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Fabrication of magnetic and recyclable In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites for visible light photocatalytic activity enhancement

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Abstract

In this work, magnetic In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites were fabricated via a two-step solvothermal process, which In$_2$S$_3$ loading amount on ZnFe$_2$O$_4$ support medium could be controlled by changing reaction mass. Investigation revealed that the photocatalytic activity of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites was superior to pure In$_2$S$_3$ and ZnFe$_2$O$_4$ for the degradation of MB driven by visible light. The improved photocatalytic activity may be stemming from the synergy effect of In$_2$S$_3$ and ZnFe$_2$O$_4$, resulting in the enhanced visible light absorbance and higher separation efficiency of the photo-generated charge carriers. Significantly, this sort of nanocomposites could rapidly be separated through an external magnetic field, and five successive cycle experiments have proved that it was stable and recyclable. Finally, a possible mechanism related to the separation of charge and photocatalytic decomposition of MB was also provided.

1. Introduction

Over the previous decades, photocatalysis technology has received so substantial attention that it has become a challenging and quickly growing area of research [1, 2]. Semiconductor photocatalyst has been proven to be a class of representative for the solar energy conversion and pollution removal owing to its efficient utilization of solar light [3, 4]. Particularly, as a typical III-VI group sulfide with a band gap of ~2.0 eV [5–7], indium sulfide (In$_2$S$_3$) has been considered as a sort of promising visible-light photocatalyst [8, 9]. On account of its excellent intrinsic optoelectronic properties [10, 11], favorable photostability [12], superior physical and chemical characteristics as well as low toxicity [8], it can be used to decompose organic contaminants and destroy bacteria for wastewater remediation and to split water for clean energy generation [13, 14]. Nevertheless, similar to other narrow-band gap semiconductor photocatalysts, the efficiency of In$_2$S$_3$ was far from satisfaction owing to the rapid recombination of photoexcited charge carriers. As a result, some efforts have been carried out to explore a number of In$_2$S$_3$-based composite materials so as to improve its photocatalytic performance, such as In$_2$S$_3$/UiO-66 (ISU) hybrids [15], ZnS@In$_2$S$_3$ core@shell composite [16], CQDs/In$_2$S$_3$ microspheres [17], In$_2$S$_3$/carbon nanofibers/Au composite [18], and so on. As can be seen clearly from the above, In$_2$S$_3$-based composite photocatalysts significantly enhanced photocatalytic activity of body photocatalyst during photochemical reaction by visible light irradiation. Despite its great potential, the fine sized nanomaterials are often limited for practical applications, because it is unfavorable for separating and recycling little particles suspended in liquid phase. Hence, it is desirable to construct innovative In$_2$S$_3$-based nanomaterial with both outstanding photocatalytic activity and prominent separable characteristics under visible light.

So far, magnetic materials, as a kind of representative substrate, have attracted considerable concern because they can be quickly separated from the suspensions only via an external magnetic field [19–21]. Notably,
magnetic complex oxides zinc ferrite (ZnFe$_2$O$_4$), with an energy band gap of about 1.9 eV, is of special interest due to its outstanding electromagnetic behavior, chemical and physical stability, as well as excellent optical characteristics [22–24]. Previously, several studies have showed that ZnFe$_2$O$_4$ can be combined with other materials to enhance photocatalytic activities [25–27]. Undoubtedly, various ZnFe$_2$O$_4$-based composites will be intriguing materials for the degradation of organic pollutants in the practical usage stemming from their magnetic and separable properties. In view of these considerations, it is attractive to attempt the combination of In$_2$S$_3$ and ZnFe$_2$O$_4$ to acquire recyclable visible-light photocatalyst. As reported, In$_2$S$_3$ and ZnFe$_2$O$_4$ have matched energy band structure, further speculating the combination of In$_2$S$_3$ and ZnFe$_2$O$_4$ could expand the spectral responsive range and improve the photocatalytic activity of each individual respectively. Specifically, the valence band (VB) of In$_2$S$_3$ is positioned between the VB and conduction band (CB) of ZnFe$_2$O$_4$ and the CB of In$_2$S$_3$ is positioned above the VB and CB of ZnFe$_2$O$_4$ [11, 28]. Accordingly, integrating In$_2$S$_3$ with ZnFe$_2$O$_4$ could be beneficial to the separation of photogenerated charge carriers owing to proper band structure, which shows great potential to be developed into a highly efficient photocatalytic system.

