can easily tunnel from the In_2S_3 nanosheet shell into the Bi_2S_3 nanoflower core; thus, the core/shell heterostructure can diminish the recombination of photoinduced electron-hole pairs, and enhance the visible-light absorption ability.

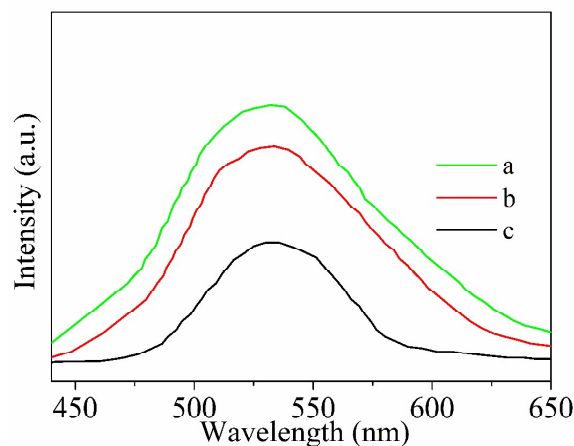


Fig. 6 Photoluminescence spectra of the different samples: Bi_2S_3 (a), In_2S_3 (b) and $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ (c).

3.4. Photocatalytic activity.

The photoactivity of the $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite was evaluated by degradation of 2, 4-dichlorophenol under visible light irradiation. For comparison, decomposition abilities of Bi_2S_3 and In_2S_3 were measured under the same experimental conditions. Bi_2S_3 and In_2S_3 showed relatively low visible light photocatalytic property (Fig. 7A a,b). After In_2S_3 nanosheets were grown on the surface of Bi_2S_3 nanoflowers, the visible light photocatalytic performance of the $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ nanoflower heterostructure is dramatically improved. The corresponding decomposition rate of optimal $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ heterostructure ($\text{Bi}:\text{In}=3:1$) increases to 92% after 90 min visible light irradiation (Fig. 7A), which is much higher than that of In_2S_3 nanosheets (31.5%) and Bi_2S_3 nanoflower (28.8%). Meanwhile, the influence of In_2S_3 nanosheets amount on the photocatalytic activity can also be confirmed (Fig. 7A c-f). When the amount of In_2S_3 nanosheets is low ($\text{Bi}:\text{In}=4:1$), In_2S_3 nanosheets can not fully cover the of Bi_2S_3 nanoflowers. So the composite can only provide relatively low surface active sites for the adsorption of reactant molecules, and the recombination chance of photogenerated electrons and holes also increased.

Adding excess In_2S_3 also reduced the catalytic efficiency of the $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite ($\text{Bi}:\text{In}=1:1$) because the additional In_2S_3 was separated from Bi_2S_3 nanoflowers, which was unfavorable to the degradation of 2, 4-dichlorophenol owing to the increased recombination of photogenerated electrons and holes.

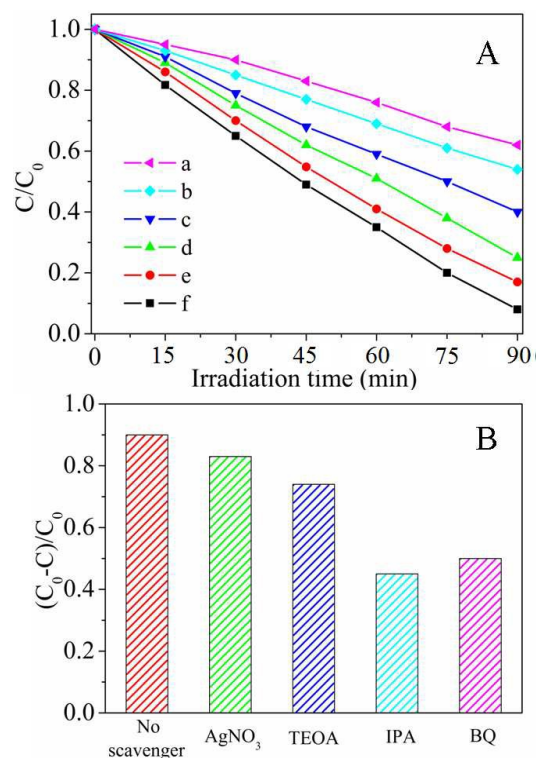


Fig. 7 (A) Comparison of photocatalytic activities of Bi_2S_3 (a), In_2S_3 (b), the hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite with different $\text{Bi}:\text{In}$ ratio, 4:1 (c), 3:1 (d), 1:1 (e), and 2:1 (f). (B) Comparison of photocatalytic activities of hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite ($\text{Bi}:\text{In}=3:1$) with different scavengers during the photocatalytic reaction under visible light irradiation.

