Materials Research Express

PAPER

In$_2$O$_3$ microspheres decorated with ZnIn$_2$S$_4$ nanosheets as core-shell hybrids for boosting visible-light photodegradation of organic dyes

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Keywords: In$_2$O$_3$, microspheres, ZnIn$_2$S$_4$ nanosheets, visible light response, photocatalysis, MB degradation

Supplementary material for this article is available online

Abstract

In this work, we firstly report the development of ZnIn$_2$S$_4$ nanosheets decorating In$_2$O$_3$ microspheres with core–shell structure by an in situ synthetic process, which is proved to be an effective method to construct promising semiconductor photocatalysts for photodegradation of methyl blue (MB) under visible–light conditions. Under visible–light illumination, the 2D/3D ZnIn$_2$S$_4$ nanosheet/In$_2$O$_3$ microsphere hybrids exhibit excellent enhancing photocactivity than that of pristine In$_2$O$_3$. The effect of ZnIn$_2$S$_4$ substitution on photoactivity was also investigated for comparative experiments and it was found that the optimized ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 hybrid exhibits the highest photocactivity of 84.5%. The experimental results indicated that the reputedly photocatalytic performance of ZnIn$_2$S$_4$/In$_2$O$_3$ can be attributed to the synergistic effect of efficient separation of photo-generated electron-hole pairs, extended visible–light response range, and the improved specific surface area. Furthermore, the roles of O$_2^-$, OH, and h$^+$ during the photodegradation process were studied to deduce the possible degradation mechanism. This work provides an effective strategy to construct the In$_2$O$_3$-based photocatalytic systems for efficient photodegradation of organic pollutants, which would be significant for the design of more In$_2$O$_3$-based systems for promising photocatalytic applications.

1. Introduction

As one of the most widely investigated organic dyes in photocatalytic areas, methyl blue (MB) is considered as refractory organic pollution due to its high toxicity and easy accumulation in the water environment [1, 2]. Till now, various semiconductors such as non-metallic carbon materials, metal oxides, and suitable composites have been reported as efficient photocatalysts for the photodegradation of MB due to their unique properties [3–5]. Among the various semiconductors, Indium oxide (In$_2$O$_3$) possesses outstanding conductivity and thermodynamic stability, which stands out as having been universally utilized in photodegradation of organic pollutants, CO$_2$ photoreduction, and hydrogen production [6–8]. However, the relatively wide bandgap (ca. 2.8 eV) and low separation/migration rate of photo-induced charge carriers of single-phase In$_2$O$_3$ markedly impede its application as a photocatalyst [9]. Therefore, the development of highly efficient In$_2$O$_3$-based photocatalysts with low bandgap and accelerated light-induced charge separation/transfer potency is of great importance.

Nowadays, the typical pathways for adjusting the separation and migration rate of photo-induced charge carriers as well as enhancing the Sunlight absorption range are delicately constructing In$_2$O$_3$-based heterojunction at the interface with other narrow bandgap semiconductors [10–12]. Among the suitable
semiconductors, ZnIn$_2$S$_4$, a widely researched ternary chalcogenides catalyst, is regarded as a promising candidate due to its narrow band gaps (ca. 2.3 eV) and well-matched band edges with In$_2$O$_3$, and the ZnIn$_2$S$_4$/In$_2$O$_3$ hybrids are indeed confirmed to exhibit enhanced photocatalytic performance than In$_2$O$_3$ in previous reports [9]. Besides, morphological control is considered as another avenue to remarkably improve the photocatalytic performance [13]. For instance, Zhu et al successfully prepared 2D/3D ZnIn$_2$S$_4$ nanosheet/In$_2$O$_3$ nanocube for photocatalytic oxidation of 2,4-dichlorophenol with remarkably enhanced photocatalytic activity than 0D/3D ZnIn$_2$S$_4$/In$_2$O$_3$ nanocube nanoparticle [9]. However, the 2D/3D ZnIn$_2$S$_4$ nanosheet/In$_2$O$_3$ microsphere has not been utilized as photocatalytic materials for exploring the possible photodegradation activity.

