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Review

Recent advances in visible light Bi-based photocatalysts

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ABSTRACT

Photocatalysis is considered to be an effective solution for the current energy and environmental crises caused by industrial development. However, the practical application of conventional oxide photocatalysts is restricted by poor visible light adsorption because of their wide band gaps. The study of photocatalysts with a narrow band gap is thus a hot topic. Among oxide photocatalysts, Bi-based photocatalysts have attracted much interest because of their high visible light photocatalytic activity. This review summarizes recent advances into the type, preparation method, morphology control, composite construction, and properties of Bi-based photocatalysts. Finally, this review ends with a discussion on the future development of Bi-based photocatalysts in this exciting research area.

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1. Introduction

Photocatalysis is a newly developed photochemical technique and has been researched since the 1970s. It is based on the promotion of oxidation-reduction reactions by photoexcited electrons and holes from semiconductors under light irradiation. It is a green technique that can be used to produce hydrogen by photocatalytic water splitting, and it can also be used for the oxidation of organic pollutants into CO₂, H₂O, and inorganic ions without secondary pollution. Therefore, photocatalysis is considered to be a promising method of environmental remediation [1–6].

TiO₂ has been widely studied since Fujishima's [4] report on the generation of H₂ and O₂ by photoelectrochemical water splitting using TiO₂ and Pt electrodes. However, because of its large band gap of ~3.2 eV, TiO₂ is only active in the UV region, which corresponds to ~4% of incident solar light. Many tech-

niques such as elemental doping, dye sensitization and composite construction have been used to modify TiO₂ for an improvement in its photocatalytic performance under visible light. Nevertheless, no significant breakthrough has been made in this area [7–10]. Therefore, the development of novel visible light photocatalysts is important in the field of photocatalysis.

Recently, much attention has been given to a series of visible light active Bi-based photocatalysts. Many Bi³⁺-containing compounds have been found to possess a narrow band gap and exhibit high visible light photocatalytic activity because of the hybridized O 2p and Bi 6s² valence bands [11–14]. Additionally, the empty 6s orbital of Bi⁵⁺ also supports Bi⁵⁺-containing compounds with high visible light photocatalytic activity [15,16]. Bi-based compounds and composites have therefore attracted much research interest in terms of their synthesis, characterization and photocatalytic properties, and they have become an important family of visible light photocatalysts.

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2. Bi-based compounds

Many Bi-based compounds have been reported and include Bi_2O_3 , Bi_2S_3 , $\text{Bi}_2\text{Ti}_2\text{O}_7$, Bi_2WO_6 , and BiOCl etc., and they can generally be classified as binary oxides or sulfides, multi-component oxides, and oxyhalides. The band gap, conduction band (CB) and valence band (VB) energies of typical Bi-based semiconductors are listed in Table 1. Most of these are active in the visible light region with a band gap of less than 3.0 eV, except for BiOF and BiOCl . The band gaps of Bi_2S_3 , BiOI and KBiO_3 are less than 2.0 eV, indicating their ability to absorb visible light of longer wavelengths. The photocatalytic activity of semiconductors is not only affected by their band gap, but also by their structures and positions. Therefore, the synthesis and photocatalytic activity of Bi-based compounds have been extensively investigated.

2.1. Bi oxides and sulfides

Bi_2O_3 , a common oxide semiconductor, is widely used in the fields of chemical engineering and electronics. Bi_2O_3 has several crystal structures including α -, β -, and γ -phases, with an indirect band gap of 2.6–2.9 eV, which differs for different crystal structures [17,32–35]. In aqueous solution, Bi_2O_3 nanoparticles can be excited under light irradiation by absorbing photons with energies higher than the band gap energy. Photoinduced electrons and holes are thus generated and react with O_2 and H_2O , forming free radicals such as $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$, respectively. These radicals have high oxidizing abilities and can oxidize organic pollutants adsorbed on the surface of Bi_2O_3 nanoparticles.

Zhang et al. [33] synthesized Bi_2O_3 nanopowders via a simple sonochemical route. They found that the obtained nano-

crystallite Bi_2O_3 effectively degraded methyl orange (20 mg/L) by 86% within 100 min under visible light illumination ($\lambda > 400$ nm). However, the photocatalytic efficiency of pure Bi_2O_3 is still not high enough. Several methods have been used to improve the photocatalytic activity of Bi_2O_3 such as metal ion doping, and multi-component composite construction. For example, Bi_2O_3 doped with Pd(II) and V(V) exhibited higher photocatalytic activity [34,36,37]. Huang et al. [38] prepared pure α - Bi_2O_3 and mixed phases of α - Bi_2O_3 , $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ and $\text{Bi}_2\text{O}_2\text{CO}_3$, using a hydrothermal method by optimizing the amount of NaOH and ammonia added. The mixed-phase samples showed higher activity than the single-phase α - Bi_2O_3 for the degradation of rhodamine B under UV light.

Bi_2S_3 , a Bi sulfide with a narrow band gap of 1.3–1.7 eV, is easily excited by visible light to generate photoinduced electron-hole pairs. It has been found that Bi_2S_3 crystals usually exist in an orthorhombic phase and have a layered structure. They have different morphologies such as nanoplates, nanorods, and nanowires [39]. Bi_2S_3 is normally synthesized by a hydrothermal method using an alcohol and/or water as the solvent, $\text{Bi}(\text{NO}_3)_3$ or BiCl_3 as the Bi source, and sulfur, thiocetamide, or sulfourea etc. as the S source. For instance, Bao et al. [40] reported the synthesis of Bi_2S_3 nanowires by a hydrothermal reaction between $\text{Bi}(\text{NO}_3)_3$ and mercaptosuccinic acid. The obtained Bi_2S_3 nanowires exhibited nonlinear current-voltage (I-V) characteristics and excellent photoresponse. The Bi_2S_3 materials prepared by the different methods have different morphologies and also different band gaps. Researchers are thus attempting to prepare Bi_2S_3 materials using various methods.

2.2. Bi-based multi-component oxides

Bi-based multi-component oxides are a series of oxysalts including $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, Bi_2WO_6 , BiVO_4 , and Bi_2MoO_6 etc., and they are considered to be hybrid oxides composed of Bi_2O_3 and metal oxides such as TiO_2 , W_2O_3 , V_2O_5 , and Mo_2O_3 etc. with stoichiometric ratio, and usually have a layered Aurivillius structure, i.e. $[\text{Bi}_2\text{O}_2]^{2+}$ layers inter-grown with metal oxide layers along the c axis.

Bi titanates are a family that includes various phases hybridized by Bi_2O_3 and TiO_2 units. While those used for photocatalysis are mainly $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Bi}_2\text{Ti}_2\text{O}_7$, and $\text{Bi}_{12}\text{Ti}_{20}\text{O}_{70}$ [6]. As shown in Fig. 1, their crystal structures consist of connected BiO_n and TiO_n polyhedrons with different n values. The VB of Bi titanates consists of a $6s^2$ filled orbital and an O 2p orbital, and the CB consists of a Ti 3d empty orbital. In contrast to TiO_2 , whose VB and CB consist of O 2p and Ti 3d orbitals, respectively, Bi titanates have a narrower band gap of 2.5–2.8 eV, and can thus be easily excited by visible light for higher photocatalytic activity [14,19]. Bi titanates can be synthesized by hydrothermal and chemical-solution-decomposition methods [42]. Treatment with microwave irradiation or sensitization can further improve the photocatalytic activity of Bi titanates. Yang et al. [43] synthesized hierarchical flower-like $\text{Bi}_{12}\text{Ti}_{20}\text{O}_{70}$ by a microwave assisted hydrothermal method. The obtained $\text{Bi}_{12}\text{Ti}_{20}\text{O}_{70}$ exhibited enhanced visible light photocatalytic per-

Table 1
Band structures of Bi-based compounds.

General formula	Compounds	E_g (eV)	E_{CB}^a (eV)	E_{VB}^b (eV)
Bi_xMO_y	Bi_2O_3	2.6–2.9 [17]	0.16 ($E_g = 2.6$)	2.76
	Bi_2S_3	1.3–1.7 [18]	0.17 ($E_g = 1.3$)	1.47
	Bi_2WO_6	2.6–2.7 [13]	0.43 ($E_g = 2.6$)	3.03
	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Bi}_2\text{Ti}_2\text{O}_7$, $\text{Bi}_{12}\text{Ti}_{20}\text{O}_{70}$	2.5–2.7 [19]	0.21 ($E_g = 2.5$)	2.71
	Bi_2MoO_6	2.3–2.7 [20]	0.51 ($E_g = 2.3$)	2.81
	BiVO_4	2.4–2.5 [21]	0.34 ($E_g = 2.4$)	2.74
	$\text{Bi}_2\text{O}_2\text{CO}_3$	3.1–3.3 [22,23]	0.31 ($E_g = 3.1$)	3.41
	BiOX			
BiOX	BiOF	3.6 [24]	0.60	4.20
	BiOCl	3.5 [25]	0.15	3.65
	BiOBr	2.6 [26,27]	0.41	3.01
	BiOI	1.8–1.9 [25,26]	0.57 ($E_g = 1.8$)	2.36
	MBiO_3			
MBiO_3	NaBiO_3	2.6 [28]	–0.29	2.31
	KBiO_3	2.1 [29]	–0.20	1.90
	LiBiO_3	1.8 [29]	0.18	1.98
	AgBiO_3	2.5 [30]	0.28	2.78

^a Calculated using $E_{CB} = \chi - E^e - 0.5E_g$ [31], based on the E_g from the reference where χ is the absolute electronegativity of the semiconductor, E^e is the energy of free electrons on the hydrogen scale of ca. 4.5 eV, and E_g is the band gap of the semiconductor.

^b Calculated using $E_{VB} = E_{CB} + E_g$.

Fig. 1. Illustration showing the crystal structures of Bi titanates.

formance toward the degradation of rhodamine B, compared to that prepared by a conventional hydrothermal method. Li et al. [44] reported the synthesis of an I-sensitized $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{TiO}_2$ heterostructure, showing enhanced photocatalytic activity for the degradation of phenol under visible light. Lin et al. [45] first prepared a precursor by the liquid phase co-precipitation method, and then $\text{Bi}_2\text{Ti}_2\text{O}_7$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_{12}\text{TiO}_{20}$ photocatalysts that were loaded with TiO_2 were obtained by a high temperature solid state reaction of the precursor. They were then used for the decomposition of gaseous benzene.

Bi tungstate (Bi_2WO_6) is a narrow band gap ($E_g = 2.6\text{--}2.7\text{ eV}$) semiconductor with a perovskite layered structure, and it is composed of WO_6 layers (including double $[\text{O}]^{2-}$ and single $[\text{WO}_2]^{2+}$ layers) and $[\text{Bi}_2\text{O}_2]^{2+}$ layers, as shown in Fig. 2. It has a strong visible light absorption ability and high stability against photocorrosion, and is thus an important material in the fields of photocatalysis and photoelectrocatalysis [35,46–48].

