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Article

A novel step-scheme BiVO₄/Ag₃VO₄ photocatalyst for enhanced photocatalytic degradation activity under visible light irradiation

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ABSTRACT

Over the past few years, the emission of organic pollutants into the environment has increased tremendously. Therefore, various photocatalysts have been developed for the degradation of organic pollutants. In this study, a step-scheme BiVO₄/Ag₃VO₄ composite was synthesized via a hydrothermal and chemical deposition process for the degradation of methylene blue. The composite showed strong redox ability under visible light. The 40%BiVO₄/Ag₃VO₄ composite showed excellent photocatalytic degradation properties with a K_{app} of 0.05588 min⁻¹, which is 22.76 and 1.76 times higher than those of BiVO₄ (0.00247 min⁻¹) and Ag₃VO₄ (0.03167 min⁻¹), respectively. The composite showed a stable performance and could retain 90% of its photocatalytic activity even after four cycles. The improved catalytic performance of the composite as compared to BiVO₄ and Ag₃VO₄ can be attributed to its novel step-scheme mechanism, which facilitated the separation of the photo-generated charges and increased their lifetime. The photoluminescence measurement results and transient photocurrent response revealed that the composite showed efficient extraction of charge carriers.

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1. Introduction

Over the past few decades, water pollution caused by heavy metals and organic pollutants has increased significantly. Therefore, it is imperative to remove these pollutants in order to protect the environment [1–11]. The photocatalytic degradation of organic material and heavy metal ions under light illumination is an efficient approach for wastewater treatment [12–14]. TiO₂ [15,16] and ZnO [17,18], which are biochemically

inert, cost-effective, and non-toxic and exhibit strong oxidation ability and excellent photostability, are the most extensively investigated photocatalysts. However, they exhibit large bandgaps, and hence respond only to the ultraviolet (UV) light [19–21]. This limits their practical applications. The UV light contributes only 5% to the solar spectrum, while the visible light accounts for about 47% of the solar spectrum. Therefore, it is imperative to fabricate novel high-efficiency photocatalysts that can be irradiated by the visible light [22–28].

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Owing to their high visible light utilization, various semiconductor-based catalysts such as $g\text{-C}_3\text{N}_4$ [29–32], $\text{Ag}_2\text{VO}_2\text{PO}_4$ [33], CdS [34,35], BiOI [36], BiOBr [37,38], Ag_3PO_4 [14,39], BiVO_4 [40], Ag_3VO_4 [41,42], and TiO_2 [43–45] have been extensively used for wastewater treatment. BiVO_4 shows a narrow bandgap (2.41 eV) [46] and responds to the visible part of the solar energy. Furthermore, the holes in the valence band (VB) of BiVO_4 exhibit strong oxidizing ability, which is favorable for degrading organic pollutants [47,48]. Moreover, it exhibits good chemical stability and non-toxicity. Unfortunately, its conduction band (CB) electrons exhibit weak oxidizing ability. In addition, it shows small surface area and easy recombination of the photogenerated carriers. These factors limit its practical applications [49,50]. Silver-based photocatalytic materials such as Ag_3VO_4 show high visible light-degradation activities owing to their suitable bandgap (~ 2.2 eV) and excellent visible-light response. Konta et al. [51] demonstrated the excellent photocatalytic properties of Ag_3VO_4 for the decomposition of water into H_2 and O_2 .

