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Structure-Property Relationships in BiOBr Photocatalysts: Impacts of Synthesis Strategies on Microstructure and Photocatalytic Performance

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Abstract. For environmental and energy applications, high-performance photocatalysts can be synthesized controllably. As a layered semiconductor with a visible-light band gap, bismuth oxybromide (BiOBr) is a promising photocatalyst. By precisely regulating crystal nucleation and growth, facet exposure and defect distribution, diverse preparation routes provide strong technical support for the construction of high-efficiency and stable BiOBr photocatalysts. This paper reviews the mainstream synthetic methods of BiOBr, with an emphasis on the growth mechanisms and performance regulation laws of solution-phase method, template-oriented method and vapor deposition method. Relying on the effects of solvent polarity, spatial confinement and chemical potential adjustment, BiOBr preparation enables precise control of crystal shape and crystallinity. Through morphology optimization, better carrier separation, and structural stabilization, performance modification strategies overcome the limitations of pure-phase BiOBr, thus enhancing photocatalytic activity and cycling stability. By examining the structure-performance relationship shaped by synthesis conditions, this paper compares the regulatory traits of various methods and highlights their key advantages and applications.

Keywords: BiOBr, Layered Structure, Photogenerated Carrier Separation, Morphology Control, Photocatalytic Activity

1. Introduction

Due to rising demand for sustainable energy and environmental remediation, efficient visible-light photocatalysts are urgently needed. However, conventional wide-bandgap semiconductors, such as TiO_2, absorb only a limited portion of solar light, motivating the development of novel materials. Exhibiting a layered $[Bi_2O_2]^{2+}/Br^-$ structure, a ~2.7 eV band gap, and an intrinsic electric field, bismuth oxybromide (BiOBr) facilitates efficient charge separation and demonstrates high activity in pollutant degradation, photocatalytic water splitting, and antibacterial applications. Despite the broad application potential of BiOBr, its photocatalytic performance remains limited by intrinsic material drawbacks. Thus, conventional synthesis typically yields irregular morphologies and wide particle size distributions, reducing surface-active sites and diminishing light-harvesting efficiency.

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Meanwhile, rapid recombination of photogenerated electron-hole pairs sharply lowers quantum yield. Laboratory-scale synthesis is difficult to scale up, and the material exhibits poor long-term stability in complex environments, significantly hindering industrial application. To overcome these limitations, adjusting synthesis parameters, applying template-assisted approaches, and using vapor deposition techniques can efficiently refine BiOBr's morphology, crystallinity, and surface area. In addition, ion doping, heterojunction construction, and surface modification can boost charge-carrier separation and improve structural stability. Nevertheless, systematic comparative studies of these strategies are limited, and their synergistic effects across the full chain from material synthesis to practical applications remain largely unexplored. Based on related studies, this paper evaluates how various synthesis methods influence BiOBr's microstructure and photocatalytic performance. Key challenges in morphology uniformity, carrier separation, and long-term stability are analyzed, and practical strategies for performance improvement are summarized. This study is expected to provide theoretical basis and methodological references for the rational design of high-efficiency, stable and scalable BiOBr-based photocatalytic materials.

2. Structural and functional characteristics of BiOBr

2.1. Material structural characteristics

BiOBr is a typical V-VI-VII ternary semiconductor with a tetragonal PbFCl-type structure (space group P4/nmm). Its structure has alternating electropositive $[Bi_2O_2]^{2+}$ layers and electronegative Br^- double layers along the c-axis [1]. Thus, weak van der Waals forces govern interlayer interactions, allowing easy cleavage along the (001) facet. This layered stacking gives BiOBr distinct cleavage properties and generates internal built-in electric fields and dipole moments between layers. These unique properties facilitate the directional migration of photogenerated electrons and holes, thereby suppressing the recombination rate of charge carriers.