Many methods have been developed to fabricate Bi_2WO_6 such as solid state reactions, liquid phase precipitations, sonochemical reactions, hydrothermal reactions, solvothermal reactions, and micro-emulsion methods etc. [48]. Solid state reactions, liquid phase precipitations, and sonochemical methods are rarely used currently since they are not suitable for the preparation of nanosized materials because of the required high temperature calcination. However, (microwave assisted) hydrothermal/solvothermal methods are extensively used and nanosized materials are easily prepared at low temperature. Yan et al. [49] fabricated nest-like, rod-like, and sheet-like Bi_2WO_6 nanomaterials using a hydrothermal method. They investigated the photocatalytic degradation of tetracycline and found that Bi_2WO_6 samples with three-dimensional structures

Fig. 2. Illustration of the crystal structure of Bi_2WO_6 .

exhibited higher activity than those with two-dimensional structures. Hu et al. [50] synthesized Bi_2WO_6 hollow nanoparticles by a solvothermal method, and the resultant Bi_2WO_6 nanoparticles showed high visible light photocatalytic activity toward the degradation of rhodamine B of up to 99% within 40 min. Zhang et al. [35] also systematically studied the controlled synthesis and enhanced properties of Bi_2WO_6 .

Bi molybdate (Bi_2MoO_6) is a kind of ternary metal oxide with a perovskite layered structure. The formula is usually $\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}$. Several phases of Bi_2MoO_6 are known and include α -, β -, and γ - Bi_2MoO_6 . As shown in Fig. 3, the crystal structure of Bi_2MoO_6 is similar to that of Bi_2WO_6 , and it is composed of $[\text{MoO}_2]^{2+}$ and $[\text{Bi}_2\text{O}_2]^{2+}$ layers connected via an intermediate $[\text{O}]^{2-}$ layer.

In early studies, Bi_2MoO_6 was used as a catalyst template for the catalytic synthesis of acraldehyde from propylene, as well as the synthesis of acrylonitrile by the oxidization of aniline. It was also studied in the fields of ionic conductors, solar cells, and gas sensors [52–55]. Recent investigations have indicated that Bi_2MoO_6 can serve as a visible light photocatalyst with excellent performance. Similar with Bi_2WO_6 , Bi_2MoO_6 can be fabricated by solid state reaction, liquid phase precipitation, sonochemical reaction, hydrothermal reaction, and solvothermal methods etc. Cuellar et al. [56] first prepared γ - Bi_2MoO_6 powders by a traditional solid-state reaction, and then a γ - Bi_2MoO_6 film with visible light photocatalytic activity was obtained from γ - Bi_2MoO_6 powder via a vapor deposition process. Wang et al. [57] prepared flower-like Bi_2MoO_6 by a hydrothermal method in the absence of surfactants, and found that the visible-light photocatalytic activity of flower-like Bi_2MoO_6 toward the degradation of rhodamine B was higher than that of those prepared by a traditional solid state reaction. Recently, an increasing amount of reports on the solvothermal synthesis of Bi_2MoO_6 have been published. Wang et al. [54] reported the synthesis of γ - Bi_2MoO_6 nanoplates by the solvothermal method in mixed solvents of ethanol and ethylene glycol, which showed high photocatalytic activity for the degradation of rhodamine B. Tian et al. [58] also prepared flower-like Bi_2MoO_6 microspheres by a solvothermal method in ethylene glycol and used it for the photocatalytic degradation of rhoda-

Fig. 3. Illustration of the crystal structure of Bi_2MoO_6 .

mine B. They found that 95% rhodamine B could be degraded within 2 h under visible light irradiation. Cruz et al. [20] found that the band gap of the Bi_2MoO_6 prepared by liquid phase precipitation was narrower than that of Bi_2MoO_6 prepared by a solid state reaction and by reflux methods.

Bi vanadate (BiVO_4) is another important ternary metal oxide, and it mainly exists in three crystalline phases--tetragonal zircon, tetragonal scheelite, and monoclinic scheelite. The tetragonal and monoclinic structures are shown in Fig. 4. The tetragonal scheelite and monoclinic scheelite phases can transform reversibly at 255 °C, while the tetragonal zircon phase will transform to the monoclinic scheelite phase irreversibly at 397–497 °C [59]. The monoclinic BiVO_4 exhibits higher photocatalytic activity than the other two phases under visible light irradiation ($\lambda > 420$ nm) because of its narrow band gap of 2.3–2.4 eV [59,60].

BiVO_4 can be fabricated by hydrothermal, sputtering, and microemulsion methods etc. Zhang et al. [61] obtained mixed-phase (tetragonal and monoclinic) BiVO_4 by the hydrothermal method, and the two phases could be controlled by adjusting the pH of the precursor solution. In particular, a pure tetragonal phase formed when $\text{pH} \leq 3.8$, while a pure monoclinic phase formed when $\text{pH} \geq 8.5$, and mixed phases formed in the pH range of 3.8–8.5. Madhusudan et al. [62] fabricated mesoporous BiVO_4 via a hydrothermal method combined with a subsequent calcination process. The obtained mesoporous BiVO_4 showed higher photocatalytic activity than nonporous BiVO_4 during the degradation of Congo red under visible light irradiation. Chen et al. [63] reported the synthesis of a V-rich monoclinic BiVO_4 thin film by sputtering. The photocurrent reached 1 mA/cm². The Bi/V ratio in the film could be effectively tuned using separate Bi_2O_3 and V sputtering targets instead of a single BiVO_4 target. The advantage of the hydrothermal method is that it is easy to prepare doped BiVO_4 or BiVO_4 based composites by changing the reactants. Ge et al. [64] found that BiVO_4 with different crystal phases could be obtained at different temperatures by microemulsion, and they further found that the mixed-phase (tetragonal and monoclinic) BiVO_4 exhibited better activity toward the photocatalytic degradation of methyl orange. Our group obtained fluorinated BiVO_4 by a hydrothermal process with NaF, and found that the photocatalytic activity of BiVO_4 was enhanced because of surface fluorination, which favored rhodamine B adsorption and hole transfer between rhodamine B molecules and the BiVO_4 photocatalyst [65]. In another report a hydrothermal method was used to prepare a $\text{BiVO}_4/\text{Bi}_2\text{O}_2\text{CO}_3$ composite photocatalyst

Fig. 4. Illustration of the crystal structures of BiVO_4 .

by adding urea into the reaction solution. The photocatalytic activity of the $\text{BiVO}_4/\text{Bi}_2\text{O}_2\text{CO}_3$ composite was found to be higher than that of both pure BiVO_4 and $\text{Bi}_2\text{O}_2\text{CO}_3$ [66].

Bismuthate, with the general formula ABiO_3 , is a series of Bi(V) containing ternary oxides. The 6s empty orbital of Bi(V) can contribute to both the top of the VB and the bottom of the CB, which may change their energies, and thus lead to a decrease in the band gap of Bi(V) containing compounds. Thus bismuthate also has high visible light photocatalytic activity [15,67]. The main type of bismuthate is an ilmenite phase composed of monovalent metal oxides and Bi(V) containing oxides such as NaBiO_3 , KBiO_3 , AgBiO_3 , and LiBiO_3 etc. NaBiO_3 has an indirect band gap with a layered structure consisting of NaO_6 octahedral and BiO_6 octahedral layers [28,67], as shown in Fig. 5. KBiO_3 and LiBiO_3 have a tunnel structure with Li^+ cations inside the tunnels, which results in KBiO_3 and LiBiO_3 having narrower band gaps of 2.1 and 1.8 eV, respectively.

To date, the synthesis of bismuthate has been relatively complicated and oxidants or high temperature have been required. Ramachandran et al. [29] added liquid bromine into the reaction solution to oxidize Bi(III) to Bi(V). Chen et al. [68] also used liquid bromine as an oxidant to fabricate NaBiO_3 hydrate. In other studies, BaBiO_3 containing both Bi(III) and Bi(V) has been synthesized. For instance, Tang et al. [69] obtained a high performance visible light BaBiO_3 photocatalyst by calcining composite oxides of Ba and Bi(III) in air at 650 °C. They proposed that Bi with different valence states favored the migration of photoinduced charge carriers.

Although Bi(V) containing compounds exhibit high photocatalytic activity, they are not stable under some conditions and suffer from photocorrosion. Chang et al. [70] found that a portion of NaBiO_3 transformed into BiOCl during the photocatalytic degradation of octyl phenol when $\text{pH} < 7$. Yu et al. [71] also found that a BiAg_xO_y photocatalyst corroded during the photocatalytic degradation of organic dyes. Bi(V) and Ag^+ in BiAg_xO_y transform into Bi(III) and Ag, respectively. The resultant Bi(III) reacts with the decomposition product CO_3^{2-} to form $\text{Bi}_2\text{O}_2\text{CO}_3$.

Bi subcarbonate ($\text{Bi}_2\text{O}_2\text{CO}_3$) has a Sillen layered structure, and was first reported by Grice et al. [72]. It consists of $[\text{Bi}_2\text{O}_2]^{2+}$ layers intercalated by CO_3^{2-} groups where the large Bi^{3+} cation with 8-coordination shows stereo active lone-pair behavior that may result in a Bi-O polyhedron with a large distortion [22], as shown in Fig. 6. $\text{Bi}_2\text{O}_2\text{CO}_3$ is widely used as an industrial additive, and is a raw material used in stomach medicine. Recent studies indicate that $\text{Bi}_2\text{O}_2\text{CO}_3$ is also a promising photocatalyst with good activity.

Zheng et al. [22] synthesized [001] facet exposed $\text{Bi}_2\text{O}_2\text{CO}_3$

Fig. 5. Illustration of the crystal structures of ABiO_3 .

Fig. 6. Illustration of the crystal structure of $\text{Bi}_2\text{O}_2\text{CO}_3$.

by controlling the growth rates of the different facets. Enhanced photocatalytic activity was observed for $\text{Bi}_2\text{O}_2\text{CO}_3$ compared to P25. Dong et al. [73] obtained $\text{Bi}_2\text{O}_2\text{CO}_3$ hollow microspheres by a template-free hydrothermal method. The photocatalytic removal of indoor NO over $\text{Bi}_2\text{O}_2\text{CO}_3$ hollow microspheres was more effective than P25, C-doped TiO_2 , and $\text{Bi}_2\text{O}_2\text{CO}_3$ particles. Madhusudan et al. [23] found that flower-like $\text{Bi}_2\text{O}_2\text{CO}_3$ microspheres prepared by a hydrothermal method exhibited higher activity than P25 for the photocatalytic degradation of rhodamine B while $\text{Bi}_2\text{O}_2\text{CO}_3$ plates showed lower activity than P25.

The band gap of $\text{Bi}_2\text{O}_2\text{CO}_3$ is dependent on the preparation method, the structure, and the morphology. For example, the band gap of the $\text{Bi}_2\text{O}_2\text{CO}_3$ synthesized by Zheng et al. [22] is 3.1

eV, whereas Madhusudan et al. [23] reported that their $\text{Bi}_2\text{O}_2\text{CO}_3$ microspheres showed an indirect band gap of 2.25 eV and a direct band gap of 3.3 eV at lower and higher energy levels, respectively.

The photocatalytic properties of Bi niobate [74], Bi tantalate [75], Bi silicate [76], and Bi phosphate [77] etc. have also been studied.

2.3. Bismuth oxyhalides

Bi oxyhalides include BiOF, BiOCl, BiOBr, and BiOI. The band structures of these Bi oxyhalides are shown in Fig. 7. The top of the VB and the bottom of the CB of BiOF are all at point Z, indicating the direct band gap structure of BiOF. For BiOCl, BiOBr and BiOI, the top of the VB is at point Z and the bottom of the CB is at point R, suggesting that they are indirect band gap semiconductors.

