Recent advances in BiOIO₃ based photocatalytic nanomaterials

Tao Jia, Yixuan Xiao, Zhonghao Ji, Run Wang, Jiang Wu*

College of Energy and Mechanical Engineering, Shanghai University of Electric Power, Shanghai 200090, China

Abstract. Semiconductor photocatalysis technology using solar energy has broad application prospects in energy conversion and environmental purification, while the photocatalytic efficiency is unsatisfactory due to limited photoresponse and recombination of charge carriers. Many researchers have made great efforts to develop new and efficient photocatalysts to solve the above problems. Among photocatalysts, bismuth-based nanomaterials have become ideal photocatalysts because of its unique layered structure, narrow band gap, better visible light response and good electron-hole separation characteristics. Particularly, appropriately modified photocatalysts shows better photocatalytic performance due to enhanced photoresponse characteristics and promoted separation and migration of electron-hole pairs. In this review, the characteristics of bismuth oxyiodate in bismuth-based photocatalysts are systematically introduced. Recent efforts for various modification strategies of bismuth oxyiodate have also been demonstrated and evaluated. Finally, this paper also briefly summarizes and forecasts the challenges and development directions of bismuth-based photocatalysts.

1 Introduction

The rapid industrialization process has caused the excessive consumption of fossil energy, resulting in a series of energy and environmental problems [1]. It is obvious that semiconductor photocatalysis technology can directly utilize solar energy has broad prospects to solve the above problems. Thus, many researchers have made great efforts to develop novel and efficient photocatalytic nanomaterials, while the performance of photocatalysts is not sufficient for the practical application [2]. The main reason is that the recombination of the charge carriers is too rapid to improve photocatalytic efficiency.

Semiconductor photocatalytic reaction mainly involves four processes which include light absorption, generation of electron-hole pairs, separation and recombination of electron-hole pairs and oxidation-reduction reaction on the surface of the semiconductor [3]. As shown in Fig.1, specifically, Semiconductor photocatalysts excitation under solar light, the electrons (e^-) migrate to conduction band (CB), and the holes (h^+) remain in valence band (VB)[3]. In these processes, recombination rate of charge carriers adversely effects on photocatalytic performance. Meanwhile, the poor light absorption rate of the semiconductor photocatalysts also makes the photocatalytic activity low. Therefore, researchers have made considerable efforts to solve the above problems, such as developing novel photocatalysts, doping and introducing heterostructure [4,5].

Recently, bismuth-based photocatalytic semiconductor materials have received widespread attention for their can use of sunlight for energy conversion and environmental purification, such as

photolysis of water to produce hydrogen, reduction of carbon dioxide and degradation of organic pollutants [5]. BiOIO₃ is one of new type bismuth-based layered polar materials, which contains Aurivillius-type (Bi_2O_2)²⁺ layer and (IO_3)⁻ pyramids. Besides, the effect of polarization field-effect on electron transfer makes it show excellent photocatalytic properties [6].

In this review, we systematically introduce the characteristics of BiOIO₃ photocatalysts. Recent efforts for various modification strategies of BiOIO₃ have also been demonstrated and evaluated. Finally, this paper also briefly summarizes and forecasts the challenges and development directions of BiOIO₃-based photocatalysts. We hope this review can help to strengthen and improve the basic theory of photocatalysis, and provide new ideas and guidelines for the development of photocatalysts with efficient.

Fig. 1. Schematic illustration of the basic photocatalytic processes on a semiconductor.

* Corresponding author: wjcf2002@163.com

2 Characteristic of BiOIO₃

In 2011, Nguyen et al. first reported and studied the polarity of BiOIO₃. BiOIO₃, generally, is a new type non-centrosymmetric and polar nanomaterial, which contains two cations of Bi³⁺ and I⁵⁺. It also exhibits Aurivillius-type (Bi₂O₂)²⁺ layer and (IO₃)⁻ pyramids (see Fig.2a,b) [6]. The unique non-centrosymmetric structure has a positive impact on electronic transmission. Moreover, the polarization electric field can promote charge carriers separation, which is favorable for improving photocatalytic performance. BiOIO₃ is a typical layered material that generally exhibiting nanoplate shape. We can simply preparation of BiOIO₃ nanoplates using Bi(NO₃)₃·5H₂O and KIO₃ via hydrothermal method.