To date, materials with microsphere structure have stimulated wide research interest due to their potential applications in the field of photocatalysis [14], dye-sensitized solar cells [15], sensor systems [16], and so on, previous studies have proved photocatalysts with a microsphere structure has a fast separation rate and prolonged lifetime of photogenerated charge carriers, thus better photocatalytic performance is achieved [17]. Recently, Liang et al reported CuWO$_4$ hollow microsphere displayed superior performance in visible-light photodegradation of methylene blue than commercial P25 [18]. Xu et al composed In$_2$O$_3$/In$_2$S$_3$ microsphere heterostructure, which exhibited excellent and stable efficiency photocatalytic nitrogen fixation under mild conditions [19]. Yuan et al recently showed that the performance of photocatalytic degradation of antibiotic pollutants can be promoted enormously by constructing a 3D In$_2$S$_3$/InVO$_4$ microsphere heterostructure [20]. Therefore, ideally for high-performance photocatalysts, materials with microsphere structure are of great significance.

In this contribution, we report a facile method to synthesize 2D/3D ZnIn$_2$S$_4$/In$_2$O$_3$ photocatalysts based on In$_2$O$_3$ microspheres supported ZnIn$_2$S$_4$ nanosheets, in which In$_2$O$_3$ microspheres was implanted as the inner shell and ZnIn$_2$S$_4$ nanosheets as the outer shell. In$_2$O$_3$ microspheres were firstly prepared by a template-free hydrothermal method with subsequent calcination of In(OH)$_3$ precursors, and then the ZnIn$_2$S$_4$ flower slices were equably generated on the surfaces of In$_2$O$_3$ microspheres via an in situ synthesis process after oil-bath heating. Results show that as-prepared 2D/3D ZnIn$_2$S$_4$/In$_2$O$_3$ hybrids exhibit remarkably enhanced photocatalytic activities for the degradation of MB in water under visible light as compared to pure ZnIn$_2$S$_4$ nanosheets and In$_2$O$_3$ microspheres. The enhanced photocatalytic activity is confirmed by a series of technical methods. Additionally, the cycle experiments were performed to detect the stability of photocatalyst, and the potential photodegradation mechanism was also discussed in detail.

2. Experimental details

2.1. Materials

Anhydrous indium chloride (InCl$_3$, 98.0%) and sodium oleate (C$_{18}$H$_{33}$NaO$_2$, 98.0%) were purchased from Shanghai Macklin Biochemical Co., Ltd Hydrochloric acid (HCl, 97.0%) and absolute ethanol (EtOH, 99.7%) were supplied by Xilong Scientific Co., Ltd Zinc chloride (ZnCl$_2$, 99.0%) and Thioacetamide (TAA, CH$_3$CSNH$_2$, 99.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd All the above-mentioned materials were used without further treatment, and the deionized water (18.2 MΩ·cm) used in the course of the experiment was obtained from a Millipore system.

2.2. Sample preparation

2.2.1. Synthesis of 3D In(OH)$_3$ microspheres

3D In(OH)$_3$ microspheres were initially prepared according to the reported method with a slight modification [21]. In a typical process, 2.055 g C$_{18}$H$_{33}$NaO$_2$ was dissolved in 100 ml EtOH by ultrasonication for 20 min with creating a surface active and alkaline environment. Thereafter, 0.655 g InCl$_3$ was added into the above solution followed by another 30 min ultrasonication. Then the mixture was transferred to a 150 ml Teflon-lined autoclave, and heated at 150 °C for 3 h. After cooling down naturally, the white In(OH)$_3$ (precursor) was retrieved by centrifugation, washed repeatedly with deionized water and EtOH, and then dried under vacuum at 60 °C overnight.

