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Sustainable Water Pollution Treatment: A Technological Breakthrough via Bismuth Halide Solid Solution Photocatalysts

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Abstract

With the rapid development of industrialization, the problem of water environment pollution is becoming increasingly serious, especially the discharge of organic pollutants such as antibiotics and dyes, which pose a serious threat to the ecosystem and human health. Traditional water treatment methods suffer from low efficiency and secondary pollution issues, while photocatalytic technology has emerged as a research hotspot due to its green and efficient characteristics. This paper shows that $BiOBr_xCl_{1-x}$ solid solutions with varying compositions were successfully synthesized via precipitation and applied to degrade the organic pollutant tetracycline (TC). Most $BiOBr_xCl_{1-x}$ solid solutions demonstrated enhanced photocatalytic activity over BiOBr and BiOCl, with the optimal sample achieving a 79.5% TC degradation efficiency within 30 min. The formation of solid solutions modulates the band structure and provides abundant active sites, facilitating the separation of photogenerated charge carriers. This study demonstrates significant potential for environmental remediation and is expected to advance sustainable pollution control strategies.

Keywords

Bismuth oxide, Solid solution, Photocatalysis, Organic pollutants, Sustainable development

Introduction

Water is the source of life, yet with the acceleration of industrialization and urbanization, water pollution has become an increasingly pressing issue. Millions of tons of organic pollutants (such as antibiotics and dyes) are discharged into water bodies annually worldwide, posing a severe threat to ecosystems and human health (Pu et al., 2024). Traditional physical, chemical, and biological treatment methods suffer from low efficiency, high energy consumption and secondary pollution issues, necessitating the development of green and efficient water treatment technologies

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(Wang et al., 2024). Photocatalysis, as an advanced oxidation process, utilizes solar energy to mineralize organic pollutants into CO_2 and H_2O. This process offers a sustainable alternative to conventional methods, characterized by its low energy consumption and absence of secondary pollution. However, traditional photocatalysts such as TiO_2 and ZnO only respond to ultraviolet light, resulting in low solar energy utilization (Wang et al., 2023). Therefore, the development of efficient and stable visible light-responsive photocatalysts has become a research focus.

Bismuth halide oxides (BiOX, X = Cl, Br, or I) are a class of semiconductor catalysts with a unique layered structure that facilitates the separation of photogenerated charge carriers, which has garnered significant attention (Luo et al., 2024). BiOX exhibits distinct advantages over conventional TiO_2 (Chen et al., 2025). Its primary benefit is a tunable visible-light response; the bandgap (1.7-3.3 eV) can be precisely engineered by adjusting the halogen composition (Cl, Br, I) to maximize solar energy utilization. Furthermore, the unique layered structure not only supplies abundant active sites but also generates an intrinsic electric field, synergistically enhancing catalytic activity by promoting charge separation. Lastly, BiOX is environmentally benign due to the low toxicity of bismuth and the material's recyclability. Nevertheless, the performance of pure BiOX is limited by rapid charge recombination and insufficient redox capabilities. To address this, solid solutions such as $BiOBr_xCl_{1-x}$ have been developed. Previous work on such catalysts has often focused on macrostructures for metal ion reduction (Deng et al., 2020). However, the systematic correlation between precise compositional control, the development of specific nanosheet morphologies, and their performance in degrading complex antibiotic molecules remains a critical knowledge gap.

Therefore, this study focuses on the $BiOBr_xCl_{1-x}$ solid solution, aiming to bridge this gap by elucidating the intrinsic relationship between its uniquely tailored nanosheet morphology and its catalytic performance for antibiotic degradation. By establishing a clear structure-activity relationship, this work not only advances the fundamental understanding of BiOX-based photocatalysts but also contributes to broader sustainable development goals (SDGs, Liu et al., 2025). The research aligns with efforts to ensure clean water (SDG 6) through efficient pollutant degradation, promote affordable and clean energy (SDG 7) by utilizing sunlight, foster innovation in environmental technology (SDG 9), and support responsible consumption (SDG 12) via a green remediation process. Ultimately, this study provides valuable insights and direction for the development of next-generation photocatalytic materials for sustainable water pollution control.

