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Article

One-pot synthesis of peony-like $\text{Bi}_2\text{S}_3/\text{BiVO}_4(040)$ with high photocatalytic activity for glyphosate degradation under visible light irradiation

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ABSTRACT

In this work, samples consisting of BiVO_4 with exposed (040) facets coupled with Bi_2S_3 ($\text{Bi}_2\text{S}_3/\text{BiVO}_4$) were prepared through a one-pot hydrothermal method, using ethylenediaminetetraacetic acid as directing agent and L-cysteine as sulfur source and soft template. X-ray diffraction, field emission scanning electron microscopy, and high-resolution transmission electron microscopy measurements indicated that the Bi_2S_3 content had a significant influence on the growth of (040) and (121) facets as well as on the morphology of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples. When the Bi_2S_3 content reached 1 mmol, the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples exhibited a peony-like morphology. The results of transient photocurrent tests and electrochemical impedance spectroscopy measurements confirmed that a more effective charge separation and a faster interfacial charge transfer occurred in $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ than BiVO_4 . The enhanced photocatalytic activity of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples could be attributed to the improved absorption capability in the visible light region and the enhanced electron-hole pair separation efficiency due to the formation of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ heterostructure. In addition, the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples showed relative stability and reusability. The simple method presented in this work could be used to fabricate composite photocatalysts with high activity for different applications, such as photocatalytic degradation of organic pollutants, photocatalytic splitting of water, and photocatalytic reduction of carbon dioxide.

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1. Introduction

Glyphosate (*N*-(phosphonomethyl)glycine) is a broad-spectrum herbicide. In March 2015, the World Health Organization's International Agency for Research on Cancer announced that glyphosate is probably carcinogenic to humans (category 2A) [1]. At present, glyphosate wastewater is generally treated using biochemical or Fenton methods [2]; however, the significant length of the corresponding biodegradation period may create secondary pollution. Since Fujishima et al. [3] reported the decomposition of H_2O by TiO_2 electrolysis in 1972, the

treatment of industrial wastewater by semiconductor photocatalysis has been widely studied [4]. The TiO_2 photocatalyst used in the photocatalytic degradation of glyphosate wastewater [4–6] only absorbs ultraviolet (UV) light; however, the solar spectrum includes a very small percentage of UV light (~5%). Therefore, extensive research has focused on developing visible light-active photocatalysts [7] for the degradation of wastewater containing organic pollutants [8,9] such as glyphosate.

Bismuth vanadate (BiVO_4) is an attractive candidate due to its high stability against photocorrosion, non-toxicity, and nar-

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row band gap [10,11]. The band gap of monoclinic BiVO_4 is about 2.4 eV, which makes it responsive to visible light. However, pure BiVO_4 exhibits poor photocatalytic activity due to its slow charge transport and rapid recombination of photogenerated charge carriers [12]. The photocatalytic activity of a photocatalyst is commonly associated with its exposed surfaces, and in particular with the arrangement and coordination of the surface atoms on the different crystal facets. Therefore, there is great interest in the design of high-performance BiVO_4 materials with different dominant exposed facets. BiVO_4 with orientational growth along the (040) direction was shown to promote charge separation and high transfer efficiency, resulting in a marked enhancement in the photocatalytic activity of BiVO_4 [13,14]. Chen et al. [15] showed that lamellar *m*- BiVO_4 samples oriented along the (040) facets, with the highest ratio between the intensities of the (040) and (121) diffraction peaks (I_{040}/I_{121}), possessed the best photocatalytic activity. Ou et al. [16] reported that the Z-scheme $\text{g-C}_3\text{N}_4/\text{Ag}/\text{BiVO}_4(040)$ photocatalyst exhibited high photocatalytic oxidation performance, due to the exposure of photogenerated electron-rich (040) facets and the high separation rate of photogenerated charge carriers. In addition, the formation of a heterojunction between BiVO_4 and other semiconductors (such as Ag_2S [17], Bi_2WO_6 [18], $\text{g-C}_3\text{N}_4$ [19,20], Ag_2CO_3 [21], BiFeWO_6 [22], or BiOI [23]) has been extensively investigated to enhance the photocatalytic activity of BiVO_4 .

Metal sulfides are attracting increasing attention due to their narrow band gaps. Most metal sulfides have been synthesized by the reaction between various metal cations and inorganic sulfur sources [24,25]. At present, the biosynthesis of nanomaterials with unique structure and excellent self-assembly properties as templates or auxiliary agents has become a key step in the preparation of materials [26]. The $-\text{SH}$ group of the L-cysteine molecule can be used as a sulfur source to synthesize sulfides. In addition, as an amino acid, L-cysteine can form peptides by condensation reactions, and then act as a template to synthesize special morphologies [27]. Using the $-\text{SH}$ group of L-cysteine and the strong self-assembly ability to synthesize the special structure of metal sulfides has attracted great interest and widespread attention.