Various efforts have been made to overcome the limitations of the abovementioned photocatalysts in order to realize their practical applications. Heterojunction structures show better photocatalytic properties such as light utilization efficiency, charge separation, and carrier lifetime than single-component semiconductors owing to the synergistic effect of their constituents [52,53]. Such heterojunction structures should exhibit the ideal coupling effect, good interface contact, adequate bandgap energy, and optimum band energy [54,55]. Photocatalysts with the step-scheme heterojunction structure show improved photocatalytic activities. The reaction of the useless electron-hole pairs to retain the useful electrons and holes in the step-scheme structure, which improves the transfer of the photogenerated electrons and holes, shows strong redox ability and enhances the activity of photocatalysts. Fu et al. [56] designed an ultrathin 2D/2D $\text{WO}_3/g\text{-C}_3\text{N}_4$ step-scheme heterojunction with excellent photocatalytic activity for H_2 -production. Jia et al. [57] prepared a high-efficiency step-scheme AgI/I-BiOAc photocatalyst, which showed 50 times higher catalytic activity than AgI . Mei et al. [58] investigated the catalytic performance of a $g\text{-C}_3\text{N}_4/\text{Ag}_3\text{VO}_4$ heterostructure for the degradation of MB. They found that the photocatalytic activity of the coupled semiconductor was higher than those of pure $g\text{-C}_3\text{N}_4$ and Ag_3VO_4 .

In this study, a novel step-scheme $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ catalyst was synthesized using a hydrothermal and chemical deposition method. The step-scheme mechanism enhanced the separation of the photogenerated charges, retained the strong VB potential of BiVO_4 and the CB potential of Ag_3VO_4 , and improved the

photocatalytic stability of the material. Compared to pure BiVO_4 and Ag_3VO_4 , the step-scheme $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ catalyst showed improved photocatalytic degradation of methylene blue (MB) and photostability under visible light. The findings of this study will not only elucidate the carrier separation mechanism of step-scheme systems but will also provide a new pathway to design narrow bandgap photocatalysts for mitigating environmental pollution.

2. Experimental

2.1. Materials

Sodium hydroxide (NaOH), ammonium metavanadate (NH_4VO_3), silver nitrate (AgNO_3), bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), MB, sodium dodecyl sulfate (SDS), sodium metavanadate ($\text{NaVO}_4 \cdot 12\text{H}_2\text{O}$), isopropanol (IPA), HNO_3 , triethanolamine (TEOA), and L-ascorbic acid (LAA) were obtained from Sigma-Aldrich. Deionized (DW, 18.25 M Ω) was used for preparing the solutions.

2.2. Preparation of BiVO_4

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (2.5 mmol) and NH_4VO_3 (2.5 mmol) were added to 20 mL of DW in a beaker. The resulting mixture (A) was stirred continuously for 1 h. SDS (0.5 g) was dissolved in 20 mL of DW and stirred for 35 min continuously to obtain solution B. Then, a NaOH solution was prepared by adding 3.2 g of NaOH in and 20 mL of DW in a beaker followed by stirring for 30 min. Solution B was slowly added to solution A. The NaOH solution was then added to the resulting reaction mixture to adjust the pH value to 7. The mixture was transferred to an autoclave, which was placed in an oven at 453 K for 24 h. The obtained precipitate was then washed with DW. Finally, the BiVO_4 sample was obtained by freeze-drying.

2.3. Preparation of the $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ catalyst

The $X\%\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ composites were obtained by chemical deposition. The schematic of the synthesis process is shown in Fig. 1. First, $X\%\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ ($X = 20, 40$, and 60) was synthesized by chemical deposition. BiVO_4 (0.1 g) was ultrasonically dispersed in 30 mL of DW for 35 min. To the resulting dispersion, 0.1743 g of AgNO_3 was added under stirring for 35 min (C). Then, 0.2736 g of $\text{Na}_3\text{VO}_4 \cdot 12\text{H}_2\text{O}$ was added to 20 mL of DW and the solution was stirred for 50 min. Finally, this solution was added dropwise to solution C, and the resulting mixture was stirred for 3 h, aged for 6 h, centrifuged with DW

Fig. 1. Schematic of the synthesis of the $X\%\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ composites.

for three times, and freeze-dried. The as-synthesized mixture was labeled as 40%BiVO₄/Ag₃VO₄. Here, 40% represents the BiVO₄:Ag₃VO₄ mass ratio. Similarly, 20%BiVO₄/Ag₃VO₄, 60%BiVO₄/Ag₃VO₄ were also obtained using the same procedure. Pure Ag₃VO₄ was also synthesized without BiVO₄.