In this contribution, a successful attempt has been carried out to fabricate magnetically separable In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites, with ZnFe$_2$O$_4$ as a support medium and tunable In$_2$S$_3$ loading amount in In$_2$S$_3$/ZnFe$_2$O$_4$ via a two-step solvothermal process. The photocatalytic activities of the as-prepared materials were evaluated by the degradation of MB solution driven by visible light. To the best of our knowledge, there are few reports in the literature about the synthesis of In$_2$S$_3$/ZnFe$_2$O$_4$ composite photocatalyst for degradation of organic pollutant under visible light. It can be distinctly found that the as-prepared In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites had dramatically enhanced photocatalytic activity as compared to pure In$_2$S$_3$ and ZnFe$_2$O$_4$ for the degradation of MB. The improved photocatalytic activity might be due to the intimate interfacial contact between In$_2$S$_3$ and ZnFe$_2$O$_4$ together with the suitable band gap structure of In$_2$S$_3$/ZnFe$_2$O$_4$, which could effectively enhance visible light absorption and accelerate the charge separation and transfer. More importantly, In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites can be easily separated from a liquid phase suspension system for recycling by virtue of an external magnetic field. The photocatalytic degradation of MB for five consecutive cycles indicated that In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites had good stability and recyclability, which was very beneficial for practical applications. In addition, a possible mechanism for the photodegradation process of MB by In$_2$S$_3$/ZnFe$_2$O$_4$ was probed and discussed. Without doubt, this work reveals the potential of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites for applications in environmental science field.

2. Experimental section

2.1. Fabrication of ZnFe$_2$O$_4$ nanopowder and In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites

All chemicals were of analytical grade and were not further purified. Deionized water was used in all experiments. ZnFe$_2$O$_4$ was prepared by a typical solvothermal method. 2 mmol of Fe(NO$_3$)$_3$·9H$_2$O was dispersed in 20 ml of ethanol with magnetic stirring and designated as solution I. 1 mmol of Zn(NO$_3$)$_2$·6H$_2$O was dispersed in 15 ml of ethanol with stirring and marked as solution II. 0.5 mmol of NaOH was dissolved in 15 ml of ethanol and labeled as solution III. Afterwards, 0.25 mmol of CTAB was slowly added to the solution II, and then the solution I was slowly added dropwise to the above solution, finally the solution III was added dropwise. The above mixed solution was poured into a Teflon-lined stainless steel autoclave and the temperature was kept at 180 °C for 10 h, naturally cooled to room temperature. Next, it was washed three times with deionized water and absolute ethanol, respectively. The obtained ZnFe$_2$O$_4$ sample was centrifuged and dried.

In a typical procedure, 1 mmol of the prepared ZnFe$_2$O$_4$ sample was dissolved in 40 ml of deionized water, and a homogeneous solution was formed after 60 min of sonication. Then, a certain amount of In(NO$_3$)$_2$·4.5H$_2$O was magnetically stirred in the ZnFe$_2$O$_4$ solution after being poured into the ultrasonic wave, and then a corresponding amount of C$_3$H$_7$O$_2$NS was added to the above solution and stirring was continued for 60 min. The mixed suspension was poured into a Teflon-lined stainless steel reaction vessel and maintained at 120 °C for 12 h, then naturally cooled to room temperature. Finally, the product was collected by centrifugation, then washed several times with absolute ethanol and deionized water, and dried. In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites with different loading amount of In$_2$S$_3$ were obtained by adjusting the amount of indium and sulfur sources. The molar ratios of In and Fe in In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites were 3:25, 3:10, and 9:20, which were labeled as InF1, InF2, and InF3, respectively.