In terms of electronic structure, BiOBr is an indirect bandgap semiconductor. The conduction band minimum is mainly contributed by Bi 6p orbitals, while the valence band maximum originates from O 2p and Br 4p orbitals [2]. For indirect bandgap semiconductors, photoinduced electron transitions require phonon participation to satisfy momentum conservation, which effectively prolongs carrier lifetime and reduces the direct recombination probability of electron-hole pairs. Furthermore, the interlayer spacing, bond length and intrinsic micro-defects of the layered structure can modulate the intensity of the built-in electric field and carrier migration pathways. Accordingly, the electron transfer rate and local surface charge distribution are precisely regulated, exerting significant influences on light absorption capacity and photogenerated carrier kinetics.

2.2. Performance and functional properties

Possessing unique crystal architecture and electronic properties, BiOBr exhibits versatile functional characteristics. It has a band gap of approximately 2.7eV and absorbs visible light below 460 nm, broadening solar spectrum use. The layered structure's built-in electric field, along with its indirect bandgap, promotes spatial separation of photogenerated electrons and holes and enhances reactive oxygen species (e.g., O_2^-) generation. Under specific conditions, these reactive oxygen species can indirectly produce hydroxyl radicals (·OH) via chain reactions, enabling efficient photocatalytic removal of water pollutants and nitrogen oxides. With good chemical stability, BiOBr maintains long-term catalytic activity in clean energy conversion processes, including photocatalytic CO_2 reduction, water splitting for hydrogen production, and photocatalytic nitrogen fixation [1].

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For antibacterial performance, light-induced reactive oxygen species can damage bacterial cell membranes, proteins and nucleic acids. Moreover, the inherent bacteriostatic effect of bismuth elements synergizes with photocatalytic oxidation, giving BiOBr strong antibacterial ability for coatings, medical dressings, and water treatment membranes. In addition, the distinctive layered structure delivers a large specific surface area and abundant surface active sites, which greatly promote the adsorption of target molecules. As a semiconductor, BiOBr's conductivity and surface photopotential are highly sensitive to adsorbates. This advantage supports the development of high-sensitivity electrochemical and photoelectrochemical sensors for the detection of heavy metal ions, organic pollutants and specific biomolecules in water environments.

3. Various BiOBr preparation strategies and their influences

3.1. Solution-phase methods and microstructure regulation

Using solution-phase synthesis, including hydrothermal, solvothermal, and chemical precipitation, the crystal shape, particle dimensions, and exposed facets of BiOBr can be finely tuned by adjusting reaction conditions, thereby affecting photogenerated charge separation and electron transport.

In hydrothermal and solvothermal systems, bismuth nitrate pentahydrate is commonly adopted as the bismuth source, while NaBr, KBr or CTAB serve as bromine sources. Water, ethanol, ethylene glycol, or dilute acetic acid serve as reaction media for high-temperature, high-pressure reactions at 120-200 °C. For example, Zhang et al. prepared BiOBr nanosheets via a simple hydrothermal route by setting the reaction pH to 9 with NaOH [3]. Similarly, Lv et al. fabricated Cu-doped flower-like BiOBr photocatalysts via a solvothermal strategy [4]. Microwave-assisted hydrothermal method can greatly shorten the reaction time to approximately 2 hours. Meanwhile, BiOBr morphology can be precisely tuned by altering solvent, reaction temperature, and microwave power. Using this method, Zhou et al. synthesized four BiOBr variants with unique shapes: microspheres, microflowers, thick nanoplates, and thin nanosheets [5]. Solvent polarity strongly affects crystal nucleation and growth orientation, thereby enabling controlled fabrication of nanosheets, hierarchical microspheres, and flower-like structures. Moreover, chelating agents such as citric acid selectively guide facet growth, promoting the formation of thick-plate structures. Thus, morphology directly influences specific surface area and facet exposure, thereby controlling the migration and separation of photogenerated electron-hole pairs.

In addition, chemical precipitation is a widely applied liquid-phase synthesis method, including co-precipitation-reflux, room-temperature ultrasonic co-precipitation, low-temperature hydrolysis, and ion exchange. Li et al. prepared BiOBr/black phosphorus nanocomposites via a co-precipitation approach. This method operates under mild conditions and can be conducted at room temperature or with oil-bath reflux. By controlling precursor concentration, pH, and bromine source, high-purity, size-tunable BiOBr nanosheets are obtained [6]. Furthermore, changes in precipitation rate and ion concentration modify grain size, exposed facets, and pore structure, hence further modulating light absorption, surface active site distribution, and electron transfer kinetics.

