

Research Progress on Bismuth-Based Semiconductors in Photocatalysis

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Abstract. With the escalating global energy crisis and environmental pollution, photocatalysis technology has emerged as a promising new avenue for development. Bismuth-based semiconductors have garnered attention as focal subjects of research in the scientific community for advancing photocatalysis technology. This article begins by introducing the crystal structure, optical properties, and electronic structure of each bismuth-based semiconductor, elaborating on their key attributes in photocatalytic applications. Through a discussion of the diverse applications of different bismuth-based semiconductors in photocatalysis, including organic compound degradation, water splitting for hydrogen generation, and redox reactions, the article analyzes their photocatalytic performance, stability, and mechanisms. This provides readers with a comprehensive understanding of the potential and limitations of these materials in practical applications. Finally, the article summarizes the challenges present in current research and outlines future directions, advocating for further exploration and innovation to propel the application of bismuth-based semiconductors in fields such as clean energy and environmental purification.

Keywords: Bismuth-based semiconductors, crystal structure, optical properties, electronic structure, photocatalysis, organic compound degradation, redox reactions.

1. Introduction

In the context of rapid global economic development, the energy issue has increasingly highlighted its particular and strategically important position in the national economy, becoming a focal point of attention in international fields such as politics, economy, military, and diplomacy. The rapid development of industry has given rise to sustained economic growth worldwide. However, accompanying this growth are severe challenges faced by fossil energy resources, such as energy crises and environmental pollution, which have become the most pressing and complex problems of the present. In such a context, how to effectively utilize natural resources, address environmental and energy issues, and promote sustainable economic development, has become a highly focused topic in the scientific community. At the same time, against the backdrop of the escalating globalization of the global economy and the rapid advancement of China's modernization process, a crucial question arises: how to profoundly understand the trends in energy development and select appropriate energy development strategies. This is an important issue that urgently requires thoughtful consideration [1].

Back in the 1960s to 1980s, research on photocatalysis primarily focused on the photodegradation and photooxidation of organic pollutants. During this period, Japanese researchers Akira Fujishima and Kenichi Honda first reported in 1972 the experimental results of using titanium dioxide (TiO_2) for photocatalytic degradation of organic substances in water [2]. This study established the significant role of semiconductor materials in photocatalysis. From the 1980s to the 1990s, titanium dioxide became the central focus of photocatalysis research. Fujishima and Honda discovered that when the surface of titanium dioxide was irradiated by ultraviolet light, it produced hydroxyl radicals and superoxide radicals, enabling the degradation of organic pollutants and the elimination of bacteria.

From the 2000s to the 2010s, researchers began exploring ways to enhance the activity and stability of photocatalysts. By manipulating factors such as catalyst crystal structure, surface morphology, and doping, they improved the photocatalytic performance of the catalysts. Additionally, the introduction of new types of photocatalytic materials opened up new possibilities for photocatalysis technology. For instance, researchers found that materials like metal oxides, semiconductor quantum dots, and

metal-organic frameworks exhibited exceptional performance in photocatalysis, expanding the range of photocatalytic applications.

After 2010, the applications of photocatalysis technology continued to expand. Beyond water and air purification, photocatalysis found use in organic synthesis, photovoltaic water splitting for hydrogen production, carbon dioxide reduction, and solar cells, among other fields [3]. Researchers also began exploring the integration of photocatalysis with other technologies, such as photoelectrocatalysis, photothermal catalysis, and photovoltaic photocatalysis, to enhance energy conversion efficiency and the sustainability of applications [4]. Photocatalysis technology is gradually maturing.

Bismuth (Bi) is a heavy metal element that is widely present and abundant in nature. Compared to other heavy metals, bismuth possesses several unique advantages, making it a green resource. Bismuth is relatively stable and can maintain chemical stability over a long period. Its lower price makes it an economically viable material choice. Furthermore, bismuth and its compounds have low toxicity, and lack carcinogenic and biotoxic properties, enhancing its safety and reliability.