Methodology

Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3•5H_2O$, ≥ 99.0%), potassium bromide (KBr, ≥ 99.0 %), potassium chloride (KCl, ≥ 99.0%), and ethylene glycol ($C_2H_6O_2$, ≥ 99.0%) were supplied by the Chengdu Chron Chemicals Co., Ltd. All chemicals were used without any further processing.

Preparation of catalysts

Two-dimensional (2D) sheet-like $BiOBr_xCl_{1-x}$ solid solutions with varying x values (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1) were synthesized via a precipitation method. Specifically, a certain amount of $Bi(NO_3)_3•5H_2O$ was dispersed in 20 mL of ethylene glycol under constant magnetic stirring for 30

min to form a clear solution. Meanwhile, KCl and KBr with a total molar amount equal to that of $Bi(NO_3)_3 \cdot 5H_2O$ were mixed at specific molar ratios and dissolved in 20 mL of deionized water. The halide salt solution was then added dropwise into $Bi(NO_3)_3 \cdot 5H_2O$ solution. The resulting mixture was maintained at 85°C in a water bath for 5 h under continuous stirring. The resulting precipitate was collected by centrifugation, washed thoroughly with deionized water and absolute ethanol several times, and finally dried at 70°C for 12 h. For comparison, pure BiOBr (x = 1) and BiOCl (x = 0) also prepared under identical conditions by using only KBr or KCl, respectively.

Characterization

The crystal structure of catalysts was analyzed by X-ray diffraction (XRD) on a DX-2700B diffractometer using Cu-Ka radiation ($\lambda = 0.154$ nm) operated at 40 kV and 30 mA. The data were collected in the 2θ range from 5° to 90° at a scanning rate of 5° min^{-1}. The microstructural properties of photocatalysts were investigated using a ZEISS Sigma 300 scanning electron microscopy (SEM).

Photocatalytic experiment

The photocatalytic activity was evaluated by degrading TC (20.0 mg L^{-1}) as target pollutants under simulated solar irradiation (500 W xenon lamp with AM 1.5G filter). Specifically, 50 mg of catalyst was dispersed in 100 mL of pollutant solution and magnetically stirred in the dark for 30 min to establish adsorption-desorption equilibrium. Subsequently, photocatalytic degradation was initiated by activating the light source, with 3 mL aliquots periodically extracted at 5 min intervals over 30 min. Finally, residual pollutant concentrations were quantified using Uv-Vis spectrophotometry (Perse TU-1901).

Results and Discussion

Characterization of catalysts

The XRD patterns of all samples (Figure 1) exhibited sharp diffraction peaks, indicating high crystallinity and phase purity. The peak positions for pure BiOBr (JCPDS 09-0393, He et al., 2021) and BiOCl (JCPDS 06-0249, Ran et al., 2024) matched their respective standard reference patterns. The continuous shift in the peak positions was observed with varying the Cl^-/Br^- ratio, which is consistent with Vegard's law (Kong et al., 2019) and confirms the formation of a homogeneous $BiOBr_xCl_{1-x}$ solid solution rather than a physical mixture. Critically, this structural modification is not merely geometric. The distortion of the crystal lattice directly influences the local electrostatic field and the orbital overlap within the $[Bi_2O_2]^{2+}$ and halogen layers, which is the fundamental reason for the modulation of the electronic band structure (Niu et al., 2024). This establishes a solid foundation for the subsequent changes in optical absorption and redox potential.