Fig. 2. Ball-and-stick representation of BiO(IO₃) (a) and polyhedral representation of the m = 2 Aurivillius phase (b).[6]

In BiOIO₃, Bi 6p, O 2p, and I 5p orbital participate in the formation of the conduction band. The Bi 6s and O 2p orbits participate in the formation of the valence band, reduce the forbidden band width, and release more active factors under the same conditions. At the same time, the O 2p and Bi 6s orbital hybridization makes the BiOIO₃ valence band more dispersed, which is beneficial to the migration of holes, delays or inhibits photogenerated electron recombination, and enhances the efficiency of photocatalytic reaction [5,7]. Although the band gap (about 3.0 eV) of BiOIO₃ is smaller than TiO₂ (about 3.2 eV), its light absorption boundary is still about 410 nm. The existence of internal electric field increases the separation rate of photogenerated electron-hole pairs. However, the large recombination rate has a detrimental effect on the photocatalytic efficiency. Therefore, the modification of BiOIO₃ can be promoted and applied to become a hot spot for many scholars.

3 Modifying photocatalysis of BiOIO₃

3.1. Surface morphological modification

Surface morphological modification is a valid way to enhance the photocatalyst performance. Because the morphology plays an crucial role in photoreaction absorption and charge carriers transfer. The modification

mainly includes adjusting the thickness or thickness of the material layer (thinning or changing the crystal face ratio), constructing the defect structure and the hierarchical structure, so that the material has a larger specific surface area and more active sites [8].

Fig. 3. SEM images of BiOIO₃-x samples prepared at different pH values: (a) BiOIO₃-0.7; (b) BiOIO₃-2; (c) BiOIO₃-3 [9].

In 2016, Qi and our group prepared a series of BiOIO₃ by a simple hydrothermal method [9]. At different pH values, BiOIO₃ exhibits different morphology and crystal structure (see Fig.3), which pH values at 2 to 3 has the optimum performance of photocatalytic oxidation for mercury removal. Usually, the specific surface area and light absorption capacity of bismuth-based materials will be increased by decreasing the thickness of the material sheet, and the photocatalytic performance of materials will be enhanced. Hence, Chen et al. prepared a suitable exposure ratio of (010) and (100) facet by controlling the acidity by hydrothermal method (Fig.4)[10]. Single crystal BiOIO₃ nanoplates with {010} facet exposure ratio of 77.4% exhibited the best photocatalytic activity for CO₂ reduction. Defect structures in photocatalytic materials also have a major impact on photocatalytic performance. Sun et al. in our group demonstrated that BiOIO₃ prepared by calcination method, which possessed oxygen vacancies to capture electrons. It can effectively remove gaseous Hg⁰ under visible light. (see Fig.5)[11].

Fig. 4. The model with photogenerated electrons and holes of the BiOIO₃ nanoplates with 35nm thick [10].

Fig. 5. Mechanism of photocatalytic oxidation gaseous Hg^0 [11].

3.2. Ion doping

When properly introduced ions, the performance of BiOIO_3 photocatalytic materials can be significantly enhanced. In addition to precious metal nanoparticles and graphite non-metallic materials, which can be used as electron trapping agents and modified by non-metallic ions, the carrier trapping effect can also be achieved [5]. Some multivalent transition metal ions can retrieve and lose electrons reversibly, and easily react with e^- and h^+ to form another valent ion, thus capturing electrons or holes.