Bismuth-based semiconductors are a class of semiconductor materials with distinctive electronic structures and excellent electrical properties. Comprising bismuth along with other elements, common bismuth-based semiconductors include bismuth oxides, bismuth sulfides, and bismuth halides. These materials exhibit diverse crystal structures and chemical compositions, leading to varying photocatalytic performances [5].

The following sections will introduce four typical Bi-based semiconductors in terms of their properties, applications, and photocatalytic performances.

2. The current research status of BiVO₄

BiVO₄ belongs to the tetragonal crystal system and exhibits a typical perovskite structure. It consists of alternating vanadium-oxygen octahedra and bismuth-oxygen octahedra. The band gap of BiVO₄ typically ranges from 2.0 to 2.5 eV, enabling it to absorb light in the visible spectrum and generate highly active electron-hole pairs for photocatalytic reactions.

BiVO₄ can be used for the catalytic degradation of organic pollutants, such as dyes and harmful compounds in wastewater, contributing to environmental protection and water purification. BiVO₄ also enables the photocatalytic water splitting reaction under visible light, offering the potential for sustainable energy research and applications. Additionally, BiVO₄'s application in optoelectronic devices and solar cells is of great interest, driving the development and utilization of optoelectronic functional materials.

Sayama K et al. synthesized porous BiVO₄ thin films using a metal-organic decomposition method and treated them with AgNO₃ aqueous solution [6]. The obtained BiVO₄ was applied to water splitting. The experimental results revealed that under visible light illumination, H₂ and O₂ were produced in a stoichiometric ratio (H₂/O₂=2) with an external bias from a Na₂SO₄ aqueous solution. Additionally, the photocurrent increased when methanol was added. Compared to conventional oxide semiconductors without Bi, the valence band edge of BiVO₄ showed a negative shift, possibly due to the hybridization effect between O 2p and Bi 6s orbitals. After treatment with AgNO₃ aqueous solution, the photocurrent of the BiVO₄ electrode was significantly improved. The maximum conversion efficiency of photocurrent reached 44% at a wavelength of 420 nm. Moreover, the AgNO₃ treatment enhanced the stability of the photocurrent, indicating that Ag⁺ ions catalyzed the intrinsic hole oxidation reaction in BiVO₄.

Zhang Fan et al. synthesized flower-like and rod-like BiVO₄ photocatalysts using an alcohol-water hydrothermal method. During the experimental process, different surfactants (CTAB, PEG10000, and SDS) were used to prepare different photocatalyst samples [7]. They performed a series of tests on the BiVO₄ photocatalysts using X-ray diffraction, scanning electron microscopy, and UV-visible absorption spectroscopy. The test data indicated that the flower-shaped nano/microparticle BiVO₄ had the smallest band gap and the highest degradation rate, demonstrating its excellent photocatalytic

activity in the degradation of Methyl Orange (MO) under visible light excitation. After three hours, its degradation rate of MO reached 91%. It exhibited good light absorption performance and high photocatalytic activity.

Liu Yufei et al. prepared oxygen vacancy-modulated BiVO_4 nanosheets using hydrothermal and sintering methods [8]. They studied the structure and photocatalytic oxygen production performance of BiVO_4 nanosheets with different oxygen vacancy contents (O_v). By regulating the oxygen vacancy content, they successfully optimized the light absorption and photoelectric properties of BiVO_4 nanosheets, greatly improving the efficiency of photocatalytic oxygen production from water splitting. The experimental results showed that the introduction of oxygen vacancies significantly enhanced the light absorption of BiVO_4 nanosheets in the visible light region, and with the increase of oxygen vacancy content, the absorption edge exhibited a noticeable red shift. The introduction of appropriate oxygen vacancies notably improved the separation of photogenerated electrons and holes, thereby increasing the utilization efficiency of photogenerated electrons.