Comparing $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite with pure Bi_2S_3 and In_2S_3 , the enhanced photocatalytic activity can be attributed to the synergistic effects of the significantly enhanced light absorption (Fig. 5) and efficient separation of photogenerated carriers (Fig. 6), which can be considered as the main reasons for the enhancement of visible light photocatalytic activity. Because In_2S_3 nanosheets on the surface of Bi_2S_3 nanoflower are ultrathin, so visible light could penetrate In_2S_3 nanosheet shell to the core of Bi_2S_3 nanoflower. Meanwhile, more abundant interfaces between In_2S_3 and Bi_2S_3 facilitate charge separation, and in the continuous interface, charge carriers are delocalized and the transport is more favorable. The synergistic effect of these factors results in a significant higher photocatalytic capability of $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composites. Under visible-light irradiation, photogenerated electrons are excited from the valence band (VB) to the conduction band (CB) of In_2S_3 and Bi_2S_3 (Fig. S4). Because the conduction band of In_2S_3 is slightly higher than that of Bi_2S_3 , the photoexcited electrons in the conduction band of In_2S_3 can be transferred to that of Bi_2S_3 easily. The electrons on the conduction band energy level (E_{CB}) of Bi_2S_3 and In_2S_3 could reduce O_2 to $\cdot\text{O}_2^-$ through one-electron reducing reaction.³⁵ Meanwhile, the remaining holes in the valence band of In_2S_3 will be trapped at surface state. All the radicals can react with organic chemicals in

the solution and improve the photoactivity.

It is known that organic pollutants can be degraded by a series of photoinduced reactive species, such as $\cdot\text{O}^{2-}$, $\cdot\text{OH}$ and h^+ , during photocatalytic degradation process. To elucidate the main reactive species responsible for the degradation of organic contaminants over $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite, a series of quenchers were employed to scavenge the relevant reactive species. As shown in Fig. 7B, the addition of AgNO_3 in the 2, 4-dichlorophenol solution has little effect on the photocatalytic activity of the hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite. The degradation rate exhibited a slight depression in the presence of triethanolamine (TEOA). This result indicates that h^+ is not the directly reactive species responsible for the degradation of 2, 4-dichlorophenol. In contrast, the introduction of isopropanol (IPA) and benzoquinone (BQ) markedly restrains the degradation of $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite nanoflower, suggesting that $\cdot\text{O}^{2-}$ and $\cdot\text{OH}$ play important role in degrading 2, 4-dichlorophenol.

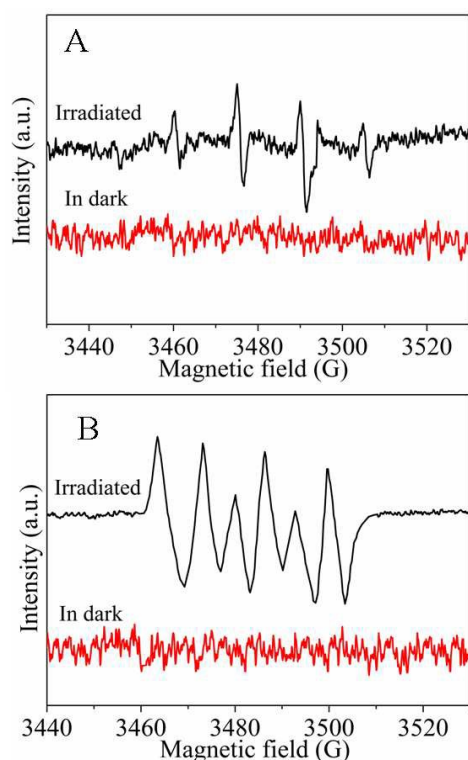


Fig. 8 DMPO spin-trapping ESR spectra recorded at ambient temperature with $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite (Bi:In=3:1) in (A) aqueous dispersion (for DMPO- $\cdot\text{OH}$), (B) methanol dispersion (for DMPO- $\cdot\text{O}^{2-}$) under visible-light irradiation ($\lambda > 420 \text{ nm}$).