2.4. Characterization

The X-ray diffraction (XRD) patterns of Ag₃VO₄, BiVO₄, and the BiVO₄/Ag₃VO₄ composites were recorded on a Rigaku D/MAX24000 diffractometer. The morphologies and elemental compositions of the photocatalysts were examined by scanning electron microscopy (SEM, Hitachi Regulus8220) and energy-dispersive X-ray spectroscopy (EDS, INCA x-act). Transmission electron microscopy (TEM, JEOL JEM-2010) was used to examine the structures of the catalysts. Photoluminescence spectroscopy (PL, FLS 920) and UV-visible diffuse reflectance spectroscopy (UV-Vis DRS, PerkinElmer Lambda 950) were used to investigate the optical properties of the synthesized catalysts. The chemical compositions of the samples were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250). The electrochemical properties of the samples were investigated using an electrochemical workstation (Shanghai Chenhua CHI-660D). The surface areas of the products were determined by obtaining their N₂ adsorption isotherms (ASAP 2040).

2.5. MB photodegradation

In a Pyrex reaction cell, a certain amount of the obtained photocatalyst was dissolved in a solution containing 30 mg of the sample and 30 mL of the MB solution (50 mg/L). A 50-W 410-nm light emitting diode (LED) was used as the light source. The distance from the light source to the MB solution surface was 1 cm, and the pH of the degradation reaction solution was 7. The time interval between the illuminations was 10 min. Meanwhile, the MB solution was centrifuged and its absorbance spectrum (721G, Shanghai Precision Instrument Co.) was obtained after each exposure.

3. Results and discussion

The crystal phase structures of the photocatalysts were investigated using XRD, and the results are shown in Fig. 2. Pure Ag₃VO₄ showed peaks characteristic of monoclinic Ag₃VO₄ (PDF No.43-0542). On the other hand, the diffraction peaks of BiVO₄ could be indexed to monoclinic BiVO₄ (PDF No.14-0688). The diffraction peaks of the X%BiVO₄/Ag₃VO₄ samples did not change significantly when BiVO₄ was composited with Ag₃VO₄. The X%BiVO₄/Ag₃VO₄ composites showed a strong BiVO₄ peak at $2\theta = 28.822^\circ$. Moreover, with an increase in the BiVO₄ content, the intensities of the diffraction peaks corresponding to the (121) and (121) crystal planes of BiVO₄ increased [59], while the intensities of the diffraction peaks corresponding to the (121) and (121) planes of Ag₃VO₄ decreased. This indicates that BiVO₄ compounded well with Ag₃VO₄.

Figure 3 shows the structures, chemical compositions, and

Fig. 2. XRD patterns of BiVO₄, Ag₃VO₄, and the X%BiVO₄/Ag₃VO₄ composites.

morphologies of the photocatalysts. It can be observed clearly that BiVO₄ showed an irregular sheet structure with a particle size of around 1 μm (SEM image in Fig. 3a). From Fig. 3b, it can be observed that Ag₃VO₄ showed irregular nanoparticles with a size of 100–200 nm. The 40%BiVO₄/Ag₃VO₄ composite showed BiVO₄ sheets and Ag₃VO₄ nanoparticles. The elemental composition of the 40%BiVO₄/Ag₃VO₄ sample is shown in Fig. 3d. The sample showed no impurities. This is consistent with the XRD results. These results indicate that the BiVO₄/Ag₃VO₄ nanocomposites were successfully prepared. Figures 3f–3i show the elemental mapping of the 40%BiVO₄/Ag₃VO₄ composite (Fig. 3e). The composite consisted of V, O, Ag, and Bi. This indicates that BiVO₄ and Ag₃VO₄ compounded well with each other. The structural characteristics of the samples were further analyzed

Fig. 3. SEM images of (a) BiVO₄, (b) Ag₃VO₄, and (c) 40%BiVO₄/Ag₃VO₄; (d) EDS spectra of 40%BiVO₄/Ag₃VO₄ and (e–i) elemental mapping of 40%BiVO₄/Ag₃VO₄.