3. The current research status of Bi_2WO_6

Bi_2WO_6 is an important bismuth tungstate composite oxide with a monoclinic crystal structure. Its crystal structure consists of two layers of bismuth tungstate connected by oxygen atoms. Each bismuth tungstate layer is composed of alternating BiO_6 octahedra and WO_6 octahedra. The connection between the bismuth tungstate layers is bridged by oxygen atoms. Bi_2WO_6 exhibits excellent photocatalytic performance with a band gap in the range of 2.8-3.1 eV, enabling it to use visible light energy to degrade organic pollutants into harmless substances. Thus, it holds promising applications in environmental protection and water treatment.

Through hybridization effects, Bi_2WO_6 undergoes significant changes in its Bi 6s and O 2p orbitals, leading to a considerable reduction in the bandgap width and the formation of a narrower bandgap structure. Due to the narrow bandgap width of Bi_2WO_6 , it can absorb more visible light and generate more electron-hole pairs. This results in higher activity and efficiency of Bi_2WO_6 in visible-light photocatalytic reactions. The outstanding performance of Bi_2WO_6 can also be attributed to its appropriate conduction band position and redox potential. The conduction band position determines the electron's oxidation ability, while the redox potential reflects the catalyst's redox capability in photocatalytic reactions. By appropriately adjusting the synthesis conditions and controlling the presence of impurities, the conduction band position and redox potential of Bi_2WO_6 can be tuned to meet the specific requirements of certain photocatalytic reactions.

Zhang Jianqiao et al. successfully introduced WSe_2 into Bi_2WO_6 using a hydrothermal synthesis method, resulting in $\text{Bi}_2\text{WO}_6/\text{WSe}_2$ with separated photogenerated electron-hole pairs at the heterojunction interface [9]. This design prevents the rapid in situ recombination of electrons and holes in the band gap of single Bi_2WO_6 catalytic nanostructures, facilitating the separation of photogenerated charge carriers and reducing the band gap.

Hu Le et al. successfully synthesized a novel visible-light-driven $\text{PW}_{12}/\text{Bi}_2\text{WO}_6$ composite material using a two-step method [10]. They tested the activity of this composite catalyst using methylene blue (MB) as a model pollutant. Experimental results showed that the introduction of PW_{12} significantly enhanced the photocatalytic activity compared to pure Bi_2WO_6 . The highest photocatalytic activity of $\text{PW}_{12}/\text{Bi}_2\text{WO}_6$ was achieved at $m(\text{PW}_{12})/m(\text{Bi}_2\text{WO}_6) = 2:8$, calcination temperature of the composite catalyst at 400°C , MB concentration of 10 mg/L, and a composite catalyst dosage of 0.1 g. After 1.5 hours of light irradiation, the removal rate of MB reached 90.87%, and after 2 hours of light irradiation, the removal rate reached 99.71%.

Yang Jinshui et al. synthesized different morphologies of Bi_2WO_6 by controlling the acetic acid content during the hydrothermal reaction [11]. They investigated the differences in photocatalytic performance using Rhodamine B as the target pollutant for degradation. The experimental results indicate that the addition of 10 mL of acetic acid as a photocatalyst Bi_2WO_6 achieved the best degradation efficiency for Rhodamine B. After 50 minutes, the degradation rate reached 99%, and

after 5 repeated uses, the degradation rate remained as high as 97%, demonstrating excellent stability. Free radical capture experiments revealed that superoxide radicals played the most important role in the entire photocatalytic process, followed by holes, and finally hydroxyl radicals.

With the continuous deepening of Bi_2WO_6 research, methods for bandgap engineering will be further enriched and improved. Researchers can explore the electronic structure and band characteristics of Bi_2WO_6 more accurately and reliably by using theoretical calculations and advanced materials characterization techniques, providing a more solid theoretical basis for bandgap engineering. Moreover, the development of material synthesis techniques will offer more possibilities for structural control of Bi_2WO_6 . Through interdisciplinary collaboration and combining advancements in nanotechnology, optoelectronics, and materials science, it is anticipated that breakthroughs in bandgap engineering of Bi_2WO_6 will be achieved, unlocking more opportunities and potential in applications such as photovoltaic conversion, catalysis, and energy storage.