Bi oxyhalides have anisotropic layered structures with $[\text{Bi}_2\text{O}_2]^{2+}$ layers intercalated by X^- ions ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$), as shown in Fig. 8. The internal electric field that forms between the $[\text{Bi}_2\text{O}_2]^{2+}$ and X^- layers can promote the separation of photoinduced electrons and holes and thus enhance their photocatalytic activity [78–80]. The band gap of Bi oxyhalides decreases with an increase in the halogen's atomic number. In particular, BiOF has the widest band gap of 3.6 eV, with no visible light photocatalytic activity. However, its UV-driven photocatalytic activity is still competitive with P25 [24]. The band gap of BiOCl is in the range of 3.2–3.5 eV, which is similar to that of TiO_2 (3.0–3.2 eV). It has been reported that dye-sensitized BiOCl has good performance in rhodamine B

Fig. 7. Band structures of the Bi oxyhalides.

Fig. 8. Illustration of the crystal structure of BiOCl.

degradation under visible light irradiation [25,79–81]. BiOBr and BiOI have narrower band gaps of 1.8–1.9 and 2.6 eV, respectively, and this enables their excellent visible light photocatalytic activity [26,27].

Bi oxyhalide preparation methods mainly include hydrolysis, hydrothermal reactions, and solid state reaction methods etc. Hydrolysis is easily done with simple equipment requirement. It is based on the reaction between soluble Bi salts ($\text{Bi}(\text{NO}_3)_3$ and BiX_3) and oxyhalides or H_2O . Shi et al. [82] found that BiOCl powders synthesized by a hydrolysis reaction between BiCl_3 and Na_2CO_3 exhibited slight higher photocatalytic activity than P25. Using the hydrolysis method, Li et al. [83] also fabricated a BiOI nanosheet thin film at room temperature. However, there are still some shortcomings of the hydrolysis method such as poor dispersion, and uncontrollable morphology. Recently, surfactants, microwave, and ultrasound have been used to assist in hydrolysis procedures resulting in better control of material size and morphology. Using surfactants, Hao et al. [84] obtained BiOI microspheres in aqueous solution by a hydrolysis reaction between $\text{Bi}(\text{NO}_3)_3$ and KI.

Hydrothermal/solvothermal methods are also frequently used for the preparation of BiOX. Under high temperature and high pressure conditions, BiOX materials with different morphology, unique structure and non-stoichiometry can be obtained. Zhang et al. [26] synthesized BiOCl, BiOBr, and BiOI microspheres with high photocatalytic activity by a hydrothermal method. Solid state reactions can also be used to prepare BiOX. However, a high reaction temperature is required, which results in the products being polluted by metal ions from the reactants and not being easily purified. Lin et al. [85] reported that some Na^+ was present in Bi oxyhalide samples synthesized by a solid state reaction. As a result, it has hardly been used recently.

3. Structure control in Bi-based photocatalysts

Most Bi-based photocatalysts possess a strong visible light absorption ability and good photocatalytic activity. However, the application of individual Bi-based photocatalysts is still restricted because of the fast recombination of photogenerated charge carriers. Some of these photocatalysts have only a lim-

ited visible light absorption ability. Therefore, researchers have tried to improve the migration and separation efficiency of photogenerated charge carriers and the visible light absorption ability of Bi-based photocatalysts by controlling their structures and morphologies. This is done to further improve their visible light photocatalytic activity [86]. The main methods are heterostructure construction and solid solution preparation.

3.1. Semiconductor/semiconductor heterojunctions

The p-n junction is the main type of heterostructure in Bi-based photocatalysts. As shown in Fig. 9(a), when p-type and n-type semiconductors are brought into close contact, an internal electric field forms at the interface. The photoinduced holes in the n-type semiconductor move to the p-type semiconductor, while photoinduced electrons in the p-type semiconductor move to the n-type semiconductor. As a result, the photoinduced electrons and holes are effectively separated, thus enhancing the photocatalytic activity of photocatalysts [87].

A Z-scheme heterojunction is a special type of junction. In the p-n junction, the photoinduced electrons migrate from the CB of the semiconductor with the more negative CB edge to the CB of the other semiconductor, and the holes migrate from the VB of the semiconductor with the more positive VB edge to the VB of the other semiconductor. In the Z-scheme junction, the photoinduced electrons migrate from the CB of the semiconductor with the less negative CB edge to the VB of the other semiconductor and the holes are scavenged, as shown Fig. 9(b). The electrons are excited to the CB of the semiconductor with the more negative CB edge for reduction reactions [88]. The Z-scheme junctions of Bi-based semiconductors are a promising method for photocatalytic H_2 evolution and CO_2 reduction.

Bi oxyhalides can be coupled with other Bi oxyhalides or other semiconductors, which makes the construction of heterojunctions for higher photocatalytic activity flexible. For example, Xiao et al. [89] synthesized BiOI/BiOCl composites with different ratios by a hydrothermal method in ethylene glycol using BiI_3 and BiCl_3 as precursors. The photodegradation rate constant of bisphenol-A in the presence of the BiOI/BiOCl composite containing 10% BiOCl was more than 4 and 20 times larger than those of pure BiOI and P25, respectively. Both the

Fig. 9. Schematic illustration of the energy band diagram and the migration of electrons and holes in a common p-n heterostructure (a) and a Z-scheme heterostructure (b).

BiOI/TiO₂ nanotube heterojunction fabricated by Dai et al. [90] and the Bi₂WO₆/Ag₂O heterojunction fabricated by Yu et al. [91] showed high photocatalytic activity. The WO₃/Bi₁₂SiO₂₀ heterostructure synthesized by Wu et al. [92] exhibited much higher activity than Bi₁₂SiO₂₀ powders for the photocatalytic degradation of gaseous benzene. Madhusudan et al. [66] found that hierarchical BiVO₄/Bi₂O₂CO₃ nanocomposites also had higher photocatalytic activity toward rhodamine B degradation than both BiVO₄ and Bi₂O₂CO₃, as shown in Fig. 10 (U6, U12, U20 refer to BiVO₄/Bi₂O₂CO₃ samples with different BiVO₄ content, U0 refers BiVO₄). When BiVO₄/Bi₂O₂CO₃ composites are excited by visible light, the photoinduced electrons in BiVO₄ migrate to the CB of Bi₂O₂CO₃, and the photoinduced holes in Bi₂O₂CO₃ migrate to the VB of BiVO₄. Therefore, the recombination of electrons and holes was effectively suppressed. In this way the photocatalytic activity of BiVO₄/Bi₂O₂CO₃ composites are highly enhanced.

Because the bottom of the CB of most Bi-containing compounds is positive (> 0 eV), they are not able to directly photocatalyze H₂ generation and CO₂ reduction. Nevertheless, when coupling Bi-containing compounds with suitable semiconductors that have CBs that are negative enough to construct Z-scheme junctions, the photocatalytic reduction activity of the composite semiconductors may be enhanced and used for H₂

generation and CO₂ reduction. This is because the photoinduced electrons in the Bi-containing compounds can migrate to the VB of the coupled semiconductors and scavenge the holes, which prolongs the lifetime of the photoinduced electrons in the coupled semiconductors. Park et al. [93] developed two different Z-scheme systems of Pt-W/Mo-BiVO₄ and Zn_{0.2}Cd_{0.8}S for photocatalytic H₂ generation by water splitting. The redox couples used in these Z-scheme configurations were I-/IO₃⁻ and S²⁻/Sn²⁻, respectively.

3.2. Solid solutions

A solid solution is a solid-state solution with a homogeneous crystalline structure. It is formed by dissolving two or more crystalline phases under solid-state conditions. Unlike a mechanical mixture of solid powders, a solid solution remains a single phase and the components hybridize at the atomic scale. The structures and properties of solid solutions may change as the components change. The band gap of some solid solutions is even narrower than that of the individual components [94]. Therefore, the photocatalytic activity of solid solutions can be tuned by adjusting the components.

Similarities of the components such as ionic radius, polarization properties, electronegativities, and crystal structures are required, and thermal treatment is normally used for the formation of a solid solution. Various Bi-based solid solutions have been reported and include a Ce_{1-x}Bi_xO_{2-δ} (x = 0.1–0.5) solid solution fabricated by Marija et al. [95] through a self-propagating method, and a (Bi_{1-y}La_y)₄(V_{1-x}Me_x)₂O_{11-y} (x, y < 0.2, Me = Zr, Ga, Fe, Cu) solid solution synthesized by Politova et al. [96] using a solid state reaction. Shangguan et al. [97,98] prepared Bi_{0.5}La_{0.5}VO₄ and BiYWO₆ solid solutions loaded with a Pt-Cr₂O₃ cocatalyst, and found that they both exhibited visible light photocatalytic activity toward H₂ production by water splitting. This is because both the La5d and Y4d orbitals contributed to the CB, resulting in a negative shift of the CB edge solid solutions to a more negative position than the reduction potential of H⁺/H₂.

Among the Bi-containing compounds, the crystal structures of BiOCl, BiOBr, and BiOI are similar, and thus solid solutions can be formed between any two or three of them. Moreover, the band gap of the as-obtained solid solutions can be continuously tuned by manipulating the halogen content [80,99,100]. Wang et al. [25] obtained BiOCl_{1-x}I_x (x = 0.2–1.0) solid solutions by a soft chemical method. Its band gap was tunable from 1.92–2.31 eV. Liu et al. [101] prepared BiOCl_{1-x}Br_x solid solutions by a hydrothermal method, and found that the absorption edges of the BiOCl_{1-x}Br_x solid solutions gradually red shifted as the amount of Br increased (see Fig. 11(b)), despite their similar sheet-like morphologies (see Fig. 11(a)). They proposed that the enhanced photocatalytic activity of BiOCl_{1-x}Br_x is due to the internal electric field that formed between the [Bi₂O₂]²⁺ and Br⁻ layers. It is noticeable that bismuth oxyhalides are superior to form solid solutions. The formation of solid solutions can tune the band structures, further to monitor the photocatalytic properties, thus is an effective way for the development of novel visible-light photocatalysts.

Fig. 10. (a) UV-vis absorption spectra and color of BiVO₄ (U0), BiVO₄/Bi₂O₂CO₃ nanocomposite (U20) and pure Bi₂O₂CO₃ nanosheets. (b) Comparison of the photocatalytic activity of the as-prepared samples for the photocatalytic decolorization of rhodamine B in water [66].

Fig. 11. SEM images (a) and diffuse reflectance spectra (b) of BiOCl_{1-x}Br_x solid solutions with different Cl/Br atomic ratios [101].

3.3. Semiconductor/conductor heterojunctions

Although semiconductor/semiconductor heterojunctions are excellent for the separation of photogenerated electron-hole pairs, challenges remain such as choosing matched semiconductor couples. The use of conductive materials as electron capture agents can also effectively suppress electron-hole recombination, and can thus improve the photocatalytic activity of semiconductors. Therefore, the preparation of conductor/Bi-based semiconductor composites is an important approach to enhance the photocatalytic activity of Bi-based photocatalysts.