3.2. Template-oriented methods and pore structure optimization

Template method constructs BiOBr with specialized morphologies and porous structures through spatial confinement and morphology-orienting effects, so as to regulate its photocatalytic and other functional properties. For hard template strategy, polyester fibers are commonly utilized as rigid templates, and BiOBr grows via in-situ deposition on the fiber surface. Polyethylene terephthalate,

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the main component of staple polyester fibers, can be hydrolyzed under alkaline conditions. After template removal, repeated washing and drying produce one-dimensional hollow fibers. And these well-defined structures have abundant pores, increasing exposed facets and active sites, extending carrier migration paths, and enhancing photocatalytic efficiency.

In terms of the soft template method, L-lysine, surfactants or small organic molecules work as structure-directing agents. These agents selectively adsorb on specific facets via functional groups, directing crystal growth and promoting oriented nanosheet assembly into hierarchical microspheres or structures with abundant exposed facets. Following this method, Li et al. synthesized BiOBr microspheres using a bio-template strategy, giving the material a loose structure and significantly increasing exposed active sites [7]. This green, non-toxic synthesis produces well-dispersed BiOBr. Moreover, optimized facet configuration and high surface area enhance electron-hole separation and surface reactivity. For example, Wu et al. used a microreactor system with Triton X-100, n-amyl alcohol, cyclohexane, and water to fabricate flower-like BiOBr microspheres (100-200 nm) through dual microemulsion mixing and room-temperature aging [8]. During this process, particle size and morphology were precisely controlled, thus resulting in high surface area and hierarchical pores that boost light absorption, reactive oxygen species generation, and photocatalytic performance.

3.3. Vapor deposition and crystal crystallinity control

Chemical vapor deposition (CVD) is employed to synthesize high-quality two-dimensional BiOBr single crystals. By optimizing reaction conditions to tailor crystallinity and defect distribution, the electron migration behavior and photocatalytic performance can be effectively improved. In this method, $BiBr_3$ serves as the bismuth source, oxygen acts as the oxygen source, and argon is used as the carrier gas. Van der Waals epitaxial growth of BiOBr is realized on diverse substrates such as mica, quartz, SiO_2/Si and FTO. The reaction temperature is generally controlled within the range of 380-440°C. By adjusting substrate position and carrier gas flow, 2D single crystals with tunable thickness (3-36 nm) and square, rectangular, or dendritic shapes can be obtained. Building on this approach, Yang et al. fabricated 2D BiOBr crystals via a chemical-potential-regulated CVD strategy. Temperature gradient, carrier gas flow, and reaction time directly control grain growth rate, facet selectivity, and interlayer uniformity [9].

On this basis, the adjustment of oxygen flow can modulate the oxygen chemical potential of the reaction system and introduce bismuth vacancies or oxygen vacancies. And these defects regulate carrier type, giving the material p-type or n-type conductivity, and reshape the local electric field and surface active site distribution, enhancing photogenerated electron-hole separation efficiency. The control of oxygen chemical potential and deposition temperature enables directional regulation of grain size and facet exposure, increases surface area, and enhances light absorption and reactive oxygen species generation. Benefiting from the precise regulation of above parameters, 2D BiOBr crystals prepared by CVD exhibit well-ordered facets, controllable defect distribution and high interlayer homogeneity at the microscale. These superior features enhance photogenerated charge separation, speed up photocatalytic reactions, and improve adsorption of organic molecules and electron transport

3.4. Comparison of preparation strategies and performance applications

The hydrothermal method, using a sealed system with minimal impurities, produces BiOBr with high crystallinity and uniform morphology, while mainstream synthesis strategies vary in efficiency, morphological control, cost, and application. Nevertheless, this approach suffers from long reaction

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duration and high energy consumption, and requires high-pressure autoclaves, making it suitable for high-crystallinity powders and composite photocatalysts. The solvothermal method enables precise regulation of crystal growth orientation and morphology by adjusting solvent polarity, obtaining materials with large specific surface area and excellent light response. However, organic solvent use raises cost and demands extra waste treatment. And this method is more applicable to the rational design of catalysts with tailored microstructures and optimized surface properties.