2.2. Characterization

The crystal structure and phase of the samples x-ray diffraction (XRD) were analyzed using the D8 ADVANCE wide-angle x-ray diffractometer from BRUKER ag, Germany, at room temperature with the copper K radiation (lambda = 1.5406 nm, 40 kV, 30 mA) with a scanning range of 10°–70°. The morphology and composition of the samples were observed using a field emission scanning electron microscope (FE-SEM, JSM-7610F) and an
energy dispersive x-ray analysis system (EDS, Oxford EDS). The surface distribution of the samples were
analyzed by transmission electron microscopy (TEM; Hitachi 600) and high-resolution transmission electron
microscopy (HRTEM). The chemical states of the elements in the samples were determined by x-ray
photoelectron spectroscopy (XPS) in a Perkin-Elmer PHI 5000 Versaprobe system with Al KI radiation of
300 W. The ultraviolet-visible absorption spectrum of the samples were measured by an ultraviolet-visible
spectrophotometer (UV-2450, Shimadzu Corporation, Japan), and the scanning range was 200 to 800 nm.
Fourier transform infrared (FT-IR) spectroscopy was performed on a Thermo Scientific Nicolet is 50 FT-IR
spectrophotometer equipped with a DTGS KBr detector and a KBr beam splitter in transmission mode. The
photoluminescence (PL) properties of the samples were measured by 325 nm light excitation at room
temperature using a HR-800 LabRam confocal Raman microscope (JY Company). The magnetic property of
the sample was measured in the range of ±50000 Oe on a vibration sample magnetometer.

2.3. Photocatalytic test
The photocatalytic performance of the as-obtained photocatalysts was evaluated at ambient temperature
through degrading MB aqueous solution under visible light. The experiments were performed in a photoreactor
with a 350 W high-pressure xenon lamp with a UV cutoff filter (λ ≥ 420 nm) as visible light source. For each
photocatalytic measurement, the suspension including the photocatalyst (0.050 g) and MB solution (50 ml,
10 mg l−1) was laid in a 60 ml of test tube. Prior to light irradiation, the test tube containing the suspension
solution was kept stirring in dark for 30 min to attain an adsorption-desorption equilibrium for MB. Next, the
above solution was illuminated by the xenon lamp equipped with a water circulation facility. During the
photocatalytic process, 4 ml of suspension was withdrawn at different time intervals, followed by centrifugation
for 10 min in a high speed centrifuge to remove photocatalyst. Then the supernatant was measured by MB
absorbance at 664 nm with a dual-beam TU-1901 ultraviolet-visible spectrophotometer. In final, the
degradation efficiency of MB was calculated by the formula: D % = (C0 − Ct)/C0 × 100%, where C0 was the
initial concentration of MB, and C was the concentration of MB at irradiation time t.

3. Results and discussion

Figure 1. XRD patterns of samples, (a) pure In2S3, (b) pure ZnFe2O4, (c) InF1, (d) InF2 and (e) InF3 nanocomposites.

The crystallinity and structure of pure In2S3, pure ZnFe2O4 and In2S3/ZnFe2O4 nanocomposites with different
proportions of In and Fe were determined by x-ray power diffraction (XRD) analysis (figure 1). As depicted from
figure 1(a), pure In2S3 shows indexed diffraction peaks at 14.2°, 23.2°, 27.4°, 32.3°, 43.6°, 44.7°, 48.1°, 56.6°,
66.3° are distinctly assigned to (111), (220), (311), (400), (511), (440), (622), (731) crystal planes of the
cubic β-In2S3 (JCPDS No.65–0459) [9, 29]. The diffraction peaks of pure ZnFe2O4 located at 2θ = 18.2°, 29.9°,
35.1°, 36.7°, 42.7°, 53.1°, 56.8° and 61.1° can be indexed to (111), (220), (311), (222), (400), (422), (511)
and (440) crystal planes (shown in figure 1(b)), which are coincident with the cubic spinel structure of ZnFe2O4
(JCPDS No. 22–1012) [26, 27]. As for In2S3/ZnFe2O4 nanocomposites, there are both ZnFe2O4 and In2S3 phases
to be observed (displayed in figures 1(c)–(e)). Doubtlessly, the strong diffraction peaks shown in XRD patterns
demonstrate that the as-prepared nanocomposites are well crystallized and the crystal structure is very perfect.
Moreover, apart from ZnFe$_2$O$_4$ and In$_2$S$_3$ phases, there are no other phases to be found in nanocomposites, illustrating the purity of the as-prepared nanocomposites. Hence, it can be concluded that In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites are successfully achieved via solvothermal route.