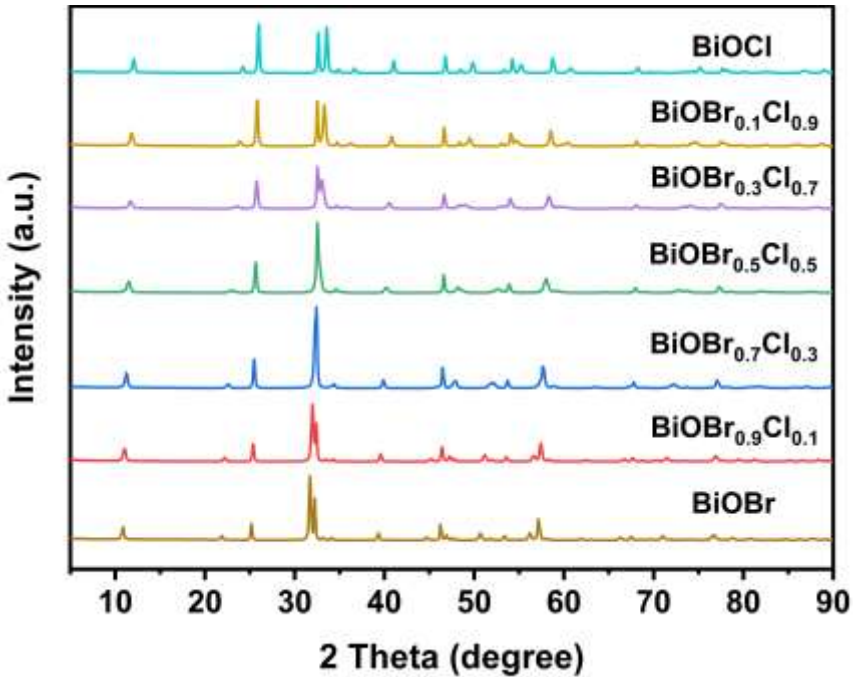

Figure 1. XRD patterns of $BiOBr_xCl_{1-x}$ catalysts

SEM analysis revealed that all $BiOBr_xCl_{1-x}$ solid solutions exhibited typical smooth 2D nanosheets. While pure BiOBr (Figure 2a) formed well-defined rectangular nanosheets, pure BiOCl (Figure 2b) consisted of smaller, irregular circular nanosheets. Notably, the $BiOBr_{0.9}Cl_{0.1}$ solid solution (Figure 2c) displayed hybrid morphological features, signifying a modulation of crystal growth kinetics by the halogen composition. This conserved 2D architecture is pivotal for photocatalysis, as it inherently promotes charge carrier separation by shortening migration pathways to the surface and simultaneously provides a large surface area for reactions (Wang et al., 2018). Thus, the solid solution strategy successfully optimizes both the electronic structure and the morphological framework for enhanced performance.

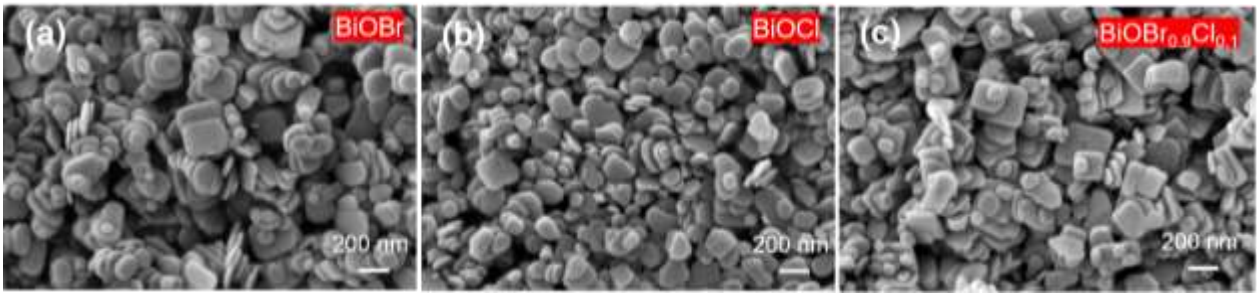

Figure 2. SEM images of (a) BiOBr, (b) BiOCl, and (c) $BiOBr_{0.9}Cl_{0.1}$ catalysts

Photocatalytic performance

The photocatalytic activity of the $BiOBr_xCl_{1-x}$ (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1) solid solutions were evaluated by the degradation of TC for 30 min (Figure 3). The degradation efficiency of pure BiOCl is relatively low (38.8%), while that of BiOBr reaches 65.0%. Notably, except for $BiOBr_{0.1}Cl_{0.9}$, the degradation efficiency of all solid solutions is superior to that of their pure samples. Additionally, the activity of $BiOBr_xCl_{1-x}$ (x = 0.1, 0.3, 0.5, 0.7, 0.9) gradually increased

with the Br^- content, with $BiOBr_{0.9}Cl_{0.1}$ reaching the highest activity of 79.5%. This value not only surpasses the performance of its pure-phase counterparts but also compares favorably with many recently reported Bi-based photocatalysts (Table 1). This significant enhancement is attributed to effective band structure engineering via Br^- incorporation. The doping narrows the excessively wide bandgap of BiOCl, improves visible light response, and optimizes band position, thereby enhancing redox capacity and degradation efficiency (Jia et al., 2018). Consequently, this intrinsic material engineering strategy provides a fundamental advantage for achieving high photocatalytic efficiency.