Under ambient temperature and pressure, chemical precipitation offers simple operation, fast reaction, low cost, and scalable production. By adjusting precipitation rate and ion concentration, grain size, facet exposure, and pore structure are controlled, though products often show severe aggregation and low crystallinity. Accordingly, this method suits low-cost, large-scale photocatalyst production. Template and microemulsion approaches use spatial confinement and morphology guidance to build materials with well-defined pores and uniform shapes. Hard and soft templates form ordered channels by directing crystal growth, while microemulsions enhance surface area and create hierarchical pores. However, these methods involve complex procedures, difficult template or surfactant removal, and relatively low yield, making them more suitable for fundamental studies of special structures and high-performance catalysts.

In contrast, chemical vapor deposition can fabricate large-area 2D BiOBr with high purity and low defects, while allowing modulation of conductivity type and defect distribution via parameter optimization. Although ideal for optoelectronic devices and 2D material research, it is limited by costly equipment, complex procedures, and low yield. Thus, synthesis route selection should match practical needs. For example, chemical precipitation enables low-cost, large-scale production, while hydrothermal synthesis ensures high crystallinity and stability. In addition, solvothermal synthesis produces specialized morphologies and enhanced catalytic activity, and template methods generate ordered channels and fine microstructures. Besides, CVD delivers high-purity materials for device applications. And future optimization should target simpler processes, lower energy use, and precise microstructure control [2, 7].

4. Preparation issues and structure-performance regulation of BiOBr

4.1. Regulation of morphology and size uniformity

In conventional liquid-phase synthesis, BiOBr often forms stacked nanosheets with uneven sizes and irregular shapes, reducing batch consistency, active site density, and light absorption. This is caused by uneven crystal nucleation and growth: elevated precursor concentration and solvent mismatch accelerate nucleation, while limited spatial confinement drives unidirectional crystal growth, resulting in particle clustering and irregular facet alignment.

To address the above issues, the morphological regularization of BiOBr is achieved through the synergistic effect of crystallization kinetics regulation and spatial confinement. Babu realized the directional morphology control of BiOBr by precisely tuning the temperature, reaction time and precursor concentration in the solvothermal process, achieving uniform, highly crystalline structures [10]. Besides, Zandi developed a BiOBr/TiO_2 heterojunction and anchored it onto a porous zeolite support. By virtue of the spatial restriction of the support and the interaction between heterojunction components, the excessive growth and agglomeration of nanosheets were effectively suppressed, improving the dispersion uniformity [11]. The regulatory mechanism entails balancing nucleation and growth rates, guiding crystal growth, and avoiding random stacking and misorientation, thereby increasing surface area, refining electric field distribution, and improving photocatalytic efficiency.

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Therefore, precise reaction control ensures high crystallinity and uniform morphology, while carrier loading with heterojunction formation promotes high dispersibility and prevents agglomeration.

4.2. Optimization of photogenerated carrier separation efficiency

Rapid electron-hole pair recombination and brief carrier lifetimes constitute the primary limitation on the quantum efficiency of BiOBr. Besides, the intrinsic electric field in pure BiOBr is too weak for effective long-range charge separation. Accordingly, lattice defects generated during synthesis serve as recombination centers, hastening the decay of charge carriers.

To break through this limitation, mainstream modification strategies focus on band engineering and interfacial structure design. Specifically, Meng et al. summarized that ion doping (Co, Ag^{+}, Er^{3+}, Zn, Cu, B) can introduce intermediate energy levels within the band gap of BiOBr. This modulation adjusts the band structure and local charge distribution, extends the spectral response range, and enhances bulk charge separation efficiency [12]. Building on this approach, Xie et al. fabricated Bi_3O_4Cl/BiOBr heterojunctions via an in-situ synthetic route. Under light irradiation, electrons and holes migrate directionally along the heterojunction interface, enabling efficient spatial separation and reduced charge recombination [13]. In addition, facet engineering and hierarchical structural design shorten charge transport pathways and lower the likelihood of interfacial recombination.