For instance, Wu et al. in our group reported an in situ reduction method for the preparation of interlining-I/ BiOIO_3 , which could control exposure to high activity (010) facets and reduce band gap [12]. Interlining-I/ BiOIO_3 effectively improves the efficiency of photoresponse and electron hole separation. The efficiency of the best sample is 92.15% (see Fig.6). N-doped BiOIO_3 was successfully prepared via calcination way, which enhanced solar light absorption and showed better photocatalytic efficiency and stability (Table 1) [13]. Replacement of I^{5+} in BiOIO_3 by V^{5+} enhanced its internal polarization, which significantly promotes the transfer of e^- and h^+ . Meanwhile, Huang et al. showed that V- BiOIO_3 could also induce the activation of oxygen actives [14].

Fig. 6. Hg^0 removal efficiency of P25 and all samples under visible light [12].

Table 1. Under LED light: the photodegradation of RhB for N- BiOIO_3 samples and BiOIO_3 [13].

Photocatalyst	Pollutant	Time (min)	Removal (%)
30% N- BiOIO_3	RhB	50	100
20% N- BiOIO_3	RhB	50	90
10% N- BiOIO_3	RhB	50	80
50% N- BiOIO_3	RhB	50	70
BiOIO_3	RhB	50	30

3.3. Constructing a heterojunction

In general, a properly designed heterojunction photocatalyst can show a higher photocatalytic activity, which can increase the visible light response, promote the charge carrier transfer, improve the stability of photocatalyst. Therefore, heterojunction is considered as a promising strategy for photocatalyst modification. Usually, heterojunctions include traditional type-II heterojunctions, p-n heterojunctions, Z-scheme heterojunctions and so on [15].

Fig. 7. Photocatalytic mechanism diagram [16].

Our group Wu et al. successfully prepared the $\text{BiVO}_4/\text{BiOIO}_3$ heterojunction hydrothermal method. It exhibits good photocatalytic activity due to high visible light responsiveness [16]. In Fig.7, we can obviously understand the photocatalytic mechanism of $\text{BiVO}_4/\text{BiOIO}_3$ heterojunction. And this is a traditional type-II heterojunction. With the development of study, researchers have found that p-n heterojunctions exhibit better electron-hole separation and transfer properties. Huang group reported that $\text{BiOI}/\text{BiOIO}_3$ heterostructures were fabricated by in situ reduction. The degradation rate of $\text{BiOI}/\text{BiOIO}_3$ heterostructures is greater than 85% under 1h irradiation, and the photocurrent density is more than 3 times that of pure samples [17]. These all benefit from the stable p-n heterojunction, which greatly promotes the separation of charge carriers (see Fig.8). In 2013, Yu Group proposed the concept of a Z-scheme heterojunction photocatalyst [18]. After that, many

scholars began to study the z-scheme heterojunction. For example, Gong et al. fabricated 2D BiOIO₃/g-C₃N₄ Z-scheme heterojunction, which performed great charge carriers separation ability and excellent redox ability. In Fig.9, It clearly shows the carrier transmission scheme of BiOIO₃/g-C₃N₄ Z-scheme heterojunction [19].

Fig. 8. Schematic diagram for the possible charge separation process of BiOI/BiOIO₃ composite [17].

Fig. 9. Schematic diagram of the different transfer pathways of photogenerated carriers in BiOIO₃/g-C₃N₄ [19].

4 Summary and outlook

BiOIO₃-based photocatalysts have unique layered structure and good visible-light photocatalytic activity. They are a kind of potential photocatalytic materials and have broad application prospects. The research on surface morphology control and modification of BiOIO₃-based photocatalytic nanomaterials has gradually become one of the hotspots in the field of photocatalysis. In recent years, researchers have carried out extensive study on the surface morphology control and surface modification of BiOIO₃-based photocatalysts, and achieved remarkable results. However, the morphology control and surface modification of BiOIO₃ photocatalysts still need to be further strengthened in the following two aspects:

1) The relationship between the process of modified catalyst and photocatalytic performance is not clear enough. Band gaps and structure control have great influence on the morphology and material morphology of BiOIO₃-based nanomaterials, and the influence mechanism needs to be further studied.

