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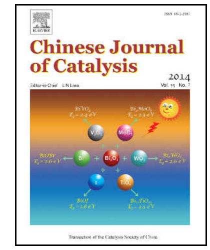

Review

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.

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 CO_2, H_2O, and inorganic ions without secondary pollution. Therefore, photocatalysis is considered to be a promising method of environmental remediation [1–6].

TiO_2 has been widely studied since Fujishima's [4] report on the generation of H_2 and O_2 by photoelectrochemical water splitting using TiO_2 and Pt electrodes. However, because of its large band gap of ~3.2 eV, TiO_2 is only active in the UV region, which corresponds to ~4% of incident solar light. Many techniques such as elemental doping, dye sensitization and composite construction have been used to modify TiO_2 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 Bi^{3+}-containing compounds have been found to possess a narrow band gap and exhibit high visible light photocatalytic activity because of the hybridized O 2*p* and Bi 6*s*^{2} valence bands [11–14]. Additionally, the empty 6*s* orbital of Bi^{5+} also supports Bi^{5+}-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, $Bi_2Ti_2O_7$, 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 $O_2{\cdot}^-$ and ·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 nanocrystallite Bi_2O_3 effectively degraded methyl orange (20 mg/L) by 86% within 100 min under visible light illumination (λ > 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, $(BiO)_4CO_3(OH)_2$ and $Bi_2O_2CO_3$, 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, $Bi(NO_3)_3$ or $BiCl_3$ as the Bi source, and sulfur, thiacetamide, 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 $Bi(NO_3)_3$ 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.

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
	$Bi_4Ti_3O_{12}$, $Bi_2Ti_2O_7$, $Bi_{12}TiO_{20}$	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
	$Bi_2O_2CO_3$	3.1–3.3 [22,23]	0.31 (E_g = 3.1)	3.41
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
$MBiO_3$	$NaBiO_3$	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 $E_{VB} = E_{CB} + E_g$.

2.2. Bi-based multi-component oxides

Bi-based multi-component oxides are a series of oxysalts including $Bi_4Ti_3O_{12}$, 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. $[Bi_2O_2]^{2+}$ 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 $Bi_4Ti_3O_{12}$, $Bi_2Ti_2O_7$, and $Bi_{12}TiO_{20}$ [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 $Bi_{12}TiO_{20}$ by a microwave assisted hydrothermal method. The obtained $Bi_{12}TiO_{20}$ exhibited enhanced visible light photocatalytic per-