2.2.2. Synthesis of 3D In$_2$O$_3$ microspheres

In the process, In$_2$O$_3$ microspheres were subsequently synthesized from the as-prepared precursor by calcination at 400 °C for 3 h in the air [22]. Afterward, the obtained powder was collected for the following synthesis of the heterojunction.
2.2.3. Synthesis of 2D/3D ZnIn₂S₄ nanosheets/In₂O₃ microspheres

2D/3D ZnIn₂S₄ nanosheets/In₂O₃ microspheres hybrids were prepared by the in situ synthesis method according to [13]. In a typical experiment, 0.075 g In₂O₃ was dispersed in 10 ml deionized water (pH = 2.5) by ultrasonication, and then 0.275 g ZnCl₂, 0.442 g InCl₃, and 0.300 g TAA were dissolved into the above solution in turn and stirred for 30 min. Subsequently, the above mixture was continually stirred and heated in an oil bath at 80 °C for 2 h. Eventually, the resultant hybrid was collected by centrifugation and washed three times with water and ethanol, respectively, and dried under vacuum at 60 °C overnight, the obtained powder was denoted as ZnIn₂S₄/In₂O₃-1:1. The other hybrids with different mass ratios of ZnIn₂S₄ were also prepared and denoted as ZnIn₂S₄/In₂O₃-2:1 and ZnIn₂S₄/In₂O₃-1:3, respectively. The above-mentioned formation procedure of ZnIn₂S₄/In₂O₃ core–shell hybrids is illustrated in figure 1. For comparison, the ZnIn₂S₄ nanosheets were also prepared using the same procedure, but without adding In₂O₃ microspheres.

2.3. Material Characterization

X-ray diffraction (XRD) patterns were acquired on a Shimadzu XRD-6100 diffractometer. Scanning electron microscope (SEM) images and energy dispersive spectrometer (EDS) mapping were obtained using a Zeiss Sigma SEM. High-resolution transmission electron microscopy (HR-TEM) and TEM images were recorded on a JEOL JEM-2100F instrument. X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific K-Alpha spectrometer. The Brunauer–Emmett–Teller (BET) specific surface areas were analyzed by N₂ adsorption-desorption isotherms measured on a Quantachrome instrument (Boynton Beach, FL 33426). UV–vis diffuse reflectance spectroscopy (UV–vis DRS) measurements were performed on a Perkin Elmer Lambda 750 spectrophotometer. Electrochemical impedance spectroscopy (EIS) and photocurrent measurements were carried out on Shanghai Chenhua CHI 660E electrochemical workstation. The concentration of residual MB solution was determined using a UV–vis PerkinElmer Lambda 35 spectrophotometer.

2.4. Evaluation of photoactivity

The photoactivity was assessed by the degradation of MB aqueous solution under visible light irradiation using a 500 W xenon lamp (Nanjing Xujiang Electromechanical Plant, China) with a 420 nm cutoff filter. Typically, each photocatalyst with an equal amount of 20 mg was added into a fresh MB solution (50 mg/l, 50 ml) using a specific quartz tube as a reactor. After establishing the adsorption-desorption equilibrium by magnetically stirring for 60 min in dark, the first sample (4 ml) was taken and filtrated, and then the concentration of MB was measured by UV–vis spectrophotometer, which was marked as C₀. After visible light irradiation (>420 nm), the specimens will be taken and filtrated for a given interval, the concentration of MB was measured and marked as Cₙ. During the measurement for the photostability of the optimized ZnIn₂S₄/In₂O₃ hybrid, the sample was washed and dried after every trial by centrifugation.