Metals such as Ag, Cu, and carbon materials like carbon nanotubes and graphene have been extensively used to construct conductor/Bi-based semiconductor composites. Reductants are mostly used to reduce metal ions to zero-valent metal nanoparticles that are embedded in semiconductors. Wang et al. [102] obtained Cu embedded Bi₂WO₆ with enhanced photocatalytic activity for phenol degradation by the hydrothermal method. Lei et al. [103] loaded Ag nanoparticles onto the surface of BiOBr_{1-x}I_x solid solutions, and found that the obtained Ag-BiOBr_{0.75}I_{0.25} composite exhibited much higher photocatalytic activity than a BiOBr_{0.75}I_{0.25} solid solution for rhodamine B degradation (see Fig. 12(b) and (h)). Here, Ag played an important role in promoting the separation of photogenerated electron-hole pairs to improve photocatalytic performance. It is not surprising that P25 showed lower activity than either Ag-BiOBr_{0.75}I_{0.25} or BiOBr_{0.75}I_{0.25} because of its wider band gap.

Carbon materials are good electron capture agents because of their high conductivity. Su et al. [104] coupled BiOI nanopar-

Fig. 12. Photodegradation curves of rhodamine B in the presence of various photocatalysts. (a) Ag-BiOBr; (b) Ag-BiOBr_{0.75}I_{0.25}; (c) Ag-BiOBr_{0.5}I_{0.5}; (d) Ag-BiOBr_{0.25}I_{0.75}; (e) Ag-BiOI; (f) blank; (g) P25; (h) BiOBr_{0.75}I_{0.25} [103].

ticles with multiwall carbon nanotubes by a solvothermal process, and found improved photocatalytic degradation efficiency toward acid orange. Graphene is a recently developed and excellent electron capture agent and it is composed of single-layer two-dimensional graphite. It has attracted much attention because of its superior electronic mobility at room temperature (1/300 the velocity of light), high Young's modulus (~1100 GPa), high thermal conductivity (~5300 W/(m·K)), excellent mobility of charge carriers at room temperature (200000 cm²/(V·s)), and extremely high theoretical specific surface area (~2600 m²/g). As shown in Fig. 13, when graphene-coupled semiconductors are excited under light irradiation the photoinduced electrons quickly transfer to the surface of the graphene and this can suppress electron-hole recombination. Recently, an increasing amount of reports have been published on graphene/Bi-based semiconductor composite photocatalysts.

The introduction of graphene into photocatalysts has been found to lead to a significant improvement in their photocatalytic performance. Fu et al. [107] found that BiVO₄/graphene composites had a much higher photocatalytic degradation efficiency toward methyl orange, methylene blue and rhodamine B than pure BiVO₄. Liu et al. [108] loaded graphene into Bi₂O₃, and found that the obtained composite possessed enhanced photocatalytic activity toward the degradation of methyl orange and methylene blue. Recently, graphene-based semiconductor photocatalysts, including Bi-based semiconductors, have

Fig. 13. Schematic illustration of photogenerated charge carrier transfer between a Bi-based photocatalyst and graphene.

been reviewed by Xiang et al. [109].

It is noteworthy that carbon materials including graphene have a strong light absorption ability, and may act as a shield against light absorption in semiconductors. Therefore, an appropriate load of carbon materials is necessary for the enhancement of photocatalytic activity. Madhusudan et al. [110] found that graphene-Bi₂O₂CO₃ composites exhibited higher photocatalytic activity than Bi₂O₂CO₃ microspheres for the degradation of rhodamine B, as shown in Fig. 14 (samples BG0, BG0.05, BG0.1, and BG0.2 were labeled based on the weight percentage of graphene used), and the graphene-Bi₂O₂CO₃ composite with 1.0 wt% graphene gave the best photocatalytic performance. Additionally, commonly used graphene is obtained by reducing graphene oxides. Researchers normally choose to prepare graphene oxide/semiconductor composites, and then graphene/semiconductor composites are prepared by reduction. The resultant graphene sometimes has a semiconductive property resulting in shift in the CB and VB of the composite photocatalysts [111,112].

Ionic liquids are also good electron capture agents because of their good ionic conductivity. Wang et al. [113] found that the visible light photocatalytic activity of BiOI toward methyl orange could be greatly enhanced by the in situ modification of the ionic liquid, 1-butyl-3-methylimidazolium iodide.

4. Morphology control of Bi-based photocatalysts

The photocatalytic properties of semiconductors are highly dependent on their morphologies and their sizes. To date, Bi-based photocatalysts with various morphologies have been synthesized using different methods (see Fig. 15). These include Bi₂S₃ nanowires [40], Bi₂O₃ nanoplates [114], Bi₂WO₆ microbelts [115], BiVO₄ hyperbranches [60], Bi₂O₂CO₃ flowers [23], BiOI hollow microspheres [116], BiOBr eggshells [117], and Bi₂MoO₆ hollow tubes [118] etc., which are generally classified as one dimensional (1D) materials (including nanowires, nanorods, nanotubes), two dimensional (2D) materials (including nanoplates, nanobelts, thin films), and three dimensional (3D) materials (including nanospheres, nanoflowers,

Fig. 14. Comparison of the photocatalytic activity of as-prepared graphene-Bi₂O₂CO₃ samples for the photocatalytic decolorization of rhodamine B in aqueous solution under ambient conditions [110].

Fig. 15. Bi-based photocatalysts with different morphologies. (a) Bi₂S₃ nanowires [40]; (b) Bi₂O₃ nanoplates [114]; (c) Bi₂WO₆ microbelts [115]; (d) BiVO₄ hyperbranches [60]; (e) flower-like Bi₂O₂CO₃ [23]; (f) BiOI hollow microspheres [116]; (g) BiOBr eggshells [117]; (h) Bi₂MoO₆ hollow tubes [118].

hollow microspheres).

Morphology control can be achieved either in the presence or absence of templates. The use of suitable templates can simplify the synthetic procedures for photocatalysts with specific morphologies. These templates include hard and soft templates. Organic and inorganic fibers are usually used as hard templates in 1D materials synthesis. 1D Bi-based photocatalysts can be prepared by loading Bi-containing precursors or compounds onto the fibers, and then removing the fibers by oxidation or thermal treatment. Zhang et al. [118] first synthesized polyacrylonitrile(PAN)/Bi₂MoO₆ hybrid microfibers as a precursor by a hydrothermal method. After removing the PAN by calcination, Bi₂MoO₆ microtubes were obtained and they gave a much higher rhodamine B degradation rate than the Bi₂MoO₆ prepared by a solid state reaction. Cui et al. [119] fabricated Bi₂WO₆ fibers by solution dipping combined with subsequent calcination at 500 °C using cotton fibers as templates. The photodegradation efficiency toward rhodamine B of the as-prepared Bi₂WO₆ fibers is ~4 times higher than that of bulk Bi₂WO₆ prepared by a solid state reaction. Tang et al. [120] prepared precursor fibers by electrospinning a mixed solution containing Bi(NO₃)₃, La(NO₃)₃, poly(vinyl pyrrolidone) and tetrabutyl titanate. Crystalline Bi_{3.25}La_{0.75}Ti₃O₁₂ fibers were then obtained by the thermal treatment of the precursor fibers. Dai et al. [90,121] fabricated BiOI/TiO₂ and Bi₂O₃/TiO₂ nanotube arrays by a novel impregnation/hydrolysis method using

TiO₂ nanotubes as templates. The as-prepared BiOI/TiO₂ and Bi₂O₃/TiO₂ nanotube arrays had much higher photocatalytic activity than pure BiOI, Bi₂O₃, and TiO₂ nanotubes in the degradation of methyl orange under visible light irradiation.

Soft-template methods are mostly used in the synthesis of 2D and 3D materials. Surfactants are used to modulate particle nucleation and growth to prepare materials with different morphologies, and they have been widely used to prepare Bi-based photocatalysts. Wang et al. [122] obtained α -Bi₂O₃ siamesed microflowers by a glycerin-involved hydrothermal method. The proposed formation process was the formation of prism-like nanorods with subsequent self-assembly to siamesed microflowers. Hao et al. [84] synthesized BiOI mesoporous microspheres through the Ostwald process in aqueous solution, using PVP as a structure directing reagent. The resultant BiOI microspheres exhibited much higher activity than BiOI nanoplates for the mineralization of tetracycline hydrochloride under visible light irradiation. This was mainly because of their high specific surface area. Apart from surfactants or polymers, some foaming agents can also be used for morphology control in photocatalysts. For example, Sun et al. [123] synthesized monoclinic BiVO₄ hollow spheres via a hydrothermal method using urea as the foaming agent. The obtained BiVO₄ hollow spheres showed higher activity toward the photodegradation of rhodamine B than the samples obtained using citric acid, ascorbic acid, and oleic acid as surfactants.

In the absence of templates, the morphology control of photocatalysts is mainly achieved by changing the concentrations of reactants and reaction conditions to control the growth direction and assembly. Bao et al. [40] prepared Bi₂S₃ nanowires via a hydrothermal method by controlling the concentration of reactants, using disodium ethylenediamine tetraacetate as a chelating agent. Chen et al. [124] reported the controllable synthesis of Bi₂WO₆ nanoplates by adjusting the pH in a hydrothermal process, with citric acid as a chelating agent. Wu et al. [125] investigated the formation of Bi₂O₃ crystals by a hydrothermal process using HNO₃ and NaOH to adjust the pH to the range of 13 and 14. The resulting crystal sizes and morphologies depended strongly on the concentrations of NO₃⁻ and NaOH. The NO₃⁻ favored the formation of long, needle-like Bi₂O₃ crystals, while increasing the NaOH concentration resulted in the formation of plate- or polyhedral-shaped Bi₂O₃ crystals. Zhu et al. [126] synthesized Bi₂MoO₆ via a hydrothermal process during which Bi₂MoO₆ nanosheets and nanorods were selectively obtained under acidic and basic conditions, respectively. The Bi₂MoO₆ nanosheets showed a 12 times higher visible light photocatalytic activity than the nanorods toward the degradation of methylene blue.

Zhang et al. [127] reported the controllable synthesis of BiOBr nanosheets with (001) exposed facets in a hydrolysis system by adjusting the reaction temperature and the solvents. They did not add a surfactant or a chelating agent. The obtained BiOBr nanosheets exhibited selective and high visible light photocatalytic activity toward rhodamine B compared to methyl orange and methylene blue. Xia et al. [116] synthesized BiOI hollow microspheres through an ethylene glycol-assisted solvothermal process in the presence of ionic liquid 1-butyl-3-

Fig. 16. Comparison of the photocatalytic activity of BiOI nanoplates, BiOI hollow spheres and P25 [116].

methylimidazolium iodine. The significantly enhanced photocatalytic degradation efficiency of methyl orange was observed for BiOI hollow microspheres, compared with those of BiOI nanoplates and P25 (see Fig. 16). This can be ascribed to the hollow structures, which have a high specific surface area leading to better communication between the photocatalysts and the dyes, and they also prolong the optical path by increasing the amount of light scattering, which generates more electrons and holes.

The effect of morphology on photocatalytic activity depends on the communication between the photocatalysts and the target reactants. Therefore, factors such as liquid movement, surface properties, and diffusion process etc. play important roles. The conclusions from different studies have been somewhat different.