Bi_2S_3 is a semiconductor with a narrow band gap of 1.19–1.5 eV; hence, it can absorb in the whole visible region [28–35]. Considering that the band gap of Bi_2S_3 is smaller than that of BiVO_4 ($E_g = 2.4$ eV), and that the valence band (VB) potential (E_{VB}) of BiVO_4 ($E_{\text{VB}} = 2.71$ eV vs. normal hydrogen electrode, NHE) is more positive than that of Bi_2S_3 ($E_{\text{VB}} = 1.42$ eV vs. NHE) [28], the energy levels of Bi_2S_3 and BiVO_4 appear to be well matched, so that a heterojunction enabling the efficient separation of photogenerated charge carriers could be formed. The formation of a heterojunction structure between BiVO_4 and Bi_2S_3 has been achieved using Na_2S [29,30], thioacetamide [31,32], and L-cysteine [33] as the sulfur source, resulting in enhanced photocatalytic activity due to the retarded recombination of photogenerated carriers.

In this work, BiVO_4 was coupled with Bi_2S_3 to form a peony-like heterojunction, which exhibited better photocatalytic activity than BiVO_4 . We report the synthesis and characteriza-

tion of BiVO_4 and of its composite with Bi_2S_3 ($\text{Bi}_2\text{S}_3/\text{BiVO}_4$). The $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ composites were prepared by a one-pot hydrothermal method using ethylenediaminetetraacetic acid (EDTA) disodium salt as a directing agent, to grow BiVO_4 sheets oriented along (040) facets, as well as L-cysteine acting as sulfur source and soft template at the same time. The flakes of BiVO_4 and Bi_2S_3 formed $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ structures with different morphologies, which showed an enhanced photocatalytic activity for glyphosate degradation compared to that of BiVO_4 .

2. Experimental

2.1. Synthesis of BiVO_4 flakes and peony-like $\text{Bi}_2\text{S}_3/\text{BiVO}_4$

$\text{Bi}_2\text{S}_3/\text{BiVO}_4$ heterojunctions were prepared by a one-pot hydrothermal method. Typically, 0.0100 mol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 5 mL of concentrated nitric acid, and deionized water was added to 20 mL of the mixture under stirring for 10 min to obtain solution A. Then, 0.0100 mol of NH_4VO_3 and 0.0068 mol of EDTA were dissolved in 20 mL of a NaOH solution (4 mol/L) with stirring for 10 min, to obtain solution B. Solution B was then added dropwise to solution A under stirring, and the pH of the resulting solution was adjusted to 5 using 2 mol/L NaOH. Afterward, a specific amount of L-cysteine (0, 0.25, 0.5, 1, 2.5, and 5 mmol) was added to the above mixture and the solution was stirred for 30 min. A 40 mL aliquot of the resulting yellow suspension was then transferred into a 50-mL Teflon-lined autoclave and heated at 180 °C for 24 h. The precipitates were filtered and washed with water and ethanol to remove impurities, and then dried at 65 °C overnight. The corresponding products were named BiVO_4 , $0.25\text{Bi}_2\text{S}_3/\text{BiVO}_4$, $0.5\text{Bi}_2\text{S}_3/\text{BiVO}_4$, $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$, $2.5\text{Bi}_2\text{S}_3/\text{BiVO}_4$, and $5\text{Bi}_2\text{S}_3/\text{BiVO}_4$, respectively.

2.2. Photocatalyst characterization

Powder X-ray diffraction (XRD) measurements were performed on a MSALXD-2 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm), employing a scanning rate of $0.02^\circ/\text{s}$ in the 2θ range from 10° to 80° . The microstructures of the samples were studied by field emission scanning electron microscopy (FESEM, FEI-Verios 460), transmission electron microscopy (TEM, FEI-Tecnai 12), and high-resolution transmission electron microscopy (HRTEM, JEM2100). Energy-dispersive X-ray (EDS) mappings of the as-prepared samples were obtained using a FEI-Verios 460 microscope. Diffuse reflectance spectroscopy (DRS) measurements were performed using a UV-vis spectrophotometer (UV-2550, Shimadzu), with BaSO_4 as a reflectance standard. Transient photocurrent and electrochemical impedance spectroscopy (EIS) measurements were carried out in a Na_2SO_4 solution (0.5 mol/L) using an electrochemical workstation (Epsilon-BAS). A 300-W xenon lamp equipped with a UV cut-off filter ($\lambda > 420$ nm) was used as visible light source. A film of the as-prepared sample on fluorine-doped tin oxide (FTO) served as the working electrode, while a Pt plate and Ag/AgCl (saturated KCl) were used as the counter and reference electrodes, respectively. Electron spin resonance (ESR)

experiments were performed on a Bruker A300 spectrometer at room temperature.