The morphologies and chemical composition of the obtained samples were investigated by scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analyses, as shown in figure 2. Clearly, figure 2(A) depicts the typical SEM micrograph of pure In$_2$S$_3$, which is composed of a large quantity of small nanoparticles stacked together and the size is in the range of 30–80 nm. Figure 2(B) displays the morphology of pristine ZnFe$_2$O$_4$ sample and is stacked and irregular nanostructures, which size is varied from tens to hundreds of nanometers. Figure 2(C) describes the SEM image of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites (InF2), it can be clearly observed that the introduction of In$_2$S$_3$ into ZnFe$_2$O$_4$ substrate does not change the morphology of pristine ZnFe$_2$O$_4$. The surface morphologies of InF1 and InF3 were similar to that of InF2 and their SEM images were displayed in figure S1 is available online at stacks.iop.org/MRX/7/015080/mmedia. Moreover, the chemical composition of the as-fabricated In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites was further determined by energy dispersive x-ray (EDX) measurement as described in figure 2(D). It can be expressly observed that In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites consist of Zn, Fe, O, In and S elements. Obviously, SEM-EDX elemental mapping of InF2 (figure 2(E)) reveals that the Fe, O, Zn, In, S elements are distributed in the same way and have the same shape as well as locations in the surface of sample, certifying the coexistence of In$_2$S$_3$ and ZnFe$_2$O$_4$ in In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites.

The microstructure of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites (InF2) was further manifested with transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). The TEM image of InF2 (figure 2(F)) demonstrates that many irregular shape particles aggregate into greater particles, so as to facilitate the formation of heterojunction structure between In$_2$S$_3$ and ZnFe$_2$O$_4$. It is worth noting that the junction in the HRTEM image of InF2 expresses two types of clear lattice fringes as depicted in figure 2(G), respectively. One set of the clear fringes with lattice spacing is ca. 0.378 nm, agreeing well with the (2 2 0) plane of cubic phase of In$_2$S$_3$. Another set of the lattice fringe separation is ca. 0.252 nm, which can be indexed to the (3 1 1) plane of cubic spinel structure of ZnFe$_2$O$_4$. Thereby, it confirms the phase formation of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites and the intimate interfacial contact between In$_2$S$_3$ and ZnFe$_2$O$_4$, which would be beneficial for the separation of photoexcited charge carriers, thus contributing to the photocatalytic activity enhancement. In addition, the presence of the diffraction rings in the selected-area electron diffraction (SAED) pattern (inset of figure 2(F)) illuminates that In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites possesses a polycrystalline structure, which is in agreement with the aforementioned XRD analysis.

The surface composition and chemical state of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites (InF2) were further analyzed by x-ray photoelectron spectroscopy (XPS), as displayed in figure 3. The fully scanned spectrum of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites (figure 3(A)) indicates that there are no signals of photoelectron peaks of other elements except Zn, Fe, In, S and O [16]. Figure 3(B) describes the high resolution XPS spectrum of Fe 2p. Using the XPS Peak fitting program, the Fe 2p XPS region is fitted to two main peaks at 726.5 and 711.1 eV [30, 31], which are attributed to Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$ of Fe$^{3+}$ in nanocomposites, respectively. As seen from figure 3(C), the peaks at 1044.2 and 1020.9 eV could be assigned to Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$, respectively, indicating a normal state of Zn$^{2+}$ [23]. In case of the XPS spectrum of O1s (figure 3(D)), it could be divided into two peaks at 531.4 eV and 529.9 eV, corresponding to the adsorbed oxygen species on the surface and the lattice oxygen in ZnFe$_2$O$_4$ [31, 32], respectively. As shown in figure 3(E), the S 2p region is decomposed into two peaks at 161.45 and 162.7 eV belonging to S 2p$_{1/2}$ and S 2p$_{3/2}$, indicating the presence of S$^{2-}$ valence state [11]. As for the In 3d spectrum displayed in figure 3(F), there are two peaks at binding energies of 444.7 and 452.3 eV, which could be assigned to In 3d$_{5/2}$ and In 3d$_{3/2}$ of In$^{3+}$ [14], respectively. In short, XPS results is in good consistent with those of XRD, SEM, EDX, elemental mapping and HR-TEM analysis, unambiguously proving the formation of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites.