5. Conclusions and prospectives

Their unique physicochemical properties have endowed Bi-based photocatalysts with excellent visible light photocatalytic activity. Studies into Bi-based photocatalysts will be beneficial for the future development of photocatalysis. Various types, structures and preparation methods for Bi-based photocatalysts have been reported. Recent investigations have indicated that Bi-based photocatalysts are very promising because of their high visible light activity. Researchers have carried out many studies on the synthesis, characterization, properties, calculations, and mechanisms of Bi-based photocatalysts, especially for the visible light photocatalytic degradation of organic pollutants. To improve the photocatalytic performance of Bi-based photocatalysts much work has been done on their composition, morphology, and structure control. Although significant progress has been made in this area, further effort is still required on various aspects to further advance the use of Bi-based photocatalysts as visible light photocatalysts. The two following aspects are of special relevance:

(1) Previous studies into Bi-based photocatalysts mainly focused on the photocatalytic degradation of organic pollutants while reports on their application in photocatalytic H₂ generation and CO₂ reduction are scarce because of their less negative

(2) The evaluation of Bi-based photocatalyst photodegradation has mostly been conducted in aqueous solutions instead of under gaseous conditions. Since visible light can be more fully utilized in the gas phase, this would favor the use of Bi-based photocatalysts. In fact, the removal of formaldehyde and benzene etc. from air is important for environmental remediation and for indoor air purification. Therefore, it will be meaningful to extend the application of Bi-based photocatalysts to the degradation of gaseous contaminants.

References

- CB edges with poor reducing abilities. The construction of Z-scheme heterojunctions between Bi-based photocatalysts and semiconductors with more negative CB edges is a promising method to investigate Bi-based photocatalysts in H₂ generation and in CO₂ reduction.
- (2) The evaluation of Bi-based photocatalyst photodegradation has mostly been conducted in aqueous solutions instead of under gaseous conditions. Since visible light can be more fully utilized in the gas phase, this would favor the use of Bi-based photocatalysts. In fact, the removal of formaldehyde and benzene etc. from air is important for environmental remediation and for indoor air purification. Therefore, it will be meaningful to extend the application of Bi-based photocatalysts to the degradation of gaseous contaminants.
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This review summarizes recent advances in the types, preparation methods, morphology control, composite construction, and properties of Bi-based photocatalysts. Some perspectives on the future development of Bi-based photocatalysts in this exciting research area are also proposed and discussed.

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可见光铋系光催化剂的研究进展

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摘要: 当前工业发展导致了严重的能源和环境危机, 光催化为这一难题提供了有效的解决方案. 然而在实际应用中, 传统氧化物光催化剂宽的带隙限制了它的可见光吸收, 于是窄带隙光催化剂成为了研究的热点. 其中铋系光催化剂以其高的可见光光催化活性引起了人们的广泛关注. 因此本文介绍了铋系光催化剂的种类、制备、形貌、复合、性能等方面的研究现状, 并展望了含铋可见光催化剂发展前景.

关键词: 光催化剂; 含铋化合物; 可见光活性

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1. 前言

光催化技术是从20世纪70年代逐步发展起来的一种新型光化学技术, 它利用半导体材料在光照下受到激发而产生电子和空穴的特性, 不断为氧化还原反应提供氧化性的空穴或还原性的电子, 使目标氧化还原反应得以进行. 利用光催化技术, 可以将水分解制得 H_2 和 O_2 , 或将有机废物氧化分解为 CO_2 , H_2O 和无机离子, 无二次污染, 因此, 光催化技术是一种具有广阔应用前景的环境治理技术^[1–6].

在众多光催化材料中, TiO_2 是研究得最多的一种. Fujishima等^[4]报道了利用 TiO_2 阳极和Pt阴极在紫外光照射下分解水制备 H_2 和 O_2 , 极大地推动了光催化的迅速发展. 目前, 每年仍有大量关于提高 TiO_2 光催化性能的研究报道. 但是由于 TiO_2 禁带宽度较大(3.0–3.2 eV), 需要在紫外光照射下发生光催化反应, 而紫外光仅占太阳光总能量的4 %左右, 从而限制了 TiO_2 的应用. 虽然人们尝试通过各种掺杂、敏化或复合的方法对 TiO_2 进行改性, 以提高其在可见光下的光催化活性, 但长期以来难有突破性进展^[7–10]. 因此, 开发新型材质的可见光光催化剂

是光催化领域的一个重要的发展趋势.

近年来, 具有可见光活性的铋系光催化剂引起了人们的广泛关注. Bi^{3+} 具有充满的 $6s^2$ 电子构型, 可与O $2p$ 轨道发生部分重叠而在半导体中形成价带的顶端, 从而使禁带宽度降低, 故 $Bi(III)$ 化合物具有较好的可见光响应性能^[11–14]. 此外, Bi^{5+} 具有空的 $6s$ 轨道, 也有较高的可见光活性^[15,16]. 因此, 包括含铋化合物及其复合物的铋系光催化剂的制备、表征及其光催化活性不断受到关注, 已逐渐成为可见光光催化剂中的重要成员.

2. 铋系化合物

目前已报道的含Bi化合物种类较多, 如 Bi_2O_3 , Bi_2S_3 , $Bi_2Ti_2O_7$, Bi_2WO_6 , $BiOCl$ 等, 大致可分成二元氧(硫)化物、多元氧化物、卤氧化物等几类. 表1列出了几种主要的含铋半导体光催化剂的禁带宽度(E_g)、导带电势(E_{CB})和价带电势(E_{VB}). 可以看出, 除了 $BiOF$ 和 $BiOCl$ 外, 其它的半导体的带隙均低于3.0 eV, 具有不同程度的可见光吸收, 均可作为可见光区的光催化剂, 特别是其中 Bi_2S_3 , $BiOI$, $KBiO_3$ 的带隙低于2.0 eV, 可吸收更宽范围的可见光. 光催化剂性能并不是简单随带隙能的减小而增加,

还与其结构密切相关,为此,围绕各种含铋光催化剂的制备和性能研究逐渐展开,现已有较多的研究报道。

2.1. 氧化物和硫化物

Bi_2O_3 为一种常见的半导体功能材料,广泛应用于化工和电子等领域。 Bi_2O_3 具有 α 、 β 和 γ 等多种晶态结构,属于间接带隙半导体,带隙宽度在2.6–2.9 eV,不同相态的 Bi_2O_3 带隙宽度不同^[17,32–35]。 Bi_2O_3 纳米颗粒在水中受到能量高于其带隙能的光照射时,会产生导带电子和价带空穴,它们分别与 O_2 和 H_2O 等反应产生具有氧化活性的自由基,如 O_2^- 和 $\cdot\text{OH}$ 等,这些自由基可与光催化剂表面吸附的有机污染物发生氧化还原反应,使其降解。

Zhang等^[33]采用超声化学法合成了 Bi_2O_3 纳米粉末,它在可见光($\lambda > 400 \text{ nm}$)照射100 min内,使20 mg/L的甲基橙溶液降解率达到86%。然而纯 Bi_2O_3 的光催化效果并不十分理想,因此,人们通过掺杂金属离子、制备多相复合材料等方法来提高 Bi_2O_3 的光催化性能,如掺杂了Pd(II)、V(V)的 Bi_2O_3 表现出更高的光催化性能^[34,36,37]。Huang等^[38]以 BiNO_3 为原料,利用水热法,通过调整加入的NaOH和氨水量制备出纯 α - Bi_2O_3 ,以及 α - Bi_2O_3 、 $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ 和 $\text{Bi}_2\text{O}_2\text{CO}_3$ 的混合相。在紫外光照射下光催化降解罗丹明B的实验中,混合相材料表现出更高的光催化活性。

Bi_2S_3 带隙较窄(1.3–1.7 eV),易被可见光激发产生电子-空穴对^[18]。研究表明, Bi_2S_3 晶体属于正交(斜方)晶系,形成的晶体为典型的层状结构,表现出的形貌有薄片状、长柱状或针状^[39]。 Bi_2S_3 纳米材料的制备通常以乙醇、水等作为溶剂,以 $\text{Bi}(\text{NO}_3)_3$ 或 BiCl_3 作为铋源,以硫、硫代乙酰胺或硫脲等含硫化合物作为硫源,通过水热法制得。如Bao等^[40]用 $\text{Bi}(\text{NO}_3)_3$ 与巯基琥珀酸水热反应制得的 Bi_2S_3 纳米线具有非线性的电流-电压性能和良好的光响应性。不同方法制备的 Bi_2S_3 材料不仅形貌有差别,带隙宽度也会有所差别,加上 Bi_2S_3 纳米材料的可见光响应性能较好,具有很多潜在应用,很多研究者都致力于通过各种方法制备纳米 Bi_2S_3 材料。

2.2. 多元氧化物

铋系多元氧化物是由 Bi_2O_3 与 TiO_2 、 W_2O_3 、 Mo_2O_3 、 V_2O_5 等金属氧化物按化学计量化合而成的复合氧化物,命名为Bi的含氧酸盐,如钛酸铋、钨酸铋、钼酸铋、钒酸铋等。这类化合物一般具有层状的Aurivillius结构:由 $[\text{Bi}_2\text{O}_2]^{2+}$ 层与相应钙钛矿的金属氧化物层沿c轴方向交替形成的层叠状构型。

钛酸铋由 Bi_2O_3 和 TiO_2 复合形成,具有多种晶相结

构,其中用于光催化领域的主要有三种: $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ 、 $\text{Bi}_2\text{Ti}_2\text{O}_7$ 和 $\text{Bi}_{12}\text{TiO}_{20}$ ^[6],其晶体结构为 BiO_n 多面体与 TiO_n 多面体相连而构成(见图1),n根据晶态不同而有所差别。钛酸铋中 Bi^{3+} 的 $6s^2$ 充满轨道和O 2p轨道共同构成了价带,导带由Ti 3d空轨道构成,与 TiO_2 相比(价带和导带分别由O 2p轨道和Ti 3d轨道构成),其带隙能较小(约为2.5–2.8 eV),较易被可见光激发,因此具有较高的可见光光催化活性^[14,19]。钛酸铋的制备可采用水热法^[41]、化学溶液分解法^[42]等,通过微波辐照、敏化等处理,还可进一步提高其光催化性能。如Yang等^[43]利用微波水热法制备了花形层状的 $\text{Bi}_{12}\text{TiO}_{20}$,其光催化降解罗丹明B的活性比传统水热法制备的 $\text{Bi}_{12}\text{TiO}_{20}$ 有明显提高。Li等^[44]通过碘敏化 $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{TiO}_2$ 异质结,增强了其对苯酚光催化降解活性。林涛等^[45]利用液相共沉淀生成前驱体,再用高温固相法制备了负载有 TiO_2 的 $\text{Bi}_2\text{Ti}_2\text{O}_7$ 、 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ 和 $\text{Bi}_{12}\text{TiO}_{20}$,并用于降解气态苯。

钨酸铋(Bi_2WO_6)为钙钛矿层状结构,如图2所示,由交替的 WO_6 八面体层(由两层 $[\text{O}]^{2-}$ 层和一层 $[\text{WO}_2]^{2+}$ 层构成)和 $[\text{Bi}_2\text{O}_2]^{2+}$ 层构成,其禁带宽度比 TiO_2 略窄,为2.6–2.7 eV,在可见光区也有较强的光吸收性能,且具有较好的光稳定性,不易发生光腐蚀^[35,46–48]。因此, Bi_2WO_6 成为光电催化和光催化领域里的一个重要研究方向。