2.3. Photocatalytic degradation experiments under visible light irradiation

The photocatalytic degradation of glyphosate was investigated under visible light irradiation ($\lambda > 400$ nm), using a 125-W high-pressure mercury lamp with 180 mL of 2 mol/L NaNO_2 solution as the filter liquor. The photocatalytic reaction system and the spectral energy distribution used in the experiments were reported elsewhere [20]. In a typical experiment, 0.2 g of the as-prepared photocatalyst was added to 500 mL of 0.1 mmol/L glyphosate aqueous solution under ultrasonic stirring for 1 min. The suspension was then stirred in the dark for 30 min to establish the adsorption-desorption equilibrium between the photocatalyst particles and the glyphosate molecules. At a given time after switching on the light source, 8 mL of the reaction solution was collected and centrifuged (3500 rpm, 10 min) to remove the photocatalyst particles. A 5-mL aliquot of supernatant was collected to analyze the final concentration of the PO_4^{3-} oxidation product by Mo-Sb-ascorbic acid colorimetry [36,37]. The relationship between PO_4^{3-} concentration (x) and absorbance (A) follows the relation $x = 63.093A + 0.0322$, where the x units are 10^{-6} mol/L. The percentage of glyphosate degradation (η) was calculated using the following equation:

$$\eta = 5C_t/C_0 \times 100\% \quad (1)$$

where C_0 is the concentration of total organic phosphorus in the reaction solution before irradiation and C_t is the concentration of PO_4^{3-} produced at the irradiation time t .

To investigate the photocatalytic reaction mechanism over the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ composites, $\text{K}_2\text{Cr}_2\text{O}_7$, EDTA, isopropyl alcohol (IPA), and benzoquinone (BQ) were added in the photocatalytic degradation solution of glyphosate as active scavengers for photogenerated electrons (e^-), photogenerated holes (h^+), hydroxyl radicals ($\cdot\text{OH}$), and superoxide radicals ($\cdot\text{O}_2^-$), respectively, under visible light irradiation for 3 h. Before irradiation, 0.2 g of photocatalyst was added to the glyphosate solution (500 mL, 0.1 mmol/L) under ultrasonic stirring for 1 min, and then the scavenger (1 mmol/L) was added. After stirring in the dark for 30 min to establish the adsorption-desorption equilibrium, the light source was turned on. After a specific time interval (30 min), 8 mL of suspension was collected and centrifuged (3500 rpm, 10 min) to remove the photocatalyst particles. An aliquot of supernatant (5 mL) was collected to analyze the final concentration of the PO_4^{3-} oxidation product via Mo-Sb-ascorbic acid colorimetry. In the ESR experiments, the $\cdot\text{OH}$ species were detected with dimethylpyridine *N*-oxide (DMPO). Typically, 0.01 g of photocatalyst was completely dispersed in 25 mL of 0.1 mmol/L glyphosate aqueous solution under stirring in the dark for 5 min. Then, 100 μL of the reaction solution was removed and irradiated by a 300-W Xe lamp (equipped with a UV cut-off filter, $\lambda > 420$ nm) for 5 min, followed by injection of 10 μL of DMPO. Capillary tubes were inserted in the ESR cavity, and spectra were recorded at 10 and

20 min during irradiation. For comparison, control experiments without photocatalyst or without light irradiation were also performed.

3. Results and discussion

3.1. Crystal phase and chemical composition

Fig. 1 shows the XRD patterns of pure BiVO_4 and of $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples with different Bi_2S_3 contents; all diffraction peaks of the pure BiVO_4 sample can be indexed to monoclinic scheelite BiVO_4 (JCPDS No. 14-0688) [38]. It is worth noting that the relative intensity of the (040) diffraction peak of pure BiVO_4 is stronger than that of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ composites, suggesting the preferential crystal growth of sheet-like BiVO_4 oriented along (040) facets using EDTA as a directing agent. When the Bi_2S_3 content is in the range of 0.25 to 1 mmol, no obvious impurity peaks are detected. However, the diffraction intensity of the (040) peak of BiVO_4 decreases and the (121) diffraction intensity gradually increases with increasing Bi_2S_3 content. This suggests that the crystal growth of sheet-like BiVO_4 oriented along the (040) facets is inhibited by the formation of Bi_2S_3 on the surface of the BiVO_4 particles. When the Bi_2S_3 content is equal or greater than 2.5 mmol, the weak intensity and broadening of the diffraction peaks suggests a low crystallinity of the $2.5\text{Bi}_2\text{S}_3/\text{BiVO}_4$ sample. In the case of the $5\text{Bi}_2\text{S}_3/\text{BiVO}_4$ sample, the characteristic diffraction peaks of Bi_2S_3 are identified at $2\theta = 22.6^\circ$, 25.4° , 28.8° , 32.0° , 33.2° , and 35.5° [JCPDS No. 17-0320] [34], matching well with the reflections of the (220), (130), (211), (221), (301), and (240) planes, respectively, which indicates that the as-prepared samples are composed of Bi_2S_3 and BiVO_4 .

3.2. Morphology and structure

The morphology, particle size, and microstructure of the BiVO_4 and $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples were analyzed by FESEM, TEM, and HRTEM, and the results are shown in Fig. 2. The morphology of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples shows significant variations when the Bi_2S_3 content is increased from 0 to 0.25, 0.5, 1, 2.5, and 5 mmol, while keeping all other reaction parameters fixed.