To further interpret the photocatalytic mechanism, the ESR spin-trap technique with 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) was employed to ascertain the active oxygen species in the $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite system. Under visible-light irradiation, $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite gives the characteristic of four peaks of DMPO- $\cdot\text{OH}$ with an intensity ratio 1:2:2:1 (Fig. 8A), similar to the previous studies of $\cdot\text{OH}$ adduct.^{36,37} Meanwhile, six characteristic peaks with intensity similar to that of DMPO- $\cdot\text{O}^{2-}$ adducts were observed only under visible-light irradiation (Fig. 8B), which is consistent with the former studies for $\cdot\text{O}^{2-}$ adduct.³⁸ These ESR tests reveal that $\cdot\text{OH}$ and $\cdot\text{O}^{2-}$ radicals exist in the

$\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite system under visible-light irradiation. The above results are consistent with the result of reactive species trapping experiments.

The stability of the hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite nanoflower was also evaluated by performing the cycling experiments under the same conditions. After four recycles, the hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite does not show obvious activity loss, indicating the better stability of this $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite (Fig. S5). The high stability can be attributed to the close interaction between Bi_2S_3 and In_2S_3 solid solution, which favors the transfer of the photogenerated electrons from the conduction band of In_2S_3 to that of Bi_2S_3 . This spatial separation of photogenerated electrons and holes is beneficial for inhibiting the reduction of In^{3+} and Bi^{3+} .

4. Conclusions

In conclusion, a facile one-step hydrothermal method was employed to synthesize hierarchical $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$ composite based on the different growth rate of sulphides. Comparative studies were carried out to evaluate the relative photocatalytic performance of $\text{Bi}_2\text{S}_3/\text{In}_2\text{S}_3$, Bi_2S_3 , and In_2S_3 . By incorporating In_2S_3 , the hybrid structures have significantly higher performance over their counterparts benefiting from enhanced light absorption and improved photogenerated electron-hole pairs separation and transportation. More importantly, in comparison with separated aggregates, In_2S_3 nanosheets exhibit more uniform distribution on Bi_2S_3 nanoflower with less agglomeration, resulting in more contact area between Bi_2S_3 and In_2S_3 , which was validated to contribute to the enhanced charge separation and transportation, and visible-light utilization.

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Notes

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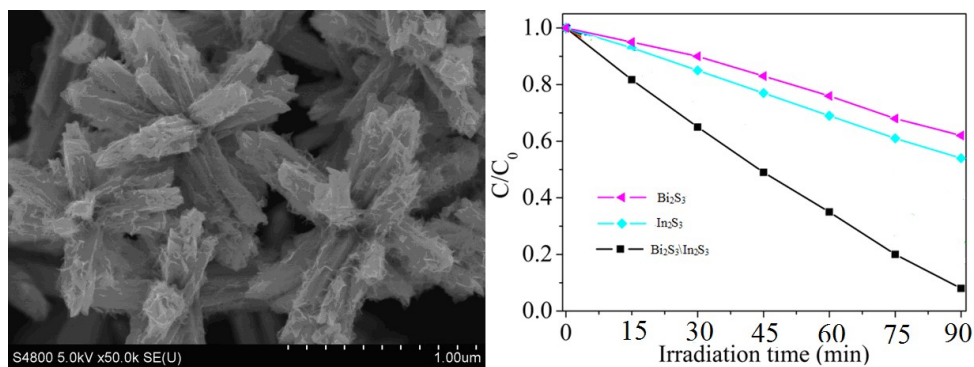
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Graphical Abstract



Hierarchical Bi_2S_3 nanoflower/ In_2S_3 nanosheet composites were prepared and showed excellent visible light photocatalytic activity