Doping introduces defect energy levels to enhance light responsiveness and bulk conductivity, while heterojunctions drive spatial charge separation relying on the interfacial built-in electric field. In addition, optimized facets and hierarchical architectures streamline charge transport pathways and mitigate recombination loss. Relevant results indicate that the synergistic effect of the above strategies can prolong carrier lifetime and significantly boost the catalytic efficiency of pollutant degradation, CO_2 reduction and other reactions.

In terms of strategy selection, ion doping with in-gap intermediate energy levels is preferable for broadening light absorption spectrum. Heterojunctions enhance spatial charge separation, with the interfacial built-in electric field directing electron and hole migration. Meanwhile, facet engineering and hierarchical structuring improve surface reaction selectivity and charge transport efficiency by optimizing transport pathways and reducing recombination.

4.3. Scalable preparation and long-term stability enhancement

When BiOBr is scaled from laboratory synthesis to industrial production, nonuniform temperature profiles and significant mass transfer gradients in reactors frequently lead to irregular morphology and poor batch reproducibility. Additionally, the layers of pure-phase BiOBr are only bonded by weak van der Waals forces, which readily causes sheet peeling, component leaching, and structural collapse in water and during cycles, resulting in rapid loss of catalytic activity.

To break through the bottlenecks of scale-up and stability, regulation should be implemented through dual pathways: process optimization and structural reinforcement. At the process level, it is necessary to achieve large-area uniform film formation by optimizing chemical vapor deposition parameters, and adopt low-temperature gradient heat treatment to regulate crystallization rate, so as to reduce defects and internal stress and improve structural consistency during the scale-up process. At the structural reinforcement level, surface coating technologies using SiO_2, Al_2O_3, or carbon layers are utilized to construct protective layers, which inhibit the leaching of bismuth and bromine components. Meanwhile, interfacial composite and heterogeneous consolidation enhance interlayer bonding force, thereby improving mechanical stability and tolerance in complex environments.

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Specifically, the mechanism of process optimization lies in matching mass transfer, heat transfer and crystallization kinetics to ensure uniform and controllable structures after scale-up. Surface and interface modification builds physical barriers and chemical bonds to enhance layer cohesion, while avoiding structural collapse and component loss. To achieve industrial scale-up, strategy should focus on continuous, low-temperature, low-defect process optimization. For long-term cycling and operation in complex aqueous environments, surface coatings and interfacial reinforcement are preferred. To balance green synthesis and sustainable production, large-scale routes without organic solvents under mild low-temperature conditions should be chosen.

5. Conclusion

This review highlights the contributions of solution-phase methods, template-directed methods, and vapor deposition methods in controlling the crystal morphology, exposed facets, defect distribution, and photocatalytic performance of BiOBr, emphasizing the pivotal role of preparation strategies in achieving synergistic optimization of structural and functional properties. By precisely adjusting solvent polarity, spatial confinement conditions and chemical potential, the crystallinity, specific surface area and morphological uniformity of BiOBr can be effectively improved. Meanwhile, the combination of ion doping, heterojunction construction, and facet engineering enables significant suppression of photogenerated carrier recombination, enhancement of photocatalytic activity and cycling stability, and provides a reliable methodological foundation for the controllable synthesis of high-performance BiOBr photocatalysts. It is worth noting that this study primarily concentrates on pure-phase BiOBr and its basic modified systems, while studies on multi-component composites and large-scale fabrication processes remain relatively limited. Future efforts include the expansion of bismuth-based multi-component composite material systems to enhance photocatalytic efficiency and enable functional diversification. Besides, the development of green and continuous large-scale preparation strategies is also essential to ensure material yield and structural consistency. In addition, the establishment of evaluation systems for stability and safety under practical conditions will promote the real-world application of BiOBr photocatalysts.

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