Fig. 1. XRD patterns of pure BiVO_4 and $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples with different Bi_2S_3 contents.

Fig. 2. FESEM images of BiVO_4 (a), $0.25\text{Bi}_2\text{S}_3/\text{BiVO}_4$ (b), $0.5\text{Bi}_2\text{S}_3/\text{BiVO}_4$ (c), $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$ (d), $2.5\text{Bi}_2\text{S}_3/\text{BiVO}_4$ (e), and $5\text{Bi}_2\text{S}_3/\text{BiVO}_4$ (f); (g) Bi, V, O, and S elemental mappings of $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$; TEM images of BiVO_4 (h) and $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$ (i); (j) HRTEM image of $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$.

Fig. 2(a) shows the SEM image of the as-prepared BiVO_4 sheets. With a Bi_2S_3 content of 0.25 mmol, a fraction of the flake-like $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ nanoparticles grows directly into peony-like particles, but some of them exhibit disk-like aggregates (Fig. 2(b)). With increasing Bi_2S_3 content, most of the $0.5\text{Bi}_2\text{S}_3/\text{BiVO}_4$ nanoparticles grow into peony-like aggregates (Fig. 2(c)), and the $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$ sample is almost entirely made of peony-like aggregates of flake-like nanoparticles (Fig. 2(d)). Upon increasing the Bi_2S_3 content (≥ 2.5 mmol), the average particle size of the $2.5\text{Bi}_2\text{S}_3/\text{BiVO}_4$ and $5\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples decreases drastically, but their peony-like morphology is maintained (Fig. 2(e) and (f)). However, some fragments are observed on the surface of the $2.5\text{Bi}_2\text{S}_3/\text{BiVO}_4$ and $5\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples, while a fraction of the peony-like $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ particles aggregate. These results indicate that the Bi_2S_3 content affects the morphology of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples, with $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$ showing a more regular peony-like morphology. The EDS elemental mappings of $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$ show that all elements (Bi, V, O, and S) are uniformly distributed throughout the scan area of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ heterojunction (Fig. 2(g)). This suggests the presence of Bi_2S_3 and BiVO_4 in the composites, resulting in the formation of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ heterojunction.

Consistent with the FESEM images, the TEM images show that BiVO_4 and $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$ exhibit a sheet-like (Fig. 2(h)) and peony-like (Fig. 2(i)) morphology, respectively. The HRTEM

image of $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$ (Fig. 2(j)) further confirms the close interfacial contact and continuity of lattice fringes between BiVO_4 and Bi_2S_3 . The fringe spacings of 0.398 and 0.272 nm correspond to the (220) and (301) planes of Bi_2S_3 (JCPDS No. 17-0320) [34], respectively, while the fringe spacing of 0.309 nm is consistent with the (121) plane of BiVO_4 (JCPDS No. 14-0688) [38]. In the hydrothermal reaction, the strong EDTA ligand not only forms a stable complex with Bi^{3+} , but also acts as the directing agent, orienting pure BiVO_4 along the (121) facet to form well-defined 2D sheets. L-Cysteine was employed as both sulfur source and soft template. As a sulfur source, L-cysteine has many functional groups ($-\text{NH}_2$, $-\text{COOH}$, and $-\text{SH}$), and the $-\text{SH}$ group has a strong tendency to coordinate Bi^{3+} . The $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ heterojunction was prepared from an ion-exchange reaction between $-\text{SH}$ and BiVO_4 [33]. Moreover, as a soft template, the $-\text{NH}_2$ group can react with the $-\text{COOH}$ group of another L-cysteine molecule to form a dipeptide or polypeptide, which preferentially grows along the (040) direction and forms Bi_2S_3 under hydrothermal treatment for 24 h [24]. Therefore, $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ does not form a sheet-like morphology such as that of pure BiVO_4 after the addition of L-cysteine, but exhibits a peony-like morphology composed of flake-like nanoparticles. However, if the Bi_2S_3 content reaches or exceeds 2.5 mmol, the growth of BiVO_4 along the (040) direction is largely suppressed due to the formation of Bi_2S_3 . A

Fig. 3. Schematic illustration of the formation mechanism of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ composites.

possible formation mechanism of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ composites proposed on the basis of the experimental results discussed above is shown in Fig. 3.

3.3. Optical absorption properties

The optical absorption properties of pure BiVO_4 and of $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples with different Bi_2S_3 contents were measured using a UV-vis diffuse reflectance spectrometer, and the results are shown in Fig. 4. Fig. 4(a) shows that the absorption edge of BiVO_4 is located at about 510 nm, within the visible light region. Compared to BiVO_4 , the optical absorption of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples in the visible region increases because Bi_2S_3 can harvest more photons due to its small band gap, resulting in a strong absorption in the visible region [24]. The band gap (E_g) of a semiconductor can be estimated by the following equation:

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

where ν is the frequency of the light, h is Planck's constant, α is the absorption coefficient, and A is a constant; moreover, n is a constant depending on the transition type of the semiconductor, and takes the values of 1 and 4 for direct and indirect transitions, respectively [39]. The band gap of the as-prepared

samples was determined from a plot of $(\alpha h\nu)^2$ vs. the photon energy ($h\nu$) (Fig. 4b) [40]. The bandgap values of BiVO_4 and Bi_2S_3 were calculated to be 2.42 and 1.27 eV, respectively. These results are in good agreement with previous reports [15,41]. The visible light absorption capacity of BiVO_4 is greatly enhanced after coupling with Bi_2S_3 ; hence, the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples are expected to show high photocatalytic activity under visible light irradiation.