3. Results

3.1. Structure and morphology characterization

The phase composition and crystal structure of the as-prepared In₂O₃, ZnIn₂S₄, and several ZnIn₂S₄/In₂O₃ hybrids were firstly characterized by XRD. As shown in figure 2, the characteristic diffraction peaks of pristine In₂O₃ centered at 2θ = 21.5°, 30.5°, 35.3°, 37.5°, 41.9°, 45.8°, 51.2°, 55.7°, and 60.7° and are identical to (211), (222), (400), (411), (332), (431), (440), (611) and (622) crystal planes of bcc-In₂O₃ (JCPDS No. 06-0416) [23]. In the case of pure ZnIn₂S₄, five diffraction peaks located at 2θ = 21.8°, 27.6°, 47.2°, 52.2°, and 55.7° can be assigned to the (006), (102), (110), (116) and (022) crystal planes of hexagonal ZnIn₂S₄ (JCPDS No. 72-0773) [24]. Concerning ZnIn₂S₄/In₂O₃ hybrids, all the diffraction peaks can be completely ascribed to that of In₂O₃ and ZnIn₂S₄, and the characteristic peaks of ZnIn₂S₄ become stronger with the increasing amount of ZnIn₂S₄.
content, nevertheless, the diffraction peaks of In$_2$O$_3$ gradually become weakened. Besides, no other impurity phase is observed in the binary hybrids, indicating the successful construction of target hybrids.

For the sake of confirming the formation of ZnIn$_2$S$_4$ on the surface of the In$_2$O$_3$ microsphere and analyze the morphology of In$_2$O$_3$, ZnIn$_2$S$_4$, and ZnIn$_2$S$_4$/In$_2$O$_3$, SEM and TEM analyses were performed on as-obtained samples. As displayed in figure 3(a), the precursor In(OH)$_3$ exhibits the structure of microspherical morphology with a smooth surface and has an average diameter of 2 μm. After annealing, In$_2$O$_3$ maintains the original microspherical morphology of In(OH)$_3$ (figure 3(b) and S1 (available online at stacks.iop.org/MRX/8/025505/mmedia)). In the case of the pristine ZnIn$_2$S$_4$, it can be seen numerous self-assembled nanosheets to form flower-like ZnIn$_2$S$_4$ spheres in figures 3(c) and S2, which is consistent with the previous reports [8, 13]. When coupled In$_2$O$_3$ nanospheres with ZnIn$_2$S$_4$ nanosheets, we can see in figure 3(d) that ZnIn$_2$S$_4$ nanosheets homogeneously grow on the surface of In$_2$O$_3$ nanospheres to obtain a 2D/3D ‘face-to-face’ structure, which contributes to maximizing the virtues of the hybrid. Compared to pure In$_2$O$_3$, the surface of ZnIn$_2$S$_4$/In$_2$O$_3$ becomes rough and the approximate diameter of the hybrids is 3 μm. Notably, there is an obvious intimate interface formed between ZnIn$_2$S$_4$ and In$_2$O$_3$ (figure 3(e)), which would be beneficial to the separation of the photo-generated carriers. Moreover, HRTEM (figure 3(f)) and EDS analyses (figure S3) were further performed.

Figure 2. XRD patterns of pure In$_2$O$_3$, ZnIn$_2$S$_4$, and ZnIn$_2$S$_4$/In$_2$O$_3$ hybrids.

Figure 3. SEM images of (a) In(OH)$_3$, (b) In$_2$O$_3$, (c) ZnIn$_2$S$_4$, (d) ZnIn$_2$S$_4$/In$_2$O$_3$-1:1, (e) TEM image of ZnIn$_2$S$_4$/In$_2$O$_3$-1:1, (f) HRTEM image of ZnIn$_2$S$_4$/In$_2$O$_3$-1:1.
to determine the lattice fringes and elemental composition, the result confirms the co-existence of ZnIn$_2$S$_4$ and In$_2$O$_3$ in the hybrids, which is in accordance with the XRD results.