The photoabsorption properties of the resultant samples were measured by UV–vis diffuse reflectance spectroscopy (UV–vis DRS). It can be distinctly found from figure 4 that these samples display strong absorption from the UV light to visible light range, which is conducive to photocatalytic performance. Specifically, pure In$_2$S$_3$ displays a broad essential absorption edge at around 630 nm [11], whereas pure ZnFe$_2$O$_4$ exhibits an intense absorption band with a steep edge at ca. 690 nm [31], indicating that both In$_2$S$_3$ and ZnFe$_2$O$_4$ can absorb visible light effectively. Evidently, In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites show strong light-absorbing ability nearly in the entire visible light region, which may be attributed to the interaction and synergetic effect between ZnFe$_2$O$_4$ and In$_2$S$_3$ in the composite system, manifesting the possibility of photocatalytic activity for them under visible light [33]. Additionally, it is known that the band gap energy (Eg) of a crystalline semiconductor follows next formula:

\[
\alpha h\nu = A(h\nu-E_g)^{n/2}
\]
where $a$, $h\nu$, $E_g$, and $A$ are the absorption coefficient, discrete photon energy, band gap energy, and a constant, respectively. In addition, the value of $n$ depends on the nature of the optical transition of semiconductor ($n = 1$ for direct transition, $n = 4$ for indirect transition) [34]. According to the literatures, the $n$ value is 1 for ZnFe$_2$O$_4$, and the $n$ value is 4 for In$_2$S$_3$. Accordingly, by applying above equation, the $E_g$ for pure ZnFe$_2$O$_4$, pure In$_2$S$_3$, InF1, InF2 and InF3 nanocomposites in this work are estimated to be about 1.87, 1.81, 1.74, 1.64, and 1.68 eV.

**Figure 2.** SEM images of (A) pure In$_2$S$_3$, (B) pure ZnFe$_2$O$_4$, (C) InF2, (D) EDX spectrum of InF2, (E) element mapping images of InF2 obtained by EDX, (F) TEM image and (G) High-resolution TEM image of InF2. The inset of figure 2(F) is the corresponding SAED pattern of InF2.
respectively. Obviously, In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites have enhanced visible light absorption, which are beneficial to photocatalytic performance.

The FTIR spectra of the as-prepared samples were depicted in figure S2. From the typical FTIR spectrum of ZnFe$_2$O$_4$, the peak at 572 cm$^{-1}$ represents a characteristic absorption of Fe–O tensile vibration. The metal-oxygen stretching frequency of (Zn–O and Zn–O–Fe) is in the range of 700–850 cm$^{-1}$, which is related to the vibration of Zn–O and Zn–O–Fe bond. Moreover, the absorption bands between 3000 and 1631 cm$^{-1}$ is caused by water molecules adsorbed on the sample surface [35, 36]. In addition, an absorption band at 1399 cm$^{-1}$ can prove the presence of nitrate groups, which was from metal nitrates for the preparation of ZnFe$_2$O$_4$ [37]. It can be seen from the FTIR spectrum of In$_2$S$_3$, there are significant absorption bands focused on about 1373 and 1610 cm$^{-1}$ as well as weak absorption peak at 620 cm$^{-1}$, which could be attributed to In–S vibration modes [17]. As for In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites, the characteristic absorption peaks related to ZnFe$_2$O$_4$ and In$_2$S$_3$ can be observed from figure S1. Besides, the absorption peak at 1434 cm$^{-1}$ could be attributed to S–O vibration in FTIR spectra of nanocomposites [38], indicating that there are certain chemical bonding between In$_2$S$_3$ and ZnFe$_2$O$_4$ component.

Photoluminescence (PL) emission spectrum is commonly used to detect the recombination of excited charge carriers on a semiconductor. It is known that a weaker PL signal presents a higher separation probability.
of photogenerated electron-hole pairs, meaning the lower recombination rate of the charge carriers, so as to cause the higher photocatalytic efficiency [26, 28]. Figure 5 presented the PL spectra of pure ZnFe$_2$O$_4$, pure In$_2$S$_3$, and In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites, which were measured with an excitation wavelength of 325 nm at room temperature. Obviously, the PL intensity of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites is much lower than that of pure ZnFe$_2$O$_4$ and In$_2$S$_3$, revealing that photoinduced electron-hole pairs could be efficiently separated in In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites in comparison with that of pure ZnFe$_2$O$_4$ and In$_2$S$_3$ due to their matching band potentials. Additionally, the PL intensity of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites first decreases with the increase of In$_2$S$_3$ content, and then increase with the increase of In$_2$S$_3$ content. The reasons could be due to that proper In$_2$S$_3$ content can act as an electron acceptor, preventing a direct recombination of electrons and holes, and excessive In$_2$S$_3$ content promote the recombination of photogenerated electrons and holes, and thereby leading to the enhanced PL intensity. It can be found that InF2 exhibits the lowest PL intensity, indicating that it possesses most efficient charge separation and the highest photocatalytic activity.