4. The current research status of BiPO_4

BiPO_4 is a bismuth phosphate composite oxide with an orthorhombic crystal structure. Its crystal structure is composed of alternating BiO_8 and PO_4 tetrahedra. BiPO_4 has a band gap in the range of 3.0-3.5 eV and exhibits excellent photocatalytic performance, enabling it to use light energy to degrade organic pollutants into harmless substances in the visible light range.

Due to its unique crystal structure and bandgap range, BiPO_4 can absorb light in the visible range, generating highly active photo-generated charge carriers, thereby exhibiting excellent performance in photocatalytic processes. It can be used to degrade organic pollutants, such as organic dyes and hazardous compounds in wastewater, converting them into harmless substances, and contributing to environmental protection and water purification. Additionally, BiPO_4 finds applications in optoelectronic devices, solar cells, and other fields. Its research contributes to the development of efficient visible-light-responsive photocatalytic materials and novel optoelectronic functional materials, offering significant practical value in addressing environmental and energy challenges.

Liu Yanfang et al. obtained a BiPO_4 photocatalytic material with a large specific surface area and excellent dye degradation performance for wastewater by adding melamine to a suspension containing BiPO_4 precursors obtained from mixing bismuth nitrate and phosphate solution [12]. This was followed by heating treatment, centrifugation, and calcination, achieving low energy consumption. The obtained composite photocatalytic material exhibits a higher removal rate for methylene blue, reaching up to 98%. Therefore, this composite photocatalyst demonstrates excellent degradation efficiency for recalcitrant organic dyes.

Ren Wang et al. prepared BiPO_4 using a hydrothermal method and then loaded AgI onto the surface of BiPO_4 through a precipitation method to form an AgI/ BiPO_4 heterojunction [13]. The AgI/ BiPO_4 heterojunction was characterized using XRD, UV-Vis DRS, and SPS to study the photogenerated charge separation characteristics. The results indicated that the heterojunction photocatalyst showed the highest photogenerated electron-hole separation rate, and the optimal AgI/ BiPO_4 molar ratio for the best Rhodamine B photocatalytic degradation performance was 1.2%. The main active radicals were $\cdot\text{O}_2^-$, while h^+ holes and $\cdot\text{OH}$ radicals played a minor role.

5. The current research status of BiOF

BiOF has an orthorhombic crystal structure. It consists of alternating BiO_6 octahedra and OF_4 tetrahedra, forming a layered structure. BiOF has a band gap in the range of 2.8-3.0 eV and exhibits excellent performance in photocatalytic processes. It efficiently absorbs light in the visible spectrum, induces charge separation, and generates high-activity oxidative radicals.

BiOF efficiently absorbs visible and near-infrared light, showing potential applications as a visible-light responsive photocatalyst. Its generation of highly active photo-generated charge carriers makes it suitable for organic pollutant degradation and wastewater treatment, contributing to

environmental protection and water purification. Additionally, BiOF finds applications in optoelectronic devices and solar cells, providing a research foundation for novel optoelectronic functional materials. In-depth research on BiOF can further optimize its performance and practical applications in environmental and energy-related fields.

Wang Jingzhen et al. effectively separated electron-hole pairs and prolonged the separation state of photogenerated electrons by limiting the mass ratio of $\text{Bi}_7\text{O}_5\text{F}_{11}$ and BiOF in the range of 7:1 to 1:1 at the $\text{Bi}_7\text{O}_5\text{F}_{11}$ /BiOF heterojunction interface [14]. This enhanced the oxidation-reduction ability of electron-hole pairs, thereby improving the photocatalytic activity. Under 60 minutes of ultraviolet light irradiation, the complete degradation of 15mg/L of $\text{C}_8\text{HF}_{15}\text{O}_2\text{S}$ can be achieved. In contrast, with an initial concentration of 15mg/L, it takes 150 minutes for In-MOF/BiOF to reach a degradation rate of 100%. This indicates that the $\text{Bi}_7\text{O}_5\text{F}_{11}$ /BiOF heterojunction photocatalyst exhibits excellent catalytic degradation performance towards $\text{C}_8\text{HF}_{15}\text{O}_2\text{S}$.