目前,制备 Bi_2WO_6 的方法较多,如高温固相法、液相沉淀法、超声合成法、水热法、溶剂热法和微乳法等^[48]。由于高温固相法、沉淀法和超声合成法制备 Bi_2WO_6 时需要在较高的温度煅焙烧,难以制备出纳米尺度的材料,故近年来较少采用,而水热法和溶剂热法等方法不需要高温焙烧,可控性较好,可得到尺度较小的材料,若以微波辅助加热可能收到更好的效果,故近期较多采用。如Yan等^[49]采用水热法可控制备了巢状、棒状、薄片状等形态的 Bi_2WO_6 纳米材料,并在光催化降解四环素的实验中,发现三维材料比二维材料表现出更高的光催化活性。Hu等^[50]利用溶剂热法制备的空心 Bi_2WO_6 纳米颗粒在可见光照射下40 min内使罗丹明B的降解率达到99%。Zhang等^[35]还对 Bi_2WO_6 的可控制备和性能增强方面的研究进行了较系统的介绍。

钼酸铋(Bi_2MoO_6)也是一种具有层状钙钛矿结构的复合氧化物,其一般的化学式为 $\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}$,具有 α 、 β 和 γ 相等多种相态^[51],其晶体结构如图3所示,中间的 $[\text{O}]^{2-}$ 层把 $[\text{MoO}_2]^{2+}$ 和 $[\text{Bi}_2\text{O}_2]^{2+}$ 连接起来,结构与 Bi_2WO_6 相似。

Bi_2MoO_6 起初被用作催化剂模板材料,用于丙烯的

选择性氧化脱氢制备丙烯醛、氨氧化制备丙烯腈等反应, 后来用于离子导体、太阳能电池、气敏等领域^[52–55]. 近年来的研究发现, Bi_2MoO_6 还是一种性能优异的可见光光催化材料. Bi_2MoO_6 光催化剂的制备方法与 Bi_2WO_6 相似, 主要有固相反应法、气相沉积、水热法、溶剂热法等. Cuellar 等^[56] 首先采用高温固相反应制备 $\gamma\text{-Bi}_2\text{MoO}_6$ 粉体, 然后将粉体再气化, 通过气相沉积法制备了具有可见光活性的 $\gamma\text{-Bi}_2\text{MoO}_6$ 薄膜. Wang 等^[57] 利用水热法, 在不加表面活性剂的条件下, 制备出花形的 Bi_2MoO_6 . 其光催化降解罗丹明B的活性高于固相反应法制备的. 溶剂热法的使用相对较少, 但近年来也开始增多, Wang 等^[54] 采用乙二醇和乙醇混合溶剂, 利用溶剂热法制备了 $\gamma\text{-Bi}_2\text{MoO}_6$ 纳米片, 在罗丹明B的降解中显示出较好的可见光活性. Tian 等^[58] 利用乙二醇溶剂热法制备了花形 Bi_2MoO_6 微球, 在其可见光光催化降解罗丹明B的实验中, 罗丹明B在2h内降解效率达到95%. Cruz 等^[20] 的研究发现, 采用液相反应方法制备的 Bi_2MoO_6 纳米颗粒的禁带宽度比固相反应法和回流法制备的更窄.

钒酸铋(BiVO_4)也是一种重要的铋系多元氧化物, 主要有四方锆石、四方白钨矿相和单斜白钨矿相等3种, 四方晶系和单斜晶系结构如图4所示. 255 °C时, 四方白钨矿结构和单斜白钨矿结构之间可进行可逆转变; 397–497 °C, 四方锆石结构会不可逆地转变为单斜白钨矿结构^[59]. 单斜晶系的 BiVO_4 带隙为2.3–2.4 eV, 在可见光照射下($\lambda > 420 \text{ nm}$) 表现出比其它两种相态更高的光催化活性^[59,60].

BiVO_4 的制备可采用水热法、溅射法、微乳法等. Zhang 等^[61] 利用水热法制备了四方晶系和单斜晶系混合相态的 BiVO_4 , 并发现通过调节溶液pH值可控制四方晶和单斜晶的生成, 即 $\text{pH} \leq 3.8$ 时, 可得到纯的四方晶相; $\text{pH} \geq 8.5$ 时, 可得到纯的单斜晶相; $3.8 < \text{pH} < 8.5$ 时, 可得到混合晶相. Madhusudan 等^[62] 利用水热方法并结合焙烧, 制备了介孔 BiVO_4 , 其光催化降解刚果红的活性明显高于非介孔的 BiVO_4 . Chen 等^[63] 利用溅射法制备了V略过量的单斜晶系 BiVO_4 薄膜, 产生的最大光电流达到 1 mA/cm^2 , 其研究还发现, 直接采用 BiVO_4 靶材溅射不易控制Bi/V比, 采用 Bi_2O_3 和V双靶溅射可有效控制Bi/V比. 在利用水热方法制备 BiVO_4 时, 改变加入的原料, 还可方便地进行掺杂和复合. 戈磊等^[64] 采用微乳法制备了 BiVO_4 , 通过调节合成温度, 可得到不同晶相的 BiVO_4 光催化剂, 在对甲基橙光催化降解实验中发现, 四方相和单斜相混合晶型的 BiVO_4 光催化性能最好. 本课题组在

水热法制备 BiVO_4 时引入NaF, 制备出表面氟化的 BiVO_4 , 表面氟化促进了 BiVO_4 对罗丹明B的吸附和空穴的迁移, 从而增加了 BiVO_4 的光催化活性^[65]. 而在水热制备 BiVO_4 时加入尿素, 还可制备出 $\text{BiVO}_4/\text{Bi}_2\text{O}_2\text{CO}_3$ 两相复合光催化材料, 其光催化活性高于单相 BiVO_4 或 $\text{Bi}_2\text{O}_2\text{CO}_3$ ^[66].

铋酸盐(ABiO_3)中Bi(V)具有6s空轨道, 不仅可参与价带构成, 还可参与导带的构成, 从而改变价带顶和导带低的位置, 减小带隙宽度, 使其具有较高的可见光活性^[15,67]. Bi(V)多元氧化物以钛铁矿型为主, 由一价金属氧化物和Bi(V)氧化物构成, 如 NaBiO_3 , KBiO_3 , AgBiO_3 , LiBiO_3 等, 其中 NaBiO_3 为间接带隙半导体, 结构为 NaO_6 八面体层和 BiO_6 八面体层交替叠加的层状结构^[28,67], 其结构见图5, 禁带宽度较窄, 而 KBiO_3 和 LiBiO_3 的结构与钛铁矿的隧道结构相似^[29], 如图5所示, 这种结构使得 KBiO_3 和 LiBiO_3 的禁带宽度比 NaBiO_3 明显更窄, 分别为2.1和1.8 eV.

目前, 该类半导体化合物的制备通常需要加入氧化剂, 或在较高的温度下进行, 制备工艺较为复杂. 如 Ramachandran 等^[29] 制备 KBiO_3 时, 利用液溴作氧化剂, 加入反应溶液中, 将Bi(III)氧化为Bi(V). Chen 等^[68] 也是采用液溴作氧化剂, 制备水合 NaBiO_3 . 还有一些研究者制备了同时含有Bi(III)和Bi(V)的混合价态的 BaBiO_3 . 如 Tang 等^[69] 利用Ba和Bi(III)复合氧化物在650 °C空气中焙烧, 制备出具有较高可见光活性的 BaBiO_3 , 并认为具有不同价的Bi共存有利于载流子的传输.

Bi(V)化合物虽然可见光活性较高, 但在一定的环境下会发生光腐蚀, 变得不稳定. 如 Chang 等^[70] 在研究 NaBiO_3 光催化降解辛基苯酚时发现, 当用盐酸将溶液的pH值调节到7以下时, 随着反应进行, 部分 NaBiO_3 会转变为 BiOCl . Yu 等^[71] 在研究 BiAg_xO_y 降解有机染料时发现, 在反应过程中, 随着有机物被氧化, BiAg_xO_y 中的 Ag^+ 会转变为单质Ag, 而Bi(V)会转化为Bi(III), 并与反应产生的 CO_3^{2-} 结合形成 $\text{Bi}_2\text{O}_2\text{CO}_3$.

碱式碳酸铋($\text{Bi}_2\text{O}_2\text{CO}_3$)具有Sillen相泡铋矿结构, 最早被Grice等^[72]报道; 它由Bi-O层和 CO_3 层交替叠层而构成, 其中8配位的 Bi^{3+} 离子具有立体活性的孤对电子, 会使Bi-O多面体产生较大的变形^[22], 如图6所示. 碱式碳酸铋通常作为工业助剂和制造胃药的原料. 近年来的研究发现, 碱式碳酸铋具有良好的光催化活性, 成为一种具有潜力的光催化剂.

Zheng 等^[22] 通过控制 $\text{Bi}_2\text{O}_2\text{CO}_3$ 不同晶面的生长速

率, 暴露其(001)面, 使其光催化活性增强, 高于P25. Dong等^[73]采用水热方法, 在不加模板剂的情况下制备了 $\text{Bi}_2\text{O}_2\text{CO}_3$ 空心微球, 其消除室内NO的光催化效果明显好于P25、碳修饰的 TiO_2 , 以及 $\text{Bi}_2\text{O}_2\text{CO}_3$ 颗粒. Madhusudan等^[23]利用水热法制备了 $\text{Bi}_2\text{O}_2\text{CO}_3$, 通过对可见光光催化降解罗丹明B的研究发现, 片状 $\text{Bi}_2\text{O}_2\text{CO}_3$ 的可见光光催化活性不及P25, 但通过形貌控制制备了花形 $\text{Bi}_2\text{O}_2\text{CO}_3$ 微球, 其可见光光催化活性大大提高, 高于P25的.

$\text{Bi}_2\text{O}_2\text{CO}_3$ 的带隙宽度与其制备方法、结构和形貌有一定关系, 例如, Zheng等^[22]制备的 $\text{Bi}_2\text{O}_2\text{CO}_3$ 带隙宽度为3.1 eV, 而Madhusudan等^[23]制备的 $\text{Bi}_2\text{O}_2\text{CO}_3$ 微球的紫外-可见吸收光谱的吸收段呈现出两段, 分别计算的带隙宽度分别为3.3和2.25 eV, 在低能位表现为间接带隙, 而在高能位表现为直接带隙.

除了上述含铋多元氧化物外, 人们还对铋酸铋^[74]、钽酸铋^[75]、硅酸铋^[76]、磷酸铋^[77]等含铋化合物的光催化性能开展了相关的探索研究.

2.3. 卤氧化铋

卤氧化铋化合物包括 BiOF , BiOCl , BiOBr 和 BiOI , 其中 BiOF 为直接带隙半导体, 而 BiOCl , BiOBr 和 BiOI 为间接带隙半导体. 图7给出了卤氧化铋化合物的能带结构图. 从图中箭头所指的价带顶和导带底的波矢位置可以看出, BiOF 的价带顶和导带底的波矢位置相同, 显示其为直接带隙半导体; 而 BiOCl , BiOBr 和 BiOI 的价带顶和导带底的波矢位置不同, 显示它们均为间接带隙半导体.