To investigate the photocatalytic activity of the obtained photocatalysts, the photocatalytic degradations of MB aqueous solution were performed under visible light. The experiments were carried out in triplicate and taken the averages or repeat values. Figure 6(A) describes that the photodegradation efficiency of pure ZnFe$_2$O$_4$, pure In$_2$S$_3$, and In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites based on C/C$_0$ as a function of reaction time. As recorded in curve a in figure 6(A), there is rarely any decomposition of MB after 180 min irradiation in the absence of sample, illustrating that the photoinduced self-decomposition of MB can be negligible. For pure In$_2$S$_3$ and
ZnFe$_2$O$_4$ (shown in curve b and c), a little photodegradation of MB can be found within 180 min. Namely, only $\sim$35.3% and 22.7% of MB can be decomposed for individual In$_2$S$_3$ and ZnFe$_2$O$_4$ after 180 min irradiation, respectively. So, it can be concluded that both pure In$_2$S$_3$ and ZnFe$_2$O$_4$ show a weak degradation capability under visible light, on account of the fast recombination of photo excited electron-hole pairs in the individual component. It is very encouraging to see that all of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites with different content of In$_2$S$_3$ display much higher photocatalytic efficiency as compared to that of the individual In$_2$S$_3$ and ZnFe$_2$O$_4$ (presented in curves d-f of figure 6(A)). One possible reason could be primarily due to the synergistic effects between In$_2$S$_3$ and ZnFe$_2$O$_4$, which are responsible for enhancing visible light absorption and accelerating interfacial charge transfer and separate between. Above all, it is distinctly observed that the photocatalytic degradation rate of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites increase primarily along with increasing the proportion of In and Fe, afterwards decrease when the proportion of In and Fe is more than 3:10. Appreciably, the photocatalytic activity of InF$_2$ sample is best one among all the samples and the degradation rate of MB reaches 86.5% within 180 min, suggesting that appropriate loading content of In$_2$S$_3$ is beneficial for the improvement of the photocatalytic activity of In$_2$S$_3$/ZnFe$_2$O$_4$. Figure 6(B) is the time-dependent absorption spectra of MB solution in the presence of InF$_2$ nanocomposites. As can be seen, the main absorption peak of MB molecule is located at 664 nm. The absorption peak decreases gradually with increasing the illumination time, and the peak almost disappears at about 180 min, meaning that InF$_2$ possesses excellent photocatalytic performance on the photodegradation of MB under visible light illumination, which is superior to related reports [14, 39]. Further tests indicate that the as-prepared nanocomposites can also work for other organic pollutants such as phenol driven by visible light. As displayed in figure S3, In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites show the enhanced photocatalytic activity in compare with pure ZnFe$_2$O$_4$ and pure In$_2$S$_3$ for the elimination of phenol in experiment duration under the identical conditions, and InF$_2$ displays the highest photocatalytic activity. The above results are the same as that of the degradation of MB.