Fig. 4. (a, b) TEM images and (c, d) HRTEM images of 40%BiVO₄/Ag₃VO₄.

using TEM (Figs. 4a–4b). The high-resolution (HRTEM) images of BiVO₄ and Ag₃VO₄ (Figs. 4c–4d) revealed that they showed the interplanar distances of 0.191 and 0.310 nm, respectively. These values correspond to the (121) and (220) crystal planes of BiVO₄ [60] and Ag₃VO₄ [61], respectively.

The valance and surface chemical compositions of BiVO₄, 40%BiVO₄/Ag₃VO₄, and Ag₃VO₄ were investigated using XPS, and the results are shown in Fig. 5. The XPS survey spectra of the samples are shown in Fig. 5a. As can be observed from the figure, the samples showed O, V, Ag, C, and Bi. The presence of C can be attributed to the extraneous pollution from the instrument. This is consistent with the elemental mapping results of the photocatalysts (Figs. 3f–3i). As can be observed from Fig. 5b, BiVO₄ showed two peaks at 158.6 and 163.9 eV corresponding to the Bi 4f_{7/2} and Bi 4f_{5/2} orbitals, respectively. The Bi 4f peaks of 40%BiVO₄/Ag₃VO₄ shifted to 158.3 and 163.6 eV because of the combination of Ag₃VO₄ and BiVO₄. Ag₃VO₄ and 40%BiVO₄/Ag₃VO₄ (Fig. 5c) showed Ag 3d peaks at 373.7 and 367.7 eV corresponding to the Ag 3d_{3/2} and Ag 3d_{5/2} orbitals,

respectively [62,63]. Furthermore, Ag₃VO₄ showed peaks at 374.8 and 369.0 eV corresponding to Ag nanoparticles [64]. BiVO₄ (Fig. 5d) showed peaks at 523.6 and 516.0 eV corresponding to the V 2p_{1/2} and V 2p_{3/2} orbitals, respectively. This also conforms to Ag₃VO₄ and 40%BiVO₄/Ag₃VO₄. It can be observed from Fig. 5e that the O 1s band of all the samples could be divided into two peaks. The O 1s peak at 530.61 eV can be attributed to the O in H₂O. The second O 1s peaks of the samples (BiVO₄ (529.06 eV), 40%BiVO₄/Ag₃VO₄ (529.43 eV), and Ag₃VO₄ (529.29 eV)) can be ascribed to the lattice oxygen [65]. This confirms the electron flow between BiVO₄ and Ag₃VO₄.

The N₂ adsorption-desorption curves of the catalysts are shown in Fig. 6a. The Brunauer-Emmett-Teller surface areas (*S*_{BET}) of the catalysts are shown in Fig. 6b [66]. The *S*_{BET} of Ag₃VO₄ (6.7 m²/g) was nearly four times higher than that of BiVO₄ (1.8 m²/g). The *S*_{BET} values of the BiVO₄/Ag₃VO₄ composites were lower than that of pristine Ag₃VO₄. Furthermore, with an increase in the BiVO₄ content, the *S*_{BET} value of the composites decreased.

The light absorption performances of the catalysts were evaluated using UV-Vis DRS. As can be observed from Fig. 7a, pure BiVO₄ and Ag₃VO₄ showed intense absorption peaks at 528 and 620 nm, respectively. With an increase in the BiVO₄ loading, the absorption peaks of the X%BiVO₄/Ag₃VO₄ composites showed a slight blue shift compared to the peaks of bare Ag₃VO₄. Silver nanoparticles were generated by the reduction reaction of BiVO₄ and Ag₃VO₄. These nanoparticles induced the surface plasmon resonance effect, which improved the light absorption capacity of the composites as compared to the pure samples. The energy bandgaps (*E*_g) of Ag₃VO₄ and BiVO₄ were calculated using the following equation [67]:

Fig. 5. XPS survey spectra of (a) BiVO₄, 40%BiVO₄/Ag₃VO₄, and Ag₃VO₄ and their high-resolution (b) Bi 4f, (c) Ag 3d, (d) V 2p, and (e) O 1s spectra.