Table 1. Comparison of the photocatalytic performance for TC degradation over various bismuth-based photocatalysts

Photocatalyst	Preparation Method	Light Source	Reaction Time (min)	Degradation Efficiency (%)	Ref.
$BiOBr_{0.9}Cl_{0.1}$	precipitation	500 W xenon lamp	30	79.5	This work
0.4-$BiOBr_xCl_{1-x}$	hydrothermal	visible light	60	80	(Cho et al., 2021)
δ-FeOOH/BiOBr	precipitation	visible light	120	81	(Li et al., 2022)
$BiOBr_{0.93}I_{0.07}$-H	precipitation	photochemical reactor	180	42.3	(Yu et al., 2021)

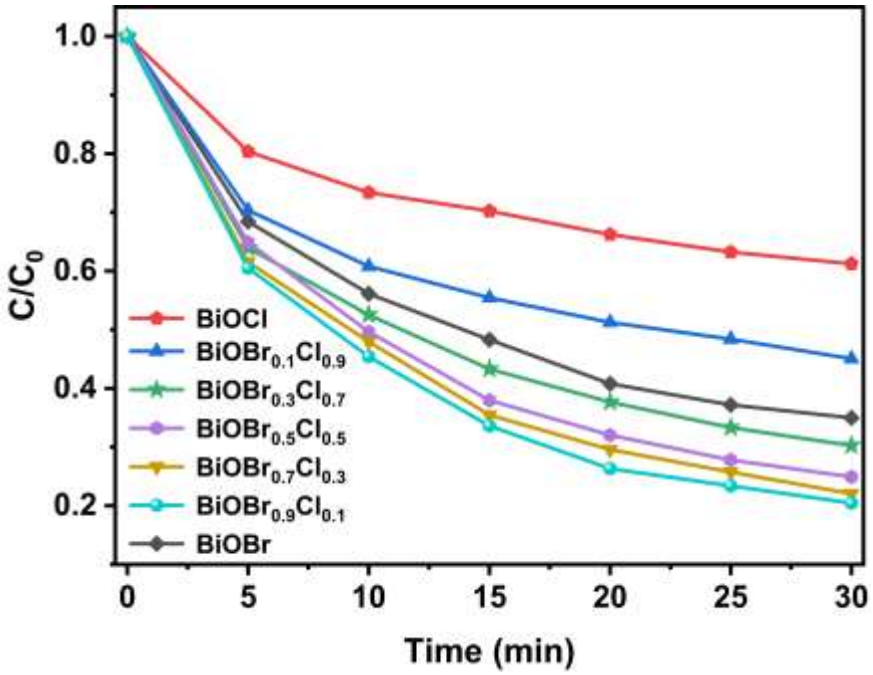

Figure 3. Photocatalytic degradation of TC over $BiOBr_xCl_{1-x}$ samples

Conclusion

In this study, sheet-like $BiOBr_xCl_{1-x}$ solid solutions were synthesized via a precipitation method. The structure and morphology of the samples were characterized using XRD and SEM, and the

catalysts were applied to the photocatalytic degradation of TC. The results demonstrate that $BiOBr_xCl_{1-x}$ solid solutions exhibit enhanced photocatalytic activity compared to pure BiOBr and BiOCl. Notably, the optimal $BiOBr_{0.9}Cl_{0.1}$ achieved 79.5% TC degradation within 30 min. This high efficiency, driven by a tailored band structure and promoted charge separation, underscores the material's significant potential for sustainable development.

Specifically, the technology's reliance on sunlight for pollutant mineralization directly supports SDG 7 (Affordable and Clean Energy) by offering a low-carbon water treatment path. Its high degradation efficacy contributes directly to SDG 6 (Clean Water and Sanitation), while its recyclability and minimal waste generation align with the principles of SDG 12 (Responsible Consumption and Production). Future work should focus on mechanistic studies and practical stability assessments to advance this technology toward real-world application.

Acknowledgements

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