Generally, the separation, reusability and stability of photocatalyst are also important parameters for evaluation its possible application. In this work, vibrating sample magnetometer (VSM) was utilized to measure the magnetically separable property of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites, and the (s-shaped) magnetization hysteresis loop of In$_2$S$_3$/ZnFe$_2$O$_4$ is displayed in figure 7(A). It can be shown that In$_2$S$_3$/ZnFe$_2$O$_4$ sample (InF$_2$) is a magnetic material with a saturation magnetization (Ms) of 12.05 emu g$^{-1}$. Meanwhile, the residual magnetization (Mr) and coercivity (Hc) values of In$_2$S$_3$/ZnFe$_2$O$_4$ sample is almost insignificant, so it can be concluded that In$_2$S$_3$/ZnFe$_2$O$_4$ possess weak superparamagnetic characteristics [22, 24, 40]. As shown in the illustration of the inset in figure 7(A), by the action of an external magnetic field, InF$_2$ can be rapidly separated from the suspension due to its magnetic characteristics, then the reaction solution of MB becomes clear and transparent. This demonstrates that In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites can be easily collected for recycling through magnetic separation. Furthermore, cycling tests for the degradation of MB solution under visible light were performed to evaluate the stability of In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites. After five consecutive photodegradation runs, InF$_2$ only exhibits a small loss of the degradation efficiency (figure 7(B)), indicating that the reused In$_2$S$_3$/ZnFe$_2$O$_4$ nanocomposites have good stability for the photocatalytic degradation of organic pollutant.
It is well known that the active species such as the free radicals and holes generated by photocatalysts played an important role in the photocatalytic process [33]. Herein, to ascertain the contributions of these active species, the quenching experiments to MB degradation by InF2 under visible light were put into effect and recorded in figure S4. Three different quenchers, p-benzoquinone (BQ), Triethanolamine (TEOA) and Tert-butyl alcohol (TBA) were used for capturing superoxide radical (·O2−), holes (h+), and hydroxyl radicals (·OH) in photocatalytic process, respectively. The quenching experiments manifest that the active species ·O2− and h+ play dominant roles in MB degradation, while ·OH is a relatively minor factor. As it were, ·O2−, h+ and ·OH all contribute to the photocatalytic reaction over In2S3/ZnFe2O4 nanocomposites under visible light.

On the basis of the UV–vis DRS experiment results and related [33, 41, 42], we proposed a possible mechanism of In2S3/ZnFe2O4 nanocomposites for photocatalytic degradation of MB, which is elucidated in figure 8. Under visible-light irradiation, both In2S3 and ZnFe2O4 in In2S3/ZnFe2O4 system could be inspired, electrons of In2S3 and ZnFe2O4 are easily transfered from their VB to CB, respectively. Under the effect of inner electric field, due to both the CB and VB potential of In2S3 is more negative than that of ZnFe2O4, the photoinduced e− on the CB of In2S3 would shift to the CB of ZnFe2O4, while the photogenerated h+ on the VB of ZnFe2O4 would shift to the VB of In2S3, and thus gives rise to the effective separation of photoinduced e− and h+. As a result, the electrons accumulated on the CB of ZnFe2O4 could reduce O2 molecules adsorbed on the surface of photocatalyst to produce ·O2− active free radicals, which is attributed to that the CB potential of ZnFe2O4 (−0.40 eV versus NHE) is lower than the standard redox potential of O2/·O2− (+0.13 eV versus NHE) [28]. Further, some ·O2− could react with H2O molecules to form ·OH group. Both O2− and ·OH are active species with strong oxidizing property, which are then involved in the photodegradation of MB. However, the VB potential of In2S3 (+1.15 eV versus NHE) is lower than the potential of OH−/·OH (+2.27 eV versus NHE) [24, 33], so the holes on the VB cannot react with H2O to yield ·OH. As result, the holes accumulated on the VB of In2S3 could diffuse to the surface of photocatalyst and oxidize the absorbed MB molecules directly. In short, these three active species including ·O2−, h+ and ·OH contribute to the superior photodegradation performance of MB over In2S3/ZnFe2O4 nanocomposites.

4. Conclusion

In summary, magnetic In2S3/ZnFe2O4 nanocomposites have been fabricated by utilizing a facile two-step solvothermal method. It was found that the photocatalytic performance of In2S3/ZnFe2O4 nanocomposites could be tuned easily by varying the In2S3 loading amount in nanocomposites. What’s more, in comparison to pure In2S3 and ZnFe2O4 nanosized powder, all In2S3/ZnFe2O4 nanocomposites have manifested superior photocatalytic performance for the decomposition of MB solution under visible light illumination. The above results may be mainly attributed to the improved visible light absorbance and higher separation efficiency of the photogenerated electron-hole pairs, namely, the synergy effect between In2S3 and ZnFe2O4. Obviously, the as-prepared nanocomposites could be conveniently separated and recycled in virtue of an external magnet, also showed stable and recyclable after five successive cycle usage. Finally, a possible mechanism for the photocatalytic decomposition of MB by In2S3/ZnFe2O4 nanocomposites was also proposed. This study implies that the obtained nanocomposites can be an ideal candidate for the application in the water purification.
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Associated content

Supplementary data associated with this article can be found in the online version.

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