Fig. 6. (a) N₂ adsorption-desorption isotherms and (b) S_{BET} values of the BiVO₄, Ag₃VO₄, and X%BiVO₄/Ag₃VO₄ catalysts.

Fig. 7. (a) UV-Vis DRS spectra of Ag₃VO₄, X%BiVO₄/Ag₃VO₄, and BiVO₄; (b) E_g values for Ag₃VO₄ and BiVO₄.

$$(\alpha h\nu)^{n/2} = A(h\nu - E_g) \quad (1)$$

where h , α , n , ν , and A are the Planck's constant, the diffuse absorption coefficient, the trait of the transition, the optical frequency, and a constant, respectively. As BiVO₄ and Ag₃VO₄ are direct transition semiconductors, the value of n was 4 [60]. The E_g values of Ag₃VO₄ and BiVO₄ were calculated to be 2.20 and 2.41 eV, respectively (Fig. 7b). Furthermore, the E_{VB} and E_{CB} values were calculated using the following equations [68]:

$$E_{CB} = X - E^c - 0.5E_g \quad (2)$$

$$E_{VB} = E_{CB} + E_g \quad (3)$$

where X is the absolute electronegativity of the catalyst. E^c was 4.5 eV. The values of X for BiVO₄ and Ag₃VO₄ were 6.16 and 5.64 eV [69,70], respectively. The E_{CB} values of Ag₃VO₄ and BiVO₄ were calculated to be 0.04 and 0.455 V, respectively.

Figure 8 shows the PL spectra of Ag₃VO₄, BiVO₄, and the X%BiVO₄/Ag₃VO₄ composites. The PL spectra of the catalysts were used to investigate their carrier separation efficiency during the photocatalytic reactions. The lower the intensity of the PL peak of a catalyst, the weaker is the recombination probability of its photoexcited carriers, and hence the higher is its charge transfer efficiency, which is favorable for the photocatalytic degradation reaction. The 40%BiVO₄/Ag₃VO₄ compo-

site showed weaker PL peaks than BiVO₄ and Ag₃VO₄, indicating that effective charge transfer occurred between Ag₃VO₄ and BiVO₄ in the composite.

The rates of electron-hole separation, migration, and recombination are important factors affecting the performance of photocatalysts. The performances of the photocatalysts were

Fig. 8. PL spectra of the BiVO₄, Ag₃VO₄, and X%BiVO₄/Ag₃VO₄ catalysts.

Fig. 9. (a) Transient photocurrent responses and (b) EIS results of Ag_3VO_4 , BiVO_4 , and $X\%\text{BiVO}_4/\text{Ag}_3\text{VO}_4$.

Fig. 10. (a) Photocatalytic degradation of MB; (b) Linear transform $\ln(C_0/C)$ of the kinetic curves for MB degradation using the catalysts; (c) The apparent pseudo-first-order rate constants (K_{app}) of the catalysts.

evaluated using electrochemical impedance spectroscopy (EIS) and by obtaining their transient photocurrent responses. The results are shown in Fig. 9. The excitation source was a 50-W LED light and the initial bias voltage was 0.3979 V. Among all the photocatalysts, the 40% $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ composite showed the highest photocurrent response (Fig. 9a). This is because BiVO_4 and Ag_3VO_4 formed a heterojunction at the interface, which improved the separation and transport of the electron-hole pairs. The EIS measurements (Fig. 9b) were carried out to investigate the electron transfer process of the catalysts. The 40% $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ composite showed the smallest arc radius among all the catalysts. This indicates that the 40% $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ composite showed the lowest resistance among all the samples. Hence, it can be stated that the charge transfer was easier at the interface of the 40% $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ composite. This suggests that the heterojunction of BiVO_4 and Ag_3VO_4 shows higher carrier transfer efficiency at the interface and better catalytic activity than pure BiVO_4 and Ag_3VO_4 .