Liu Wen et al. prepared BiOF: Tm^{3+} Yb^{3+} by using a mixed solution of pentahydrated bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and ammonium fluoride (NH_4F) as precursors through a solvothermal method [15]. The prepared BiOF: Tm^{3+} , Yb^{3+} was then mixed with the precursor solution of Bi_2WO_6 , and the reaction was carried out in a high-temperature and high-pressure reaction kettle, followed by natural cooling in an oven. After centrifugation and washing three times, the mixture was dried in the oven to obtain the Bi_2WO_6 /BiOF: Tm^{3+} , Yb^{3+} composite photocatalyst. This method is simple, mild in conditions, and cost-effective, showing significant degradation efficiency for organic pollutants under visible and near-infrared light irradiation.

Cao Jiangxing et al. prepared a hydrogen production system by mechanically ball-milling and heat-treating a mixture of reduced metals and silicon powder in molar ratios of 0.01-2 for one or more of lithium, potassium, sodium, calcium, barium, and magnesium as the reduced metals, 0.03-0.3 for one or more of other reduced metals and magnesium, 0.01-0.15 for bismuth salt and silicon, and 0.01-0.2 for ammonium salt and silicon. The mixture was then combined with an ammonium salt. The resulting material with the highest hydrogen production rate upon reaction with water was obtained, with magnesium metal being an essential component, and the bismuth salt comprising one or two of BiCl_3 , BiF_3 , BiBr_3 , BiOCl , BiOF, and BiOBr , and the ammonium salt comprising one or two of NH_4F , NH_4Cl , NH_4Br , $(\text{NH}_4)_2\text{CO}_3$, and NH_4HCO_3 , as confirmed by testing [16].

6. Conclusion

This article provides a comprehensive analysis and summary of the research status of four bismuth-based semiconductors: BiVO_4 , Bi_2WO_6 , BiPO_4 , and BiOF. Bismuth-based semiconductors have attracted widespread research interest due to their unique band structures and excellent photoelectric properties. BiVO_4 exhibits superior light absorption and charge carrier mobility in the field of photocatalysis, making it a promising photocatalyst for efficient water splitting and carbon dioxide reduction. Bi_2WO_6 is of interest for its good visible light response and efficient photogenerated charge separation, making it suitable for water purification and organic waste degradation. As a novel visible-light-responsive semiconductor, BiPO_4 shows outstanding performance in the photocatalytic degradation of organic pollutants. BiOF, with a tunable band structure, demonstrates excellent photocatalytic performance, holding potential for applications in organic pollutant degradation and water purification.

Despite exhibiting favorable photoelectric properties, some bismuth-based semiconductors have relatively low absorption efficiency in the visible light region, limiting their photocatalytic and optoelectronic device efficiency. The stability and lifespan issues of the four bismuth-based semiconductor materials still exist, especially susceptible to degradation and deactivation in complex environments. Additionally, current preparation methods and processes require further optimization to achieve large-scale and high-efficiency production.

To overcome the limitations of bismuth-based semiconductors and expand their applications, future research can focus on several aspects: utilizing advanced material design and computational

methods to optimize the band structure of bismuth-based semiconductors and enhance photoelectric conversion efficiency; exploring novel synthetic methods and processes to achieve controllable preparation and large-scale production of bismuth-based semiconductors; integrating other functional materials to construct composite structures, improving catalytic performance and stability. Furthermore, in-depth mechanistic research can deepen the understanding of the photocatalytic and electrocatalytic behaviors of bismuth-based semiconductors. Alongside this, it is essential to emphasize environmental friendliness and ecological safety assessment to ensure the sustainable development of bismuth-based semiconductors in practical applications.

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