卤氧化铋化合物均具有各向异性的层状结构, 卤素原子X夹在 Bi_2O_2 层之间(见图8), 形成的 $[\text{Bi}_2\text{O}_2]^{2+}$ 正电层和 X^- 负电层之间会形成内部电场, 使光生电子和空穴得到有效分离, 从而提高其光催化活性^[78–80]. 卤氧化铋的禁带宽度随卤素的原子序数的增加而不断减小. BiOF 的禁带宽度最宽, 为3.6 eV, 几乎没有可见光活性, 但其紫外光光催化活性接近商品P25^[24]. BiOCl 禁带宽度比 BiOF 的窄, 在3.2–3.5 eV, 与 TiO_2 相当(3.0–3.2 eV), 但经染料敏化后在可见光下可实现对RhB的高效降解, 表现出较高的可见光催化活性^[25,79–81]. BiOBr 和 BiOI 的禁带较窄, 其宽度分别为1.8–1.9和2.6 eV, 具有良好的可见光光催化活性^[26,27].

卤氧化铋的制备方法主要有水解法、水热法和固相反应法等. 水解法操作较为简单, 对设备要求不高, 利用 $\text{Bi}(\text{NO}_3)_3$ 和 BiX_3 等可溶性Bi盐与卤化物或水反应得到

BiOX . Shi等^[82]利用水解法, 向 BiCl_3 的盐酸溶液中加入 Na_2CO_3 溶液, 得到了 BiOCl 粉末, 其性能略优于P25. Li等^[83]通过水解法在室温下制备出 BiOI 纳米片薄膜. 水解法虽然简单, 但制备的样品分散度差、形貌不易控制, 故近年来的研究大多辅以软模板剂、微波和超声处理, 以便制备出尺寸较为均一、具有一定规则形貌的样品. 如Hao等^[84]利用 $\text{Bi}(\text{NO}_3)_3$ 与KI在溶液中反应, 在表面活性剂作引导剂的条件下, 制备出了 BiOI 微球.

水热法或溶剂热法也是制备 BiOX 的常用方法, 通过高温、高压等极端环境, 不仅可制备具有独特结构和形貌的产品, 还能得到非化学计量的卤氧化铋材料. 例如Zhang等^[26]利用水热法合成了 BiOCl , BiOBr 和 BiOI 微球样品, 发现水热法制备的样品均有良好的光催化活性. 固相反应法也可制备 BiOX , 不过通常需要较高的温度, 由于得到的产物不利于洗涤, 产物中常常混有原料所含的金属离子. 如Lin等^[85]用固相反应制备的卤氧化铋样品中含有一定比例的 Na^+ . 在近年来制备 BiOX 的研究中, 该方法已经较少采用.

3. 铋系光催化剂的结构控制

含铋化合物的共同特点和优势在于其强的可见光吸收和良好的光催化性能, 但其单独使用仍存在光生电子-空穴容易结合、部分含铋化合物可见光吸收范围有限等问题, 限制了铋系光催化剂的应用. 因此, 通过结构和形貌控制可进一步提高其光生电子迁移效率, 抑制光生电子-空穴的复合, 拓宽可见光吸收范围, 提高催化剂的可见光光催化活性是研究的重点^[86]. 在结构控制方面主要通过制备异质结、固溶体等途径.

3.1. 半导体/半导体异质结

半导体异质结主要采用p型半导体和n型半导体组成的p-n结, 结构如图9(a)所示, 通过p型半导体和n型半导体界面处形成的内建电场, 使n型半导体产生的空穴向p型半导体迁移, 同时使p型半导体产生的光生电子迁移到n型半导体, 从而实现光生电子-空穴的有效分离, 延长光生电子和空穴的寿命, 提高光催化剂的光催化性能^[87].

Z型异质结是一种特殊的异质结. 对于一般p-n型异质结, 光生电子从导带位置较负的半导体的导带流向导带位置较正的半导体的导带, 而空穴则由价带位置较正的半导体移向价带位置较负的半导体的价带. 而Z型异质结的电子流动方向是由导带位置较正的半导体的导带流向导带位置较负的半导体的价带, 与相应价带的空

穴复合, 电子传输过程如图9(b)所示, 这样的电子传输方式, 可减少导带位置较负的半导体上光生电子与空穴的复合机会, 使光生电子能用于物质的还原^[88]. 这类半导体异质结在制H₂和CO₂还原方面有较好的应用前景.

BiOX异质结材料, 既可以用BiOX与其它材料复合, 构成异质结, 也可以不同卤素的卤氧化铋相互复合构成异质结, 材料选择范围较宽, 有利于光催化效果的提高. Xiao等^[89]利用溶剂热法, 同时加入BiCl₃和BiI₃, 以乙二醇为溶剂, 制备了不同摩尔比的BiOI/BiOCl复合材料, 发现BiOCl比例为10%的异质结在可见光降解双酚A过程中, 反应速率常数分别是纯BiOI和P25的4倍和20倍. Dai等^[90]制备了BiOI/TiO₂异质结纳米管, Yu等^[91]制备了Bi₂WO₆/Ag₂O异质结, 这些异质结光催化剂都表现出较好的光催化性能. 吴大旺等^[92]将WO₃和Bi₁₂SiO₂₀复合构成WO₃/Bi₁₂SiO₂₀异质结, 进行光催化降解气态苯, 发现异质结光催化剂的光催化性能明显高于单一Bi₁₂SiO₂₀粉末. Madhusudan等^[66]通过制备BiVO₄/Bi₂O₂CO₃异质结, 使得对罗丹明B的光催化降解效率明显提高, 见图10 (U6, U12, U20为不同比例的BiVO₄/Bi₂O₂CO₃异质结光催化剂, U0为BiVO₄), 当BiVO₄/Bi₂O₂CO₃异质结受可见光激发后, BiVO₄上的光生电子向Bi₂O₂CO₃的导带移动, 而Bi₂O₂CO₃上的光生空穴向BiVO₄移动, 有效降低了光生电子和空穴的复合, 从而使光催化剂的性能得到很大提高.

由于大部分含铋化合物的导带位置为正值(> 0 eV), 不能直接用于制H₂和CO₂还原, 不过若将含铋化合物与比H₂和CO₂还原电位更负的半导体构成Z型异质结, 则能增强相应半导体的光催化性能, 即利用含铋化合物的光生电子与相应半导体的光生空穴复合, 延长该半导体的光生电子的寿命, 异质结可用于制H₂和CO₂的还原反应. Park等^[93]制备了Pt-W/Mo-BiVO₄和Zn_{0.2}Cd_{0.8}Se两个体系的Z型异质结, 分别在Γ⁺/IO³⁻或S²⁻/Sn²⁺环境介质中使用, 才能表现出Z型电子传导方式, 可以通过光催化分解水得到H₂.

3.2. 固溶体

固溶体是两种或两种以上的晶体在固态条件下溶解形成的均匀、组成可变的晶态固体相. 与机械混合不同, 固溶体不同组分的基本单元是原子尺度混合的, 不破坏主晶相的结构和对称性, 为单一结构. 固溶体的组成结构和性能都可随成分的变化而变化, 两种带隙较宽的半导体形成固溶体后其带隙甚至有可能比两者带隙都要窄^[94], 因此, 可以通过改变固溶体的组成可改善其

光催化性能.

固溶体形成的要求比异质结要高, 它要求不同晶体的离子半径、极化性能和电负性比较接近, 晶格的形状和大小也要接近, 通常在固溶体的制备过程中还要进行热处理. 目前, 已经有多种含Bi的固溶体的报道. Marija等^[95]通过室温快速自蔓延方法制备了Ce_{1-x}Bi_xO_{2-δ} (x = 0.1–0.5)固溶体. Politova等^[96]采用固相反应法制备了钒酸铋基固溶体(Bi_{1-y}La_y)₄(V_{1-x}Me_x)₂O_{11-y} (x, y < 0.2, Me = Zr, Ga, Fe, Cu). 上官文峰等^[97,98]制备了Bi_{0.5}La_{0.5}VO₄固溶体和BiYWO₆固溶体, 并负载Pt-Cr₂O₃作为共催化剂, 在可见光照射下可以分解水产生H₂, 其主要原理是分别利用La 5d轨道和Y 4d轨道参与导带构成, 使材料导带位置比H⁺/H₂的还原电位更负引起的.

在含铋化合物中, BiOCl, BiOBr和BiOI的晶体结构相似, 都为四方的氟氯铅矿晶系, 可形成完全的固溶体, 既可两两组成固溶体, 也可三者共同形成固溶体. 且由于卤素元素的比例可以通过原料的配比进行调节, 而卤素元素的比例与固溶体的禁带宽度密切相关, 故可通过调节卤素元素的比例调节固溶体的禁带宽度和价带顶和导带底的位置^[80,99,100]. 如Wang等^[25]采用软化学方法制备了BiOCl_{1-x}I_x (x = 0.2–1.0)固溶体, 其禁带宽度可在1.92–2.31 eV范围调整. Liu等^[101]制备的BiOCl_{1-x}Br_x固溶体的紫外-可见光吸收边界随Br的增加而不断红移, 如图11(b)所示, 而固溶体的形貌较为接近, 均成薄片状(见图11(a)). 他们认为, 卤氧化铋高的光催化活性与[Bi₂O₂]²⁺阳离子层和卤素阴离子层间的内部电场有关. 由此可见, 卤氧化铋在固溶体制备方面有着独特的优势. 通过形成固溶体调控光催化材料的能带结构进而调控材料的光催化性能, 是开发新型可见光响应光催化材料的一条有效途径.

3.3. 半导体/导体异质结

虽然半导体异质结可以有效地分离半导体所产生的电子-空穴对, 达到延长其寿命、增加光催化活性的目的, 但组成异质结的两个半导体还是要有一定的匹配度, 以满足电子和空穴移动的需要. 利用导电性较好的材料作为电子捕获剂, 与半导体材料进行复合, 将半导体上的光生电子及时转移到导体材料上, 同样也能实现光生电子和空穴的有效分离, 达到增强材料光催化活性的目的, 因此, 利用良好的导电材料与铋系半导体复合也是制备高效光催化剂的一个重要途径.

目前, 用于和铋化合物复合的材料主要为Ag, Cu等金属和碳纳米管、石墨烯等碳材料. 在制备金属/半导体

复合材料的时候,通常是选择较易被还原的Ag, Cu等金属离子,通过适当的还原剂将其还原为单质,形成纳米颗粒,嵌在半导体中. Wang等^[102]采用水热方法在 Bi_2WO_6 中引入Cu纳米颗粒,增强了光催化剂对苯酚降解的活性. Lei等^[103]通过溶液方法在 $\text{BiOBr}_{1-x}\text{I}_x$ 固溶体中引入Ag纳米颗粒,制备了 $\text{Ag-BiOBr}_{0.75}\text{I}_{0.25}$ 复合共催化剂,其光催化降解罗丹明B的性能明显高于 $\text{BiOBr}_{0.75}\text{I}_{0.25}$ 的性能(见图12中曲线(b)和(h)),其主要原因在于Ag有效地捕获固溶体的光生电子,使得固溶体的光生电子和空穴有效分离,延长了光生空穴的寿命,从而提高了光催化活性,而 $\text{Ag-BiOBr}_{0.75}\text{I}_{0.25}$ 和 $\text{BiOBr}_{0.75}\text{I}_{0.25}$ 可见光活性显著高于P25的原因主要在于 $\text{BiOBr}_{0.75}\text{I}_{0.25}$ 固溶体本身较窄的带隙.