The catalytic performances of the catalysts were evaluated by carrying out the photodegradation of MB using them. As can be observed from Fig. 10a and Table 1, pure BiVO_4 showed the worst photodegradation performance among all the catalysts. The photodegradation performance of Ag_3VO_4 was better than that of BiVO_4 , but was poorer than that of the $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ composite. The 40% $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ composite showed better MB photodegradation performance than pure BiVO_4 , Ag_3VO_4 ,

and the physical mixture of BiVO_4 and Ag_3VO_4 ($\text{BiVO}_4 + \text{Ag}_3\text{VO}_4$). It could degrade 93.48% of MB in 50 min. As can be observed from Fig. 10b, $\ln C_0/C$ and t showed a linear relationship:

$$\ln C_0/C = K_{\text{app}}t \quad (4)$$

where C_0 , C , and K_{app} are the concentration of the original MB solution, concentration of the MB solution after the illumination time T , and apparent pseudo-first-order rate constant, respectively. The K_{app} values of the catalysts were calculated using Eq. 4 and the results obtained from Fig. 10b. The K_{app} of 40% $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ was 0.05588 min^{-1} (Fig. 10c). The K_{app} values of Ag_3VO_4 and BiVO_4 were only 0.03167 and 0.00247 min^{-1} , respectively. The K_{app} of 40% $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ was 1.76 and 22.6 times higher than those of Ag_3VO_4 and BiVO_4 , respectively. The photocatalytic degradation performance parameters of the catalysts for the degradation of MB are listed in Table 1.

Table 1

Degradation rates and K_{app} values of the catalysts (degradation time: 50 min).

Sample	Degradation rate (%)	K_{app} (min^{-1})
Ag_3VO_4	83.77	0.03167
BiVO_4	16.31	0.00247
20% $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$	84.89	0.03377
40% $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$	93.48	0.05588
60% $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$	84.46	0.03012
$\text{BiVO}_4 + \text{Ag}_3\text{VO}_4$	87.00	0.03511

Fig. 11. (a) MB degradation activities of the photocatalysts after four cycles; (b) XRD patterns of the fresh and used 40%BiVO₄/Ag₃VO₄ catalysts.

To evaluate the photostability of the catalysts, the cyclic degradation of MB was carried out. As shown in Fig. 11a, after four cycles of photocatalytic degradation, BiVO₄ showed very stable photocatalytic activity. However, it showed almost no degradation properties. On the other hand, 40%BiVO₄/Ag₃VO₄ not only exhibited very stable photocatalytic properties, but could retain more than 90% of its photocatalytic degradation activity after four cycles. Unfortunately, the photocatalytic degradation activity of Ag₃VO₄ was unstable. The excellent stability of 40%BiVO₄/Ag₃VO₄ can be attributed to the formation of a heterojunction between BiVO₄ and Ag₃VO₄, which improved the separation of carriers and reduced the possibility of carrier recombination. This indicates that 40%BiVO₄/Ag₃VO₄ was more stable than BiVO₄ and Ag₃VO₄. Furthermore, the XRD patterns of the fresh and used 40%BiVO₄/Ag₃VO₄ catalysts are shown in Fig. 11b. It can be observed from the figure that the XRD pattern of 40%BiVO₄/Ag₃VO₄ did not change significantly after the cyclic degradation (four cycles) experiment. This indicates that 40%BiVO₄/Ag₃VO₄ could be reused.

Fig. 12. MB degradation rate of 40%BiVO₄/Ag₃VO₄ in the presence of different capture agents.