The information of the surface chemical states of all the elements in ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 was in-depth investigated by XPS characterization. The high-resolution spectrum of In 3d shows the two prominent peaks of In 3d$_{5/2}$ and In 3d$_{3/2}$ at 444.6 and 452.1 eV, separately, corresponded to In$^{3+}$ of In$_2$O$_3$ (figure 4(a)) [15]. The high-resolution spectrum of O 1s (figure 4(b)) splits into the two peaks at 529.5 and 531.4 eV, which can be attributed to the oxygen in In-O-In (O$_{\text{lattice}}$) and the oxygen defects in metal oxide support (O$_{\text{defect}}$), separately [25]. The Zn 2p XPS spectrum (figure 4(c)) exhibits two peaks of Zn 2p$_{3/2}$ (1021.7 eV) and Zn 2p$_{1/2}$ (1044.8 eV), consistent with the values of Zn$^{2+}$ in ZnIn$_2$S$_4$ [15]. As shown in figure 4(d), the curve of S 2p can be also decomposed into two peaks at the binding energies of 161.6 and 162.4 eV, corresponding to S$^{2-}$ in ZnIn$_2$S$_4$ [26]. Above all, the XPS results further prove that the chemical states of elements in the ZnIn$_2$S$_4$/In$_2$O$_3$ hybrids are In$^{3+}$, O$^{2-}$, Zn$^{2+}$, and S$^{2-}$.

3.2. Photoelectrochemical and Optical properties

The transient photocurrent responses were carried out for six on/off cycles to further investigate the separation and transport efficiency of photo-induced charge carriers under visible light irradiation. As disclosed in figure 5(a), the photocurrent-time curves exhibit that the monomer In$_2$O$_3$ possesses low photocurrent intensity owing to its intrinsic deficiency. In contrast, it can be observed that the surface modification of ZnIn$_2$S$_4$ significantly improves the photocurrent intensity of bare In$_2$O$_3$, suggesting the enhanced charge carriers separation and transport efficiency in the hybrid photocatalyst [27]. To further confirm the charge carrier separation and transport behavior, the EIS plots and PL spectra of bare In$_2$O$_3$ and ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 are also measured. As given in figure 5(b), ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 displays a smaller arc radius than pure In$_2$O$_3$, indicating a lower suppressed charge transfer and separation process than that of In$_2$O$_3$ [28]. Simultaneously, the result of PL spectra is consistent with the above-mentioned results, with lower PL intensity is observed for
ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 hybrid (figure 5(c)), indicating its high carriers separation efficiency. All the results unanimously clarify that the ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 hybrid exhibits better charge separation efficiency compared with monomer In$_2$O$_3$. Therefore, it is expected that the photocatalytic activities would be improved by constructing ZnIn$_2$S$_4$/In$_2$O$_3$ hybrids.

The optical absorption properties of ZnIn$_2$S$_4$, In$_2$O$_3$, and ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 were analyzed by UV–vis DRS. As displayed in figure 6(a), pure In$_2$O$_3$ mainly absorbs UV light with wavelengths below 400 nm, which makes an adverse influence on its visible-light photoactivity, in contrast, the pristine ZnIn$_2$S$_4$ possesses a wider visible-light response range with an absorption edge of 480 nm. The narrow bandgap of ZnIn$_2$S$_4$ nanosheets is responsible for the broadening response range of ZnIn$_2$S$_4$/In$_2$O$_3$ in the visible-light region. In consequence, this enhanced visible-light adsorption can produce more photoinduced electron–hole pairs in the ZnIn$_2$S$_4$/In$_2$O$_3$ hybrid, which is favourable for the enhancement of photocatalytic performance. Furthermore, the bandgap energies of the specimens can be estimated according to the Tauc plots [29]. As illustrated in figure 6(b), the band gaps of ZnIn$_2$S$_4$, In$_2$O$_3$, and ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 were recognized as 2.47, 2.80, and 2.58 eV, separately. Due to the homogeneous dispersion of ZnIn$_2$S$_4$ with a small bandgap, the bandgap of the synthesized hybrid became smaller than that of In$_2$O$_3$, which indicated that the target ZnIn$_2$S$_4$/In$_2$O$_3$ hybrids have been constructed successfully.