3.4. Photocatalytic performance

To investigate the effects of the Bi_2S_3 content on the photocatalytic activity of BiVO_4 , we tested the degradation of a glyphosate solution by P25, BiVO_4 , and $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples with different Bi_2S_3 contents under visible light irradiation. As shown in Fig. 5(a), pure BiVO_4 shows a degradation percentage of 36%, while P25 TiO_2 exhibits a lower degradation rate of 24%. The degradation rate increases with increasing Bi_2S_3 content; in particular, the $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$ sample shows the highest photocatalytic activity, with a degradation rate of 79% after 180 min. The enhanced photocatalytic activity of $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ can be attributed to the formation of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ heterostructure with exposed (040) facets, which

Fig. 4. (a) UV-vis diffuse reflectance spectra of pure BiVO_4 and $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples with different Bi_2S_3 contents; (b) Kubelka-Munk plots of BiVO_4 and Bi_2S_3 .

Fig. 5. Photocatalytic degradation of glyphosate under visible light irradiation of P25, BiVO₄, and Bi₂S₃/BiVO₄ samples.

results in high light absorption efficiency and efficient separation of electron-hole pairs [15,42,43]. However, when the Bi₂S₃ content reaches or exceeds 2.5 mmol, the glyphosate degradation rate decreases and becomes lower than that of pure BiVO₄. This might be attributed to the decrease of the contact interface (that reduces the separation efficiency of electrons and holes), the poor charge transport in Bi₂S₃ [30], and the low-lying valence band of Bi₂S₃, which cannot drive the photocatalytic oxidation reaction. This result indicates that an optimum amount of Bi₂S₃ is required to achieve the best photocatalytic performance in the Bi₂S₃/BiVO₄ heterostructures. Moreover, cycling runs were carried out for the 1Bi₂S₃/BiVO₄ sample because of its importance in practical applications. Fig. 5(b) shows that the degradation rates of glyphosate in the second and third run are 66% and 59%, corresponding to 84% and 75% photocatalytic activity retention, respectively. This suggests that 1Bi₂S₃/BiVO₄ exhibits relative stability and reusability during the photocatalytic reaction process. In addition, the corresponding XRD pattern (Fig. 5(c)) reveals that there are no changes in the crystal structure of 1Bi₂S₃/BiVO₄ after three cycles, further confirming the relative stability of the photocatalyst.

3.5. Mechanism of enhanced photocatalytic performance

In order to confirm the possible mechanism of the enhanced photocatalytic performance under visible light irradiation, we investigated the exposure of the (040) crystal facets and carried out transient photocurrent tests as well as EIS measurements.

3.5.1. Exposure of (040) crystal facets

The effect of the Bi₂S₃ content on the ratio of the intensities of the (040) and (121) diffraction peaks (I_{040}/I_{121}) and on the photocatalytic degradation rate of glyphosate over the Bi₂S₃/BiVO₄ samples is illustrated in Table 1. The amount of Bi₂S₃ has no effect on the crystal phase of BiVO₄, because all Bi₂S₃/BiVO₄ samples are monoclinic (Fig. 1). However, the Bi₂S₃ content has a major influence on the morphology of the Bi₂S₃/BiVO₄ samples (Fig. 2), the I_{040}/I_{121} ratio, and the photocatalytic degradation rate of glyphosate (Table 1). It is worth noting that a gradual decrease in relative intensity and sharpness is observed for the (040) diffraction peak with the increase of the Bi₂S₃ content, and the I_{040}/I_{121} ratio decreases

with increasing Bi₂S₃ content. This suggests that the growth along the (040) direction stopped due to the coupling with Bi₂S₃. Because the VB and conduction band (CB) energy levels of the (040) and (110) facets are different, the photoinduced electrons and holes, which transfer to the (040) and (110) facet, respectively, can be separated [44]. In addition, the (040) facets on the surface of monoclinic BiVO₄ are multi-electron transfer centers and serve as active sites for the photocatalytic reaction [16]. Chen et al. [15] showed that BiVO₄ samples with a greater I_{040}/I_{121} ratio exhibit higher photocatalytic activities, because BiVO₄ sheets with a shorter time and migration distance for photogenerated carriers to reach the surface lead to a more efficient separation and transport of photogenerated electrons and holes. However, in this study the I_{040}/I_{121} ratio is not consistent with the measured degradation rates of glyphosate over the Bi₂S₃/BiVO₄ samples, because of the coupling with Bi₂S₃.