To identify the major active species in the photodegradation process, capture experiments were carried out. For these experiments, TEOA (2 mL, 0.13 mol/L), IPA (2 mL, 0.25 mol/L), and LAA (50 mg) were used for capturing hydroxyl holes (h⁺), radicals (·OH), and superoxide ions (·O₂⁻) [71], respectively. The results are shown in Fig. 12. When no capture agent was added, the efficiency of the 40%BiVO₄/Ag₃VO₄ catalyst for the degradation of MB was as high as 90%. On the other hand, when TEOA, IPA, and LAA were used as the capture agents, the degradation efficiencies of the catalyst were 0.9%, 79.9%, and 74.3%, respectively. This indicates that in the case of the 40%BiVO₄/Ag₃VO₄ composite, h⁺ played the most important role in the photocatalytic degradation process, while the effects of ·OH and ·O₂⁻ were secondary.

On the basis of these results, the photocatalytic mechanism of BiVO₄/Ag₃VO₄ heterostructures was proposed. As shown in Fig. 13, under light irradiation, the electrons (e⁻) in the VBs of

Fig. 13. Step-scheme charge carrier flow for the composite.

BiVO_4 and Ag_3VO_4 (narrow bandgaps of 2.41 and 2.20 eV, respectively) are excited to their CBs leaving behind h^+ . However, since BiVO_4 and Ag_3VO_4 exhibit narrow bandgaps, their photo-generated e^- and h^+ recombine rapidly. However, from Fig. 12, it can be observed that h^+ play an important role in the degradation of MB. Hence, we proposed the step-scheme mechanism [56,57]. When BiVO_4 and Ag_3VO_4 are in close contact to form a heterojunction, the e^- in Ag_3VO_4 spontaneously move to BiVO_4 through their interfaces, generating an internal electric field at the interface. The internal electric field and Coulomb interaction accelerate the recombination of certain electrons (CB from BiVO_4) and holes (VB from Ag_3VO_4) while separating certain electrons (CB from Ag_3VO_4) and holes (VB from BiVO_4). As shown in Fig. 13, the CB position of Ag_3VO_4 is lower than the $\text{O}_2/\cdot\text{O}_2^-$ potential (-0.33 V vs. NHE). Hence, the e^- in the CB of Ag_3VO_4 cannot reduce O_2 to $\cdot\text{O}_2^-$ radicals. This is consistent with the observation made from Fig. 12 that $\cdot\text{O}_2^-$ plays a small role in the degradation of MB using $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ heterostructures. Meanwhile, the VB potential of BiVO_4 is 2.865 V, which is higher than the standard redox potential of $\text{OH}^-/\cdot\text{OH}$ (2.4 V vs. NHE). Hence, the adsorbed H_2O molecules could be oxidized to $\cdot\text{OH}$ by the photogenerated h^+ in the VB. From Fig. 12, it can be observed that $\cdot\text{OH}$ showed a little effect on the degradation of the MB solution, suggesting that the h^+ in the VB of BiVO_4 play a major role in oxidizing MB into CO_2 and H_2O . The e^- in the CB of Ag_3VO_4 may react with H^+ and O_2 to produce H_2O_2 .

On the basis of this discussion, we elucidated the photodegradation mechanism of the $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ step-scheme heterojunction. In this heterojunction, the relatively useless e^- (from CB of BiVO_4) combined with h^+ (from VB of Ag_3VO_4) [72] so that the useful e^- in the CB of Ag_3VO_4 and h^+ in the VB of BiVO_4 were completely utilized. This indicates that the $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ heterostructure developed in this study was a step-scheme sys-

tem, and its excellent redox performance can be attributed to its carrier separation ability.

4. Conclusions

In summary, a step-scheme $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ composite was prepared using a hydrothermal and chemical deposition method. The 40% $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ composite showed the best MB degradation performance among all the catalysts investigated in this study. This indicates that the formation of the $\text{Ag}_3\text{VO}_4/\text{BiVO}_4$ heterojunction improved the photocatalytic activity of the composite. This stepped heterojunction accelerated the recombination of unwanted carriers, thereby suppressing the recombination of useful electrons and holes. It extended the lifetime of the photoexcited carriers, thus increasing the photocatalytic activity of the catalysts. The findings of this study will be helpful for understanding, designing, and preparing step-scheme heterojunctions for the photodegradation of environmental pollutants.