### 3.3. Photocatalytic efficiency

All the as-obtained specimens are subsequently evaluated for the photocatalytic activity towards MB under visible-light irradiation, and the results are illustrated in figure 7(a). It can be seen that the concentration of MB has hardly changed in the absence of any catalysts, which indicates that the self-degradation of MB can be neglected under visible-light irradiation. With regard to the individual In$_2$O$_3$, it can be observed that the concentration of MB diminished inconspicuously owing to the relatively wide bandgap of In$_2$O$_3$. Compared to In$_2$O$_3$, ZnIn$_2$S$_4$ exhibits relatively higher photocatalytic activity, which is assigned to its narrow band gaps. As expected, the study of the effect of ZnIn$_2$S$_4$ in ZnIn$_2$S$_4$/In$_2$O$_3$ hybrid shows that the ZnIn$_2$S$_4$/In$_2$O$_3$ display significantly enhanced photocatalytic activity, and the photocatalytic activity of the optimized sample ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 is improved to 84.5%, which is 11.4% higher than that of pristine ZnIn$_2$S$_4$ and almost 5 times higher than that of pristine In$_2$O$_3$, separately. The stability and reusability of ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 in the
photocatalytic process were further investigated as shown in figure 7(b), it can be seen that the degradation activity is no obvious changed after four cycles lasting for 16 h, indicating the ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 hybrid has an excellent photo-stability and lifetime for photodegradation of organic pollutant. Besides, the TEM image, XRD spectra, and EDS spectrum of ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 after the fourth run are further utilized to verify the phase stability (figures S4, S5, and S6). Comparing with these of ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 before the recycling experiment, it is observed that the morphology, crystalline phase, and structure of the hybrid remain unchanged after the recycling experiments, further demonstrating that the hybrid is quite stable during the photocatalytic process.

### 3.4. Photocatalytic performance enhancement mechanism

The photocurrent, EIS, and PL results have proved that constructing ZnIn$_2$S$_4$/In$_2$O$_3$ hybrids can promote effectively the transfer and separation of the photogenerated charges for producing more radical species, therefore, capture experiments were carried out to detect the exact roles of active species in the visible-light photocatalytic reaction by using several scavengers for analyzing the possible photodegradation mechanism in depth. Triethanolamine (TEOA, 1 mM), 1,4-benzoquinone (BQ, 1 mM) and tertiary alcohol (t-BuOH, 1 mM) are used as the hole (h$^+$), superoxide radical (·O$_2^-$) and hydroxyl radical (·OH) scavenger, separately. As shown in figure 8, compared with the photodegradation efficiency (84.5%) without any capture agents, once BQ or TEOA was added to the photoreaction system, an evident decline (59.1% for BQ or 35.9% for TEOA) is observed. However, the addition of t-BuOH displays only a slight inhibition in the photodegradation process (81.3%). The above results indicate that ·O$_2^-$ and h$^+$ radicals are the two main active substances in the photodegradation process, while ·OH radical is a minor active species.

**Figure 7.** Photocatalytic degradation curves of MB by as-synthesized photocatalysts (a); Recycling experiments of photocatalytic MB degradation over ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 (b).