3.5.2. Photoelectrochemical properties

In order to evaluate the photogenerated charge separation efficiency and charge transport properties under visible light irradiation ($\lambda > 420$ nm), transient photocurrent tests and EIS measurements were carried out, and the results are shown in Fig. 6. The transient photocurrent response measurements were employed to compare the photoinduced charge separation efficiency of pure BiVO₄ and Bi₂S₃/BiVO₄ samples with different Bi₂S₃ contents. As shown in Fig. 6(a), the BiVO₄ and Bi₂S₃/BiVO₄ samples exhibit a stable photocurrent response for several on-off cycles under visible light irradiation. The photocurrent is generated immediately after the light source is switched on, due to the separation of electron-hole pairs at the

Table 1

Effect of the Bi₂S₃ content on the ratio of the intensities of the (040) and (121) diffraction peaks and on the photocatalytic degradation rate of glyphosate over Bi₂S₃/BiVO₄ samples.

Sample	XRD I_{040}/I_{121}	Degradation rate of glyphosate (%)
BiVO ₄	0.95	36
0.25Bi ₂ S ₃ /BiVO ₄	0.68	51
0.5Bi ₂ S ₃ /BiVO ₄	0.56	69
1Bi ₂ S ₃ /BiVO ₄	0.56	79
2.5Bi ₂ S ₃ /BiVO ₄	0.30	29
5Bi ₂ S ₃ /BiVO ₄	0.22	21

Fig. 6. Transient photocurrent responses (a) and EIS Nyquist plots (b) of BiVO₄ and Bi₂S₃/BiVO₄ samples under visible light irradiation.

electrode/electrolyte interface [20,37,45]. Once the light source is turned off, the photocurrent rapidly decreases to zero. With the exception of 2.5Bi₂S₃/BiVO₄, the Bi₂S₃/BiVO₄ samples exhibit a stronger transient photocurrent than BiVO₄, indicating an improved interfacial charge transfer due to the formation of the Bi₂S₃/BiVO₄ heterostructure, thus inhibiting the recombination of photogenerated charges and extending the lifetime of the photoinduced electrons and holes. The 1Bi₂S₃/BiVO₄ sample shows the highest transient photocurrent density among all photocatalysts, resulting in the best photocatalytic activity for glyphosate degradation.

Because the charge transport properties at the electrode/electrolyte interface play an important role in the photocatalytic activity, EIS measurements were performed under visible light irradiation. The Nyquist plots of pure BiVO₄ and of Bi₂S₃/BiVO₄ samples with different Bi₂S₃ contents, reflecting the charge-transfer resistance at the electrode/electrolyte interface, are shown in Fig. 6(b). The radius of the arc is related to the charge-transfer resistance occurring on the surface of the electrode, with a smaller arc radius denoting a higher charge-transfer efficiency [45]. Fig. 6(b) shows that the arc radius of the 1Bi₂S₃/BiVO₄ electrode is the smallest among all photocatalyst electrodes, confirming that the fastest charge transport takes place in the 1Bi₂S₃/BiVO₄ electrode. Furthermore, with the exception of 2.5Bi₂S₃/BiVO₄, the Bi₂S₃/BiVO₄ samples exhibit a smaller arc radius than that of the BiVO₄ electrode. These findings are similar to the transient photocur-

rent results. As mentioned above, a more effective charge separation and faster interfacial charge transfer occurs in 1Bi₂S₃/BiVO₄, greatly contributing to its enhanced photocatalytic performance.

3.5.3. Active species in the glyphosate degradation

In addition, active species trapping experiments and ESR measurements were performed to identify the reactive species in the photocatalytic process. Fig. 7 shows the photocatalytic degradation of glyphosate over 1Bi₂S₃/BiVO₄ in the absence and presence of scavengers (IPA, BQ, EDTA, and K₂Cr₂O₇) under visible light irradiation for 3 h. When charge carrier scavengers (EDTA for h⁺ or K₂Cr₂O₇ for e⁻) were added in the reaction system [46,47], the photocatalytic degradation of glyphosate was significantly inhibited. These results suggest that photogenerated electrons and holes are the main active species involved in the photocatalytic reaction process. Moreover, the addition of radical scavengers (IPA for ·OH and BQ for ·O₂⁻) resulted in a decrease in the photocatalytic reaction rate. These results indicate that the photocatalytic oxidation of glyphosate over 1Bi₂S₃/BiVO₄ is mainly driven by photogenerated electrons and holes. The presence of ·OH was further confirmed by the ESR analysis, as shown in Fig. 8. In comparison, no ESR signals were detected when the reaction was carried out in the dark. Similarly, no ESR signal was observed

Fig. 7. Photocatalytic degradation of glyphosate with 1Bi₂S₃/BiVO₄ in the absence and presence of scavengers under visible light irradiation for 3 h.