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Graphical Abstract

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A novel step-scheme $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ photocatalyst for enhanced photocatalytic degradation activity under visible light irradiation

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A step-scheme $\text{BiVO}_4/\text{Ag}_3\text{VO}_4$ heterojunction was successfully fabricated using a hydrothermal and chemical deposition process. The formation of the heterojunction improved the photocatalytic activity of the composite by separating electron-hole pairs and improving their transmission efficiency.

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梯型BiVO₄/Ag₃VO₄光催化剂的构建及其可见光光催化性能

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摘要: 近年来, 有机污染物的问题变得越来越严重. 为了解决该问题, 人们研究和开发了许多有效的光催化剂. 本工作采用水热法和化学沉积法合成了BiVO₄/Ag₃VO₄梯型半导体材料, 该复合材料在可见光下具有很强的氧化还原能力. 其中40%BiVO₄/Ag₃VO₄具有最佳的光催化降解性能, 其降解速率为0.05588 min⁻¹, 分别是BiVO₄和Ag₃VO₄的22.76和1.76倍. 并且其性能稳定, 经过四次循环后其降解率仍可保持90%以上. BiVO₄和Ag₃VO₄复合后, 其催化性能得到增强, 归因于形成了新型的梯型光催化机制, 该方法促进了光生电荷的分离并延长了电荷的寿命, 且通过PL测试和瞬态光电流响应证明了电荷的有效转移.

X射线衍射(XRD)可以观察到Ag₃VO₄和BiVO₄物相, 没有其他成分. 用扫描电子显微镜(SEM)和透射电子显微镜(TEM)进一步观察了该催化剂的结构和形貌, 从SEM可以看出, Ag₃VO₄生长在BiVO₄的上面, 能谱分析也证明该催化剂仅包含Ag₃VO₄和BiVO₄的各种元素, 而不含其他杂质, TEM进一步证明了两种物质复合在一起, 而不是机械混合. 通过紫外-可见光漫反射光谱(UV-vis)测试可以得到BiVO₄和Ag₃VO₄的吸收带边, 进一步计算BiVO₄的带隙和导带分别为2.41和0.455 eV, Ag₃VO₄的带隙和导带分别为2.20和0.04 eV, 二者组成的异质结的带隙满足降解的条件. 用荧光光谱(PL)和光电流研究了样品的光电特征, 结果表明BiVO₄/Ag₃VO₄光催化剂具有很高的载流子分离效率和很低的光电流电阻, 这有助于光生载流子的运输.

光催化降解甲基蓝实验表明, BiVO₄/Ag₃VO₄具有很强的光催化降解速率(0.05588 min⁻¹), 是BiVO₄的22.6倍, Ag₃VO₄的1.76倍, 而且经过四次循环后仍能保持很高的活性. 通过XRD发现使用后的催化剂并没有发生变化, 说明该催化剂具有良好的稳定性. 高分辨X射线光电子能谱(XPS)不仅进一步说明了该催化剂成功复合后没有其他杂质元素, 而且从各元素的结合能变化可以看出构成异质结后电子的流向, 证实了光催化机制为梯型机制. 光照射后, BiVO₄和Ag₃VO₄产生电子空穴对, 当催化剂受光激发后, 电子从价带被激发到导带, 并在价带留下空穴. 当BiVO₄和Ag₃VO₄复合后, 在接触界面形成内电场, 由于库仑相互作用, 能带边缘弯曲等作用加速了Ag₃VO₄价带上某些空穴和BiVO₄导带上电子的复合, 从而阻止了Ag₃VO₄和BiVO₄内部电子空穴对的复合, 这有助于Ag₃VO₄导带上的电子和BiVO₄价带上的空穴参与氧化还原反应. 从捕获实验可以看出, 本实验中空穴在光催化降解中起着最重要的作用, 这与上述结论一致.

关键词: 梯型光催化剂; BiVO₄; Ag₃VO₄; 光催化活性; 亚甲基蓝

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