**Figure 8.** The capture experiments of active species during the photodegradation of MB over ZnIn$_2$S$_4$/In$_2$O$_3$-1:1 in the presence of different scavengers.
On the basis of the above results, a possible mechanism is presented to explain the enhanced performance of the ZnIn$_2$S$_4$/In$_2$O$_3$ photocatalysts (figure 9) with the following equations:

\[
\text{In}_2\text{O}_3 \rightarrow \text{In}_2\text{O}_3(h^+ + e^-) \quad \text{ZnIn}_2\text{S}_4 \rightarrow \text{ZnIn}_2\text{S}_4(h^+ + e^-)
\]

\[
\text{In}_2\text{O}_3(h^+ + e^-) + \text{ZnIn}_2\text{S}_4(h^+ + e^-) \rightarrow \text{In}_2\text{O}_3(e_{\text{total}}^-) + \text{ZnIn}_2\text{S}_4(h_{\text{total}}^+)
\]

\[
\text{In}_2\text{O}_3(e_{\text{total}}^-) + \text{O}_2 \rightarrow \text{In}_2\text{O}_3 + \cdot\text{O}_2^-
\]

\[
\cdot\text{O}_2^- + \text{MB} \rightarrow \text{colorless products}
\]

\[
\text{ZnIn}_2\text{S}_4(h_{\text{total}}^+) + \text{MB} \rightarrow \text{colorless products}
\]

According to the above-mentioned UV–vis DRS analysis, the band gaps of pure ZnIn$_2$S$_4$ and In$_2$O$_3$ are 2.47 and 2.80 eV, separately, which indicates that In$_2$O$_3$ can only absorb a small amount of visible light to produce charge carriers, in contrast, ZnIn$_2$S$_4$ can easily capture photons and generate charge carriers under visible light irradiation (equation (1)). Since the energy levels of the conduction band (CB) and valence band (VB) of In$_2$O$_3$ are lower than those of ZnIn$_2$S$_4$ [30], the intimate contact between ZnIn$_2$S$_4$ and In$_2$O$_3$ allows the light-induced $e^-$ on the CB of ZnIn$_2$S$_4$ transfer easily to the CB of the In$_2$O$_3$, simultaneously, the photo-excited $h^+$ on the VB of In$_2$O$_3$ tend to migrate to the VB of ZnIn$_2$S$_4$ (equation (2)). Subsequently, $e^-$ stored in CB of In$_2$O$_3$ are able to react with molecular oxygen to form reactive ·O$_2^-$ radical (equation (3)), because the $e^-$ possess more negative potential than that of O$_2^-$ (-0.33 eV versus NHE), while the $h^+$ potential on the VB of ZnIn$_2$S$_4$ is not positive enough to convert OH$^-$ into ·OH radical (2.4 eV versus NHE) [31]. Finally, the ·O$_2^-$ and $h^+$ radicals are able to directly degrade MB due to their high oxidative capacity (equations (4) and (5)), and thus the enhancement of photoactivity can be attributed to the effective transfer and separation of carriers in ZnIn$_2$S$_4$/In$_2$O$_3$ hybrids.

4. Conclusions

In this contribution, a 2D/3D ZnIn$_2$S$_4$ nanosheet/In$_2$O$_3$ microsphere hybrid has been successfully fabricated by a simple three-step reaction process and applied to efficient visible-light photodegradation of MB. The ZnIn$_2$S$_4$ nanosheets are in situ assembled and uniformly generated on the surface of the In$_2$O$_3$ microsphere. Under visible-light irradiation, the photodegradation activity of the ZnIn$_2$S$_4$/In$_2$O$_3$ hybrid is significantly enhanced than these of pure In$_2$O$_3$ and ZnIn$_2$S$_4$. The enhanced photocatalytic performance is mainly attributed to the construction of hybrid, thus improving the separation and transfer of light-generated charge carriers and extending the visible-light response range. This work is expected to provide design ideas for constructing efficient 2D/3D In$_2$O$_3$-based photocatalysts for environmental restoration.
Acknowledgments

Financial supports from the National Natural Science Foundation of China (No. 41763020), the Natural Science Foundation of Jiangxi Province (Nos. 20202BAB214040, 20171BAB206008, 20202BAB213014), and the Foundation of Jiangxi Educational Commission (Nos. GJJ180596, GJJ190620) are gratefully acknowledged.

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