

Structure, synthesis methods and photocatalytic applications of Halide perovskites: a mini review

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Abstract

This mini review provides an examination of Halide perovskites, a class of materials that have captured significant attention in recent years due to their exceptional optoelectronic properties. The paper not only offers an overview of the crystal structure and stoichiometry of Halide perovskites but also explores various synthesis methods and their potential applications in optoelectronics, photocatalysis, and environmental remediation. Furthermore, the review delves into the challenges associated with Halide perovskite synthesis, including stability and toxicity concerns, and emphasizes the ongoing research efforts aimed at addressing these issues.

The potential of Halide perovskites as a promising class of materials for practical applications is a key focus of this paper. It highlights the significance of these materials in various fields and provides valuable insights into their potential impact on technological advancements and environmental sustainability. This review serves as a comprehensive resource for researchers and professionals seeking to understand the capabilities and challenges of Halide perovskites.

1. Introduction

Halide perovskites are a class of materials that have garnered significant attention in the fields of photovoltaics, light-emitting devices, and other optoelectronic applications due to their exceptional optoelectronic properties. These materials are defined by their crystal structure, which consists of a network of corner-sharing BX_6 octahedral with a general ABX_3 stoichiometry. The A-site is typically occupied by large monovalent alkali metals (such as cesium) or small organic cations like methylammonium (MA) or formamidinium (FA), while the B-site is occupied by divalent cations like lead (Pb^{2+}) or tin (Sn^{2+}) [1].

The term "perovskite" originates from the mineral CaTiO_3 , which was named after the Russian nobleman and mineralogist Count Lev Alekseyevich von Perovski. The crystal structure was later defined as a general term for a group of crystal structures by Victor Goldschmidt in 1926 [1].

Halide perovskites have been extensively studied for their remarkable properties, including high charge carrier mobilities, long carrier lifetimes, and high absorption coefficients, making them promising candidates for efficient solar cells and light-emitting devices. These materials exhibit tunable bandgaps in the visible spectrum and near-infrared (NIR), which is advantageous for their use in photovoltaic and light-emitting applications [2].

The subgroup of halide perovskites discussed in the document consists of heavier halides such as chlorine (Cl), bromine (Br), and iodine (I). This subgroup includes fully inorganic halide perovskites, as well as hybrid organic-inorganic halide perovskites. The document also mentions the existence of natural perovskite minerals as oxides, fluorides, chlorides, hydroxides, arsenide, and intermetallic compounds, highlighting the adaptability of the perovskite crystal lattice across the periodic table [1].

It is important to note that deviations from the ABX_3 stoichiometry can lead to variations in the crystal lattice structure, such as vacancy-ordered perovskites or the formation of double or quadruple perovskites. The crystal structure of halide perovskites can also exhibit reduced symmetry due to lattice distortions, distorted octahedral, ordered cations, vacancies, or the presence of organic cations or inorganic clusters [2].

In summary, halide perovskites represent a versatile class of materials with promising optoelectronic properties, and their study and development continue to be a focus of research in the fields of photovoltaics, light-emitting devices, and beyond [2].

2. Types of perovskite structures

The perovskite supergroup encompasses various types of perovskite structures, including:

- **Ideal Perovskite Structure:** The ideal perovskite structure is represented by the general formula ABX_3 , where the A-site cations are larger than the B-site cations and similar in size to the X-site anions. This structure consists of a cubic close-packed array of X anions with one quarter of these replaced by A-site cations in an ordered manner. The A-site cations are surrounded by 12 anions in twelve-fold cubo-octahedral coordination, and the B-cations are surrounded by 6 anions in octahedral coordination. The X anions are coordinated by two B-site cations and four A-site cations [1].
- **Single and Double Perovskites:** Single perovskites refer to the number of symmetrically non-equivalent A and B sites, while double perovskites involve ordered distributions of cations at the B-site. The A-site can be filled or vacant, forming A-site deficient single or double perovskites, and the B-site can be partially or entirely vacant [1].
- **Cation- and Anion-Deficient Varieties:** Synthetic perovskites can be classified according to a hierarchy of structural types ranging from simple ABX_3 compounds and ordered variants through cation- and anion-deficient varieties to layered complex derivatives. This classification is applicable to naturally-occurring perovskite supergroup minerals and can be used to predict the structural and compositional variants of perovskites that might be expected to occur in nature [1].

These structures exhibit significant solid solution and can occur as oxides, fluorides, chlorides, hydroxides, arsenide, antimonides, intermetallic compounds, and silicates [1].

3. Synthesis

Various conventional ceramic reaction methods are employed for synthesizing the most commonly used perovskite phases [3].