2) Research on theoretical calculations and modeling methods is needed in the future. In order to understand more deeply the mechanism and charge transfer kinetics of BiOIO₃ photocatalyst, we need to study further theoretical calculations to reveal the true state of the photocatalytic process in photocatalyst.

Acknowledgement

This work was partially sponsored by National Natural Science Foundation of China (51106133).

References

1. X.M. Sun, J. Lu, J. Wu, D.Y. Guan, Q.Z. Liu, N.Q. Yan, J. Colloid Interf. Sci. **546**, 32 (2019)
2. Y. Su, L. Zhang, W.Z. Wang, Int. J. Hydrog. Energy **41**, 10170 (2016)
3. H. Li, J. Li, Z.H. Ai, F.L. Jia, L.Z. Zhang, Angew. Chem. Int. Ed. **57**, 122 (2018)
4. H.W. Huang, H.L. Ou, J.W. Fen, X. Du, Y.H. Zhang, Colloid Surf. A-Physicochem. Eng. Asp. **518**, 158 (2017)
5. H. Zhang, C.G. Niu, S.F. Yang, G.M. Zeng, RSC Adv. **6**, 64617 (2016)
6. S.D. Nguyen, J. Yeon, S.H. Kim, P.S. Halasyamani, J. Am. Chem. Soc. **133**, 12422 (2011)
7. T. Xiong, F. Dong, Y. Zhou, M. Fu, W.K. Ho, J. Colloid Interf. Sci. **447**, 16 (2015)
8. G.L. Xiang, Y.G. Wang, D. Wu, T.Y. Li, J. He, J. Li, X. Wang, Chem. Eur. J. **18**, 4759 (2012)
9. X.M. Qi, M.L. Gu, X.Y. Zhu, J. Wu, H.M. Long, K. He, Q. Wu, Chem. Eng. J. **285**, 11 (2016)
10. F. Chen, H.W. Huang, L.Q. Ye, T.R. Zhang, Y.H. Zhang, X.P. Han, T.Y. Ma, Adv. Funct. Mater. **28**, 1804284 (2018)
11. X.M. Sun, J. Wu, Q.F. Li, Q.Z. Liu, Y.F. Qi, L. You, Z. Ji, P. He, P.F. Sheng, J.X. Ren, W.B. Zhang, J. Lu, J.J. Zhang, Appl. Catal., B **218**, 80 (2017)
12. J. Wu, K. Xu, Q.Z. Liu, Z. Ji, C.H. Qu, X.M. Qi, H. Zhang, Y. Guan, P. He, L.J. Zhu, Appl. Catal., B **232**, 135 (2018)
13. L.Y. Huang, Y.Q. Wang, Y.P. Li, S.Q. Huang, Y.G. Xu, H. Xu, H.M. Li, Mater. Lett. **246**, 219 (2019)
14. H.W. Huang, S.C. Tu, C. Zeng, T.R. Zhang, A.H. Reshak, Y.H. Zhang, Angew. Chem. Int. Ed. **56**, 11860 (2017)
15. H.J. Li, Y. Zhou, W.G. Tu, J.H. Ye, Z.G. Zou, Adv. Funct. Mater. **25**, 998 (2015)
16. J. Wu, L.J. Zhu, F.G. Tian, Q.Z. Liu, L.L. Zhao, Y. Guan, F.Q. Li, Z.Z. Guan, H. Zhang, Catal. Lett. **148**, 3193 (2018)
17. H.W. Huang, K. Xiao, K. Liu, S.X. Yu, and Y.H. Zhang, Cryst. Growth Des. **16**, 221 (2015)
18. J.G. Yu, S.H. Wang, J.X. Low, W. Xiao, Phys. Chem. Chem. Phys. **15**, 16883 (2013),
19. Y. Gong, X. Quan, H.T. Yu, S. Chen, H.M. Zhao, Appl. Catal., B **237**, 947 (2018)