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Review

Bismuth-based photocatalytic semiconductors: Introduction, challenges and possible approaches

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ABSTRACT

Bismuth-based semiconductors are a unique and promising group of recently developed advanced photocatalytic materials. They have been widely applied in several areas including the generation of H_2 by splitting water, decomposition of organic and inorganic pollutants in both wastewater and polluted air, and organic synthesis through harvesting the energy of light. The electronic structure of bismuth-based semiconductors confers them with a suitable band gap for visible-light response and a well-dispersed valence band composed of hybrid orbitals of Bi*6s* and O*2p*, making them a promising candidate when compared to other metal oxide semiconductors. In addition, they are simple to operate and prepare with controlled morphologies, making them attractive as potential photocatalysts. The purposes of this review are (1) summarization of advanced bismuth-based compounds that have been applied to date, (2) statement of challenges facing this material and possible approaches to overcome them, and (3) suggestions for future work.

Contents

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1. Introduction

Photocatalysis is an advanced oxidation process (AOPs) involving the participation of photons that has been widely extended into areas such as the generation of hydrogen by splitting water and the protection of the environment. Unique properties such as an inexpensive energy source and a wide range of applications make it attractive for further research. Photocatalytic materials as the basis are also extensively developed. When compared to early photocatalytic materials, namely TiO_2 [1], recently developed materials possess several advantageous properties such as visible-light responses, controllable structures, and higher photo-quantum yields. The intrinsic electronic band structure of TiO_2 is a well-known shortcoming of the material, and results in a large band gap of about 3.2 eV. Given that only UV light possesses enough energy to activate TiO_2 and trigger a photocatalytic process, use of this material is uneconomical. Approaches to overcome this barrier usually include either modification of TiO_2 to narrow the band gap (such as doping [2]) or development of other novel visible-light-responsive materials.

Bismuth-based semiconductors are a promising new candidate for visible-light-responsive photocatalysts. Their electronic structure results in a valence band consisting of hybrid orbitals of O *2p* and Bi *6s*, while that of TiO_2 is composed solely of O *2p* orbitals. It has been reported that the well-dispersed Bi *6s* orbital increases mobility of photogenerated charge carriers and decreases the band gap [3,4]. As a result, bismuth-based compounds usually possess band gaps less than 3.0 eV. A variety of bismuth-based substances have been prepared and tested as photocatalysts, *e.g.* Bi_2O_3, Bi_2MO_6 (M = Cr, Mo and W), $BiVO_4$, BiOX (X = Cl, Br and I), $BiPO_4$, $(BiO)_2CO_3$, and pentavalent bismuthates. In terms of environmental protection applications, bismuth-based semiconductors have been used for degradation of organics in wastewater such as dye pollutants [5–8], oxidation of gaseous pollutants such as NO [9], and photo reduction of CO_2 [10]. Studies on photocatalytic water splitting to generate H_2 and O_2 have also been reported [11–15].

In this review, current bismuth-based photocatalysts and their applications are summarized. Next, main challenges in their application are presented along with possible approaches for overcoming them. Finally, future work in this area is proposed.

2. Bismuth-based photocatalytic materials

2.1. Bi_2O_3 and Bi_2S_3

Bismuth trioxide (Bi_2O_3) is the simplest and most significant bismuth compound. It has potential applications, among others, in a wide range of gas sensors and ceramic glass solid oxide fuel cells [16]. It has also been implemented as a photocatalyst in both the splitting of water and in the decomposition of organic pollutants [17]. Bi_2O_3 as a semiconductor has a band gap that varies from 2.1 eV to 2.8 eV, making it a viable visible-light-responsive photocatalyst. Polymorphs of Bi_2O_3 include the alpha (monoclinic), beta (tetragonal), gamma (body-centered cubic), delta (face-centered cubic), and omega (triclinic) phases. These metastable phases can be easily transformed to α phase at low temperatures and δ phase at high temperatures (Fig. 1). Further transformation to $(BiO)_2CO_3$ [18] has also been observed, and this chemical instability represents the main obstacle for further applications of Bi_2O_3 as a photocatalyst. Approaches including metal doping, ion doping, and establishing composites have been attempted, but have yet to overcome this intrinsic disadvantage.

Bi_2S_3 has a bulk band gap of 1.7 eV and is an ideal light-harvesting photocatalytic material due to its activation by visible and near-IR light. A variety of Bi_2S_3 nanocrystals have been prepared, ranging from 1D nanorods and 2D nanosheets (Fig. 2a and b) by standard oxygen-free and hot injection techniques [19,20], to 3D urchin-like spheres (Fig. 2c) by solvothermal method [10]. The photogenerated holes on the valence band of Bi_2S_3 with a flat potential of 1.62 eV, as well as the production of hydroxyl radicals (•OH) may be the oxidants for decomposing most dye pollutants [19]. Photocatalytic reduction of CO_2 to methyl formate (MF) in the presence of Bi_2S_3 [10] has also been reported. Bi_2S_3 has a narrow band gap and if combined with other photocatalysts such as TiO_2 [21], Bi_2WO_6 [22] and CdS [23], the recombination rate of e^-/h^+ pairs could be decreased resulting in further improvements to photocatalytic performance under visible light irradiation.

2.2. Bi_2MO_6 (M = Cr, Mo, W)

Bi_2MO_6 (M = Cr, Mo, W) is the simplest member in the Aurivillius family, the general formula for which is $Bi_2A_{n-1}B_nO_{3n+3}$ (A = Ca, Sr, Ba, Pb, Bi, Na, K; B = Ti, Nb, Ta, Mo, W, Fe). Theoretically, the electronic structure of Bi_2MO_6 can be simulated based on density functional theory (DFT) [24]. The crystal structure of Bi_2MO_6 falls under the orthorhombic space group *Pca2(1)*. Simulated results suggest that both the valence band and conduction band of Bi_2MO_6 are composed of hybridized Bi *6p*, O *2p* and M *nd* (n = 3, 4, and 5 for Bi_2CrO_6, Bi_2MoO_6 and Bi_2WO_6, respectively) orbitals. Band structures of Bi_2MO_6 are illustrated in Fig. 3, and the predicted bandgaps shown are 1.245 eV, 1.96 eV and 2.2 eV for Bi_2CrO_6, Bi_2MoO_6 and Bi_2WO_6, respectively [24]. These predictions are smaller than experimental results, which determiend the band gaps to be 2.16 eV, 2.63 eV and 2.77 eV for Bi_2CrO_6, Bi_2MoO_6 and Bi_2WO_6 [25,26]. The discrepancy is due to well-known limitations of GGA. However, both suggest that Bi_2MO_6 compounds are suitable for visible-light-activated photocatalysts. It should also be noted that Bi_2CrO_6, despite having the narrowest band gap in Bi_2MO_6, is not suitable for photocatalysis due to easy recombination of the photo-