Fig. 8. ESR spectra obtained from samples containing BiVO₄ or Bi₂S₃/BiVO₄ along with the DMPO spin probe under visible light irradiation. The controls consist of the sample containing the spin probe alone under visible light or the sample containing the spin probe and the photocatalysts before exposure to visible light.

when no photocatalyst was added. These findings suggest that no $\cdot\text{OH}$ radicals were formed. However, the four characteristic peaks of DMPO- $\cdot\text{OH}$ adducts (in 1:2:2:1 intensity ratio, consistent with previous studies of $\cdot\text{OH}$ adducts [52–54]) appeared when the BiVO_4 photocatalyst was added. This suggests the formation of strong and nonselective $\cdot\text{OH}$ radicals. $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$ exhibited stronger signals due to the higher concentration of produced $\cdot\text{OH}$ radicals compared to BiVO_4 , indicating that a larger amount of $\cdot\text{OH}$ radicals is formed in the presence of $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$ than BiVO_4 . Furthermore, the intensity of the DMPO- $\cdot\text{OH}$ signals increased with increasing irradiation time.

To determine the origin of the high photocatalytic activity of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples, we investigated the energy level alignment of the photocatalysts. The conduction (E_{CB}) and valence band potentials (E_{VB}) of Bi_2S_3 and BiVO_4 were calculated empirically using the following equations:

$$E_{\text{CB}} = \chi - E_{\text{e}} - 0.5E_{\text{g}} \quad (3)$$

$$E_{\text{VB}} = E_{\text{CB}} + E_{\text{g}} \quad (4)$$

where E_{g} is the band gap of the semiconductor, E_{e} is the energy of free electrons on the hydrogen scale (4.5 eV), and χ is the absolute electronegativity of the semiconductor. The χ value of a compound semiconductor is calculated as the geometric mean of the absolute electronegativity of the constituent atoms. Taking the absolute electronegativity values for Bi, V, S, and O as 4.69, 3.6, 6.22, and 7.54, respectively, the calculated χ values of Bi_2S_3 and BiVO_4 are 5.56 and 6.16 eV, respectively. The calculated VB potential of BiVO_4 ($E_{\text{VB}} = 2.87$ eV vs. NHE) is more positive than that of Bi_2S_3 ($E_{\text{VB}} = 1.69$ eV vs. NHE), while the calculated CB potential of Bi_2S_3 ($E_{\text{CB}} = 0.42$ eV vs. NHE) is more negative than that of BiVO_4 ($E_{\text{CB}} = 0.45$ eV vs. NHE) [29,32]. Therefore, the energy levels of Bi_2S_3 and BiVO_4 are well matched and the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ heterojunction could be formed, favoring the separation of photogenerated charge carriers. On the basis of the above results, a possible mechanism for the enhanced photocatalytic activity of $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ is schematically illustrated in Fig. 9. Upon irradiation with visible light, the electrons of both BiVO_4 and Bi_2S_3 are promoted from the VB into the CB, leaving holes behind. As the visible light absorption capacity of $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ is better than that of BiVO_4 , a higher

number of electron-hole pairs are generated over $\text{Bi}_2\text{S}_3/\text{BiVO}_4$. The photogenerated electrons in the CB of Bi_2S_3 transfer to BiVO_4 [29], then react with adsorbed O_2 to yield $\cdot\text{O}_2^-$, and subsequent redox reactions may occur. The photogenerated holes formed in the VB of BiVO_4 react with the adsorbed $\text{H}_2\text{O}/\text{OH}^-$ ions to produce $\cdot\text{OH}$ or directly oxidize glyphosate. Therefore, the photogenerated electrons and holes can be efficiently separated at the interfaces of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ heterostructures. Eventually, the $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals also drive the glyphosate oxidation reaction to form PO_4^{3-} and other ions; in this work, the PO_4^{3-} concentration was determined to assess the photocatalytic degradation percentage of glyphosate. As a result, the photocatalytic activity of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ heterostructures was greatly enhanced due to the formation of the heterostructure and the improved absorption of visible light.

4. Conclusions

$\text{Bi}_2\text{S}_3/\text{BiVO}_4$ (040) heterojunctions with various morphologies were successfully synthesized by a one-pot hydrothermal method using L-cysteine as sulfur source/soft template and EDTA as directing agent. BiVO_4 showed an enhanced visible light absorption capacity after coupling with Bi_2S_3 , owing to the formation of a $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ heterojunction. The coupling with Bi_2S_3 had a significant influence on the growth of (040) and (121) facets, as well as on the morphology of the $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ samples. When the amount of added L-cysteine reached 1 mmol, $1\text{Bi}_2\text{S}_3/\text{BiVO}_4$ assumed a peony-like morphology. Photoelectrochemical performance tests highlighted the enhanced charge separation and efficient transport of photogenerated charge carriers in $\text{Bi}_2\text{S}_3/\text{BiVO}_4$. The enhanced photocatalytic activity of $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ could be attributed to the enhanced visible light absorption and the formation of the heterojunction structure. In addition, $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ exhibited relative stability and reusability. The simple method presented in this work could be used to fabricate composite photocatalysts with high activity for different applications, such as photocatalytic degradation of organic pollutants, photocatalytic splitting of water, and photocatalytic reduction of carbon dioxide.