- **Solid State Reaction**

The predominant process involves thoroughly mixing oxides (or carbonates and oxides) and then subjecting them to firing at temperatures exceeding two-thirds of the melting point for periods of up to ten hours. However, this method presents challenges, particularly in cases where one oxide, especially a toxic one like Pb, may partially vaporize during the prolonged reaction times [3].

- **Solution Technologies - Sol-Gel and Others**

Beginning in 1950, sol-gel techniques, developed by Roy at Penn State in 1948 [4], were likely used to create several perovskite phases, possibly marking the first instances of such nonsilicate ceramics. These methods were routinely applied to various aluminate, titanate, and complex mixed cation phases by the mid-1950s [5-8]. In recent decades, sol-gel techniques have garnered increased attention, particularly for producing thin films at low temperatures. Notably, these techniques have been successfully employed to grow highly oriented perovskites, such as SrTiO₃ on SrTiO₃ "single crystals," at temperatures as low as 600 °C from thin gel layers spun onto substrates [3,9-12].

- **Hydrothermal**

This method was utilized early on to synthesize and assess the thermodynamic stability of BaTiO₃ and numerous other perovskites in the 1950s [3,13]. Recent efforts have focused on producing BaTiO₃ at very low temperatures using this approach [3,14,15].

- **Hydrothermal-Electrochemical**

Building on the work of Hawkins and Roy, Yoshimura et al. [16], demonstrated the ability to synthesize BaTiO₃ using an electric field in a hydrothermal bomb at temperatures ranging from 100 to 200 °C [17].

- **Microwave Synthesis**

In a conventional furnace, the reaction of $\text{BaCO}_3 + \text{TiO}_2$ at 1200 °C typically forms Ba_2TiO_4 initially, followed by a gradual transformation into increasing amounts of BaTiO_3 . However, the use of a 2.450 GHz microwave field has led to remarkable differences, including the formation of BaTiO_3 in one to two minutes and the emergence of hexagonal BaTiO_3 , previously unheard of at these temperatures. This method has shown potential for commercialization, particularly for Pb-containing perovskites, as it minimizes Pb-loss [3,18].

- **PVD Methods - Laser Ablation, MBE**

As the trend toward integrating the capacitive function into silicon circuitry continues, established thin film methods, including PVD techniques, are routinely applied to perovskites. Thin film ferroelectrics represent a significant area of research, as evidenced by references to symposium proceedings and journals showcasing the extensive work in this field [3].

4. Photocatalytic properties of Halide perovskites

Photocatalysis, the process of using light to drive chemical reactions, has garnered significant attention in recent years due to its potential applications in environmental remediation, energy production, and synthesis of value-added chemicals.

Among the various photocatalysts, halide perovskites (HPs) have emerged as a promising candidate for photocatalysis applications, thanks to their excellent optoelectronic properties and the potential for low-cost solution processing. In this essay, we will delve into the potential of HPs for photocatalysis, focusing on their optoelectronic properties, fabrication approaches, and the challenges that need to be addressed for their widespread adoption in photocatalytic applications [19].

HPs have gained attention in the field of photocatalysis due to their unique properties, including high carrier mobility, long carrier diffusion lengths, and tunable bandgaps. These properties make HPs highly efficient in absorbing light and generating charge carriers, which are essential for driving photocatalytic reactions. Moreover, the low-cost solution processing techniques make HPs an attractive option for large-scale production of photocatalysts, further enhancing their potential for practical applications [19].

One of the key factors that determine the efficiency of HPs in photocatalysis is their fabrication approach. Thin films and nanostructures of HPs have been the focus of recent research efforts, aiming to improve their performance as efficient photocatalysts. Thin films offer a large surface area for light absorption and catalytic reactions, while nanostructures provide enhanced charge carrier separation and transport, both of which are crucial for efficient

photocatalysis. By exploring different fabrication techniques and optimizing the morphology of HPs, researchers aim to enhance their performance and expand their applicability in a wide range of photocatalytic reactions [19].

HPs photocatalysis holds significant potential for various applications in industry and environmental remediation. Some of these applications include:

- **CO₂ reduction reactions:** Halide perovskite photocatalysts can be utilized to convert carbon dioxide into valuable chemical fuels, contributing to efforts to mitigate climate change and reduce greenhouse gas emissions [19].

The findings of these studies demonstrate the potential of hybrid perovskites as highly effective catalysts for the reduction of carbon dioxide (CO₂), resulting in the production of carbon monoxide (CO) and methane (CH₄) at notably high yields [19]. For instance, one study documented a yield of 1.05 μmol cm⁻² h⁻¹ for the conversion of CO₂ to CO by utilizing GO-wrapped methylammonium lead bromide (MAPbBr₃) quantum dots (QDs) [19,20].