碳材料也有良好的导电性,可有效捕获光生电子. 例如Su等^[104]将制备的BiOI微粒与多壁碳纳米管复合,提高了对酸性橙的降解效率. 在碳材料中,石墨烯是近来兴起的一种优良的电子捕获剂,石墨烯是一种由碳原子以 sp^2 杂化轨道组成六角型呈蜂巢晶格的平面薄膜,只有一个碳原子厚度的二维材料,石墨烯是目前已知导电性能最出色的材料,其电子的运动速度达到了光速的 $1/300$,远远超过了电子在一般导体中的运动速度;此外它还具有较高的杨氏模量($\sim 1100 \text{ GPa}$)、热导率($\sim 5300 \text{ W/(m}\cdot\text{K)}$)、较高的载流子迁移率($200000 \text{ cm}^2/(\text{V}\cdot\text{S})$)和巨大的比表面积(理论计算值 $\sim 2600 \text{ m}^2/\text{g}$)^[105,106]. 如图13所示,半导体颗粒受到光激发产生的光生电子可及时传输到石墨烯表面,由于石墨烯具有独特的二维结构,将铋系光催化剂与石墨烯复合的研究报道也不断增加. 研究发现,石墨烯对光催化剂的性能提升比较明显. 如Fu等^[107]发现,将制备的 BiVO_4 与石墨烯复合后,其降解甲基橙、亚甲基蓝、罗丹明B的光催化性能均高于纯 BiVO_4 的光催化性能. Liu等^[108]将 Bi_2O_3 与石墨烯复合,明显提高了其降解甲基橙和亚甲基蓝的. 向全军等^[109]曾对包括铋系光催化剂在内的多种半导体与石墨烯复合的研究情况进行了综述.

需要指出的是,包括石墨烯在内的碳材料本身对光有吸收,故碳的引入,一方面及时转移光催化剂的光生电子,延长了光催化剂光生电子-空穴对的寿命,有利于增加光催化剂性能;另一方面,碳材料对光的吸收,会减弱到达光催化剂表面的光强,这不利于光催化剂提高性能,故一般会有一个较为合适的引入量. 如Madhusudan等^[110]将制备的花状 $\text{Bi}_2\text{O}_2\text{CO}_3$ 与石墨烯复合,明显提高了花状 $\text{Bi}_2\text{O}_2\text{CO}_3$ 光催化降解罗丹明B的性能,如图14所

示(BG0, BG0.05, BG0.1, BG0.2等样品为根据引入石墨烯的质量百分比作的样品标记),通过调整石墨烯的引入量,光催化效果存在最佳值,且相应样品的光催化性能提升较为明显. 另外,虽然纯的石墨烯与石墨一样具有导电性,但通常商品化的石墨烯是采用的氧化石墨烯还原制备得到,许多研究者也是先将光催化剂与氧化石墨烯复合,再进行还原处理,故样品中的石墨烯通常具有一定的半导体性质,不是完全意义上的导体,所制备的复合材料有时会出现光催化剂的导带和价带偏移的现象^[111,112].

另外,由于离子液体具有较好的离子传导特性,也可作为电子捕获剂,故用离子液体对光催化剂表面进行修饰,也能达到增强光催化剂光催化性能的效果. Wang等^[113]用1-丁基-3-甲基咪唑啉碘化物离子液体修饰BiOI表面,在进行甲基橙降解中,明显增强了BiOI催化剂的可见光活性.

4. 铋系光催化剂的形貌控制

目前,人们已经探索了各种途径对铋系光催化剂进行形貌控制,制备出了形貌各异的光催化材料,如图15所示的 Bi_2S_3 纳米线^[40]、 Bi_2O_3 纳米片^[114]、 Bi_2WO_6 微带^[115]、树枝状 BiVO_4 ^[60]、花状 $\text{Bi}_2\text{O}_2\text{CO}_3$ ^[23]、BiOI空心微球^[116]、蛋壳状 BiOBr ^[117]、 Bi_2MoO_6 空心管^[118]等. 这些铋系光催化剂的形貌大致可分为一维纳米结构材料(纳米线、纳米棒、纳米管等)、二维结构材料(纳米片、纳米带、薄膜等)和三维结构材料(纳米微球、微花、空心球等).

对材料形貌的控制,既可以利用模板剂的引导,也可以在没有模板剂引导的情况下进行. 选择合适的模板(硬模板或软模板)可以较为方便地进行材料形貌控制. 例如制备一维纳米结构光催化材料时,常利用无机或聚合物纤维作硬模板,将含铋化合物(或含铋前驱体)负载到前驱体纤维上,再通过氧化、热处理等方法去除前驱体纤维,得到线形光催化材料. Zhang等^[118]以聚丙烯腈(PAN)纳米纤维为先驱体,通过水热反应在PAN纤维上原位生成了 Bi_2MoO_6 ,再焙烧除去PAN纤维,得到了 Bi_2MoO_6 微管;与固相法制备的块体 Bi_2MoO_6 相比, Bi_2MoO_6 微管具有更高的可见光活性. 如Cui等^[119]利用棉线作模板,将制备的 Bi_2WO_6 悬浮液浸渍于棉线上焙烧,制备出 Bi_2WO_6 纤维,其可见光光催化降解罗丹明B的效率比块体 Bi_2WO_6 (固相反应法制备)的提高了约4倍. Tang等^[120]配制了含有 $\text{Bi}(\text{NO}_3)_3$ 、 $\text{La}(\text{NO}_3)_3$ 和钛酸丁酯的

前驱体混合液,采用静电纺丝法制备了纤维状先驱体,再经焙烧去除模板剂,可形成晶态的 $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ 纤维。戴高鹏等^[90,121]进一步以 TiO_2 纳米管阵列作为模板,利用浸渍-分解法制备得到了 BiOI/TiO_2 纳米管阵列和 $\text{Bi}_2\text{O}_3/\text{TiO}_2$ 纳米管阵列复合光催化剂,该复合光催化剂在可见光降解甲基橙的实验中,表现出比单一光催化剂更好的光催化性能。

软模板法也常用来制备二维和三维光催化材料,利用表面活性剂来引导光催化材料的成核与生长,可制备出形貌各异的光催化材料,是铋系光催化剂形貌控制用得较多的方法。如Wang等^[122]以甘油为引导剂,利用水热法制备出连体微花形的 $\alpha\text{-Bi}_2\text{O}_3$,产物的形成经历了纳米片的形成和纳米片组装两个步骤。Hao等^[84]在制备 BiOI 介孔微球时,以PVP为引导剂,利用Ostwald熟化原理,通过液相反应实现了对 BiOI 光催化材料的形貌控制。通过对盐酸四环素的降解研究发现, BiOI 介孔微球具有比片状 BiOI 更高的可见光催化活性;反应动力学结果表明,光催化性能的提高主要是由于比表面积增加所致。在软模板法中,除了利用上述表面活性剂和高分子引导外,也可利用发泡剂对光催化材料进行形貌控制。如Sun等^[123]以尿素为发泡剂,通过水热法制备了单斜晶型的 BiVO_4 空心球,其光催化降解罗丹明B的活性比采用柠檬酸、油酸和维生素C模板剂制备的样品高。

在不加模板剂的情况下,对光催化材料的形貌控制主要利用光催化材料的取向生长和组装来实现,操作时通过控制反应物的浓度和反应条件来进行形貌控制。如Bao等^[40]采用水热法,以二乙胺四乙酸钠为螯合剂,控制反应物离子浓度,制备了 Bi_2S_3 纳米线。陈渊等^[124]以柠檬酸为螯合剂,采用水热方法通过调整反应体系pH值实现了对 Bi_2WO_6 纳米片尺寸的控制。Wu等^[125]采用水热法,通过调节反应体系中加入 HNO_3 和 NaOH 的量来控制pH值在13–14范围内,制备出了针形、片状和多面体形状的 Bi_2O_3 ,结果显示, NO_3^- 有利于形成针形外观,而 NaOH 有利于片状和多面体的形成。朱永法等^[126]在不加表面活性剂的情况下,利用水热法通过调节反应体系的pH值,分别在酸性和碱性条件下选择性地制备出 Bi_2MoO_6 纳米薄片和 Bi_2MoO_6 纳米棒,并发现在亚甲基蓝的降解反应中, Bi_2MoO_6 纳米薄片的可见光活性比 Bi_2MoO_6 纳米棒高12倍。

Zhang等^[127]在不加表面活性剂和螯合剂的情况下,通过调整反应体系的温度和溶剂,制备出了暴露(001)晶

面的 BiOBr 薄片,在对罗丹明B、甲基橙和亚甲基蓝的降解实验中发现,制备的 BiOBr 薄片对罗丹明B的光催化降解效果明显优于对甲基橙和亚甲基蓝,显示出较好的光催化选择性。Xia等^[116]采用离子液体,在没有表面活性剂的情况下制备出 BiOI 空心微球,其降解甲基橙的性能比片状 BiOI 有明显提高(见图16),认为空心结构不仅具有较大的比表面积,有利于反应物充分接触,且可增加对光的吸收,产生更多光生电子和空穴,因而 BiOI 空心微球的光催化性能显著优于片状 BiOI 的光催化性能。

由于光催化剂的形貌在实际反应过程中对光催化反应的影响,最终还与反应物接触光催化剂的实际效果有关,故受到液体流动、表面性质、扩散等因素影响,故不同研究者得到的不同形貌光催化剂的性能比较结果也不尽相同,不能一概而论。

5. 结论与展望

铋系光催化剂具有独特的物理和化学性质,使其具有良好的可见光响应性能,符合光催化剂未来发展的趋势。铋系光催化剂的种类较多、结构多样,制备方法较为灵活,近年来的研究显示铋系光催化剂的可见光光催化活性普遍较高,极具应用潜力。近年来,在铋系光催化剂制备、表征、性能测试、结构计算、机理研究等方面,特别是在可见光光催化降解有机污染物方面取得了一些可喜的进展。可通过调控组成、形貌和结构等多种方法进一步提高铋系光催化剂的光催化性能,其国内研究者的研究工作较为突出。不过铋系光催化剂的研究仍存在较大的探索空间:

(1) 以前铋系光催化剂的研究主要集中在有机物降解,对于光催化分解水制备氢气和 CO_2 还原方面的研究还不多见,这主要是由于铋系光催化剂的导带位置较正,还原能力较弱引起的。利用复合的方法将含铋化合物半导体与导带位置较负的半导体复合构成Z型光催化剂,即可用于光催化分解水产 H_2 和 CO_2 的还原反应,这是拓展含铋化合物还原能力的主要方法之一。

(2) 在现有的铋系光催化性能研究中,大多以水溶液为研究体系,而气态污染物降解的研究较少。由于气相环境中,可见光的照射更为充分,应更能发挥铋系光催化剂的优势,而空气中的甲醛、苯等挥发性有机物去除是环境治理和室内空气净化中的重要内容,故有关铋系光催化剂在气态污染物光催化降解方面的研究今后还需要加强。