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Fig. 9. Mechanism for the enhanced photocatalytic activity of $\text{Bi}_2\text{S}_3/\text{BiVO}_4$.

Graphical Abstract

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One-pot synthesis of peony-like Bi₂S₃/BiVO₄(040) with high photocatalytic activity for glyphosate degradation under visible light irradiation

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Peony-like Bi₂S₃/BiVO₄ was prepared using EDTA as directing agent and L-cysteine as sulfur source and soft template; the enhanced photocatalytic activity of Bi₂S₃/BiVO₄ could be attributed to its improved absorption capability and charge separation.

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一锅法合成在可见光下具有高效降解草甘膦的牡丹状 $\text{Bi}_2\text{S}_3/\text{BiVO}_4(040)$ 复合光催化剂

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摘要: 草甘膦是一种广谱除草剂, 2015年世界卫生组织国际癌症研究机构宣布草甘膦可能对人类致癌(2A类)。单斜白钨矿型 BiVO_4 是一种较广泛研究的可见光光催化剂, 但由于其光生电子和空穴迁移慢且容易复合而导致其光催化活性低。此外, 有研究表明, BiVO_4 的(040)晶面易于光生载流子分离, 从而提高其光催化性能。 Bi_2S_3 的带隙能为1.27 eV, 能被全可见光(400–800 nm)激发。 Bi_2S_3 的导带和价带位置与 BiVO_4 匹配, 能形成异质结, 从而提高其光催化活性。

本文以EDTA为导向剂, L-半胱氨酸为硫源和软模板, 采用一锅水热法制备了单斜白钨矿型 BiVO_4 , 主要以(040)晶面为暴露面的 $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ 复合光催化剂。采用钼锑抗分光光度法测定草甘膦最终光催化降解产物之一 PO_4^{3-} 浓度, 来计算草甘膦的降解率。X射线衍射(XRD)结果表明, $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ 复合光催化剂只含 Bi_2S_3 和 BiVO_4 两种成分, 没有其他晶相存在。场发射扫描电子显微镜(FESEM)显示, 纯 BiVO_4 为片状结构, 随着 Bi_2S_3 复合量增加, $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ 的形貌为小片组成的牡丹状; 但 Bi_2S_3 复合量进一步增加, $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ 颗粒聚集严重。XRD, FESEM和高分辨透射电子显微镜(HRTEM)结果表明, Bi_2S_3 复合量对 $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ 样品(040)和(121)面晶生长及形貌有显著影响。 Bi_2S_3 的复合提高了 $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ 对可见光的吸收能力, 经计算 BiVO_4 和 Bi_2S_3 带隙能分别为2.42和1.27 eV。随着 Bi_2S_3 复合量增加, $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ 的光催化活性逐渐提高, 至1 mmol时最高, 对草甘膦的降解率为纯 BiVO_4 的2.2倍; 但随着 Bi_2S_3 复合量进一步增加, $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ 的光催化活性反而下降, 可能是由于 Bi_2S_3 量太多包覆在 BiVO_4 表面而 Bi_2S_3 光催化性能很差的缘故。

瞬态光电流测试和电化学阻抗谱的结果证实, $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ 比 BiVO_4 具有更有效的电荷分离和更快的界面电荷转移能力。活性成分捕获剂实验表明, 加入空穴捕获剂EDTA或电子捕获剂 $\text{K}_2\text{Cr}_2\text{O}_7$ 完全抑制了草甘膦的降解。ESR谱证明羟基自由基·OH的存在。通过计算, 得出 BiVO_4 的价带电位($E_{\text{VB}} = 2.87 \text{ eV vs. NHE}$)比 Bi_2S_3 ($E_{\text{VB}} = 1.69 \text{ eV vs. NHE}$)正, 而 Bi_2S_3 ($E_{\text{VB}} = 0.42 \text{ eV vs. NHE}$)的导带电位比 BiVO_4 ($E_{\text{VB}} = 0.45 \text{ eV vs. NHE}$)负, 能带匹配, 即光生电子从 Bi_2S_3 迁移至 BiVO_4 , 光生空穴从 BiVO_4 迁移至 Bi_2S_3 , 从而将光生电子与空穴有效分离利用, 达到提高其光催化性能的目的。 $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ 样品对草甘膦的光催化降解活性提高, 主要是由于 $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ 异质结结构的形成提高了其对可见光的吸收能力和电子空穴对的分离效率。此外, $\text{Bi}_2\text{S}_3/\text{BiVO}_4$ 具有相对稳定性和可重复使用性。该方法简单, 可制备用于光催化降解有机污染、光催化裂解水和光催化还原二氧化碳等不同领域的高活性复合光催化剂。

关键词: $\text{BiVO}_4(040)$; $\text{Bi}_2\text{S}_3/\text{BiVO}_4(040)$; 异质结; 光催化; 草甘膦

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