Another investigation revealed that CsPb(BrxCl_{1-x})₃ exhibited remarkable selectivity towards CO and CH₄, achieving a selectivity rate as high as 99% [21]. Furthermore, a study employing CsPbBr₃ QDs and metal-organic frameworks (MOFs) resulted in the development of a nanocomposite that displayed significantly enhanced photocatalytic performance for CO₂ conversion [22]. Collectively, these outcomes strongly indicate that HPs hold significant promise as effective catalysts for the reduction of CO₂ [19].

- **Hydrogen evolution reaction:** Halide perovskite photocatalysts can be employed to produce hydrogen through water splitting, offering a clean and sustainable source of energy [19].

HPs have emerged as promising candidates for efficient photocatalysts in various electrochemical reactions, particularly the hydrogen evolution reaction (HER) [19].

Research has shown that methylammonium lead iodide (MAPbI₃) has the capability to produce hydrogen from hydriodic acid in dynamic equilibrium with an aqueous solution [23]. Additionally, a separate study delved into the photocatalytic hydrogen evolution activity of mixed-halide perovskite CH₃NH₃PbBr_{3-x}I_x, and discovered that the bandgap funneling of charge carriers could significantly enhance the material's photocatalytic activity [24].

These findings collectively indicate that HPs hold significant potential as efficient photocatalysts for the HER [19].

- **Wastewater treatment:** These photocatalysts have the potential to degrade pollutants and purify wastewater through photocatalytic degradation processes, thereby addressing environmental pollution concerns.

Gao et al. [25], reported a groundbreaking study on the photoactivity of HPs for degrading organic dyes. The researchers utilized all-inorganic CsPbX₃ HPs for the photocatalytic degradation of methyl orange (MO), a common organic pollutant found in wastewater. Their findings revealed that the percentage of MO degradation increased from 50% to 90% within 80 minutes when the amount of CsPbCl₃ was increased from 0.1 mg to 2 mg, demonstrating the

remarkable photocatalytic degradation activity of CsPbX_3 . Furthermore, the study also investigated the degradation of 2-mercaptobenzothiazole (MBT) as evidence for the photocatalytic activity of CsPbBr_3 . This research laid the foundation for the application of HPs in wastewater treatment and highlighted their potential for addressing water pollution challenges [19,25].

Environmentally Friendly CsSnBr_3 HPs for Dye Removal In 2018, Reyes-Pérez et al. [26], successfully synthesized CsSnBr_3 HPs, a more environmentally friendly alternative to their Pb-containing counterparts, and used them for the removal of crystal violet dye. The HPs exhibited good light absorption in the visible spectral region, making them suitable for photocatalytic applications. This study not only expanded the range of HP materials available for wastewater treatment but also underscored the importance of developing environmentally sustainable alternatives to traditional HPs. The successful synthesis and application of CsSnBr_3 HPs represented a significant step forward in the pursuit of eco-friendly and effective photocatalytic treatment methods [19,26].

Superior Photocatalytic Activity of Ordered Macro-Mesoporous CsPbBr_3 In a related development, Stefan et al. [27], demonstrated the superior photocatalytic activity of ordered macro-mesoporous CsPbBr_3 for the decay of organic pollutants. This study emphasized the importance of surface area and charge carrier diffusion length in improving photocatalytic activity. By engineering the structure of CsPbBr_3 to enhance its surface area and charge carrier transport properties, the researchers were able to achieve enhanced photocatalytic performance. This research contributed valuable insights into the design and optimization of HP-based photocatalysts for efficient wastewater treatment [19,27].

Enhanced Stability and Efficiency Using $\text{Cs}_2\text{AgBiBr}_6$ HPs Furthermore, Zhang et al. [28], made significant strides in improving the stability of HPs and developed an alcohol-based photocatalytic system based on $\text{Cs}_2\text{AgBiBr}_6$, a lead-free HP. This novel approach exhibited high efficiency in degrading various ionic dyes, offering a promising alternative to traditional HPs. The efficiency of the $\text{Cs}_2\text{AgBiBr}_6$ photocatalyst was further enhanced by depositing noble metals on its surface to facilitate photogenerated carrier separation. This study not only addressed the stability concerns associated with HPs but also showcased the potential of lead-free HPs for sustainable and effective wastewater treatment [19,28].

Conclusion The advancements in photocatalytic wastewater treatment using HPs represent a significant leap forward in the quest for sustainable and efficient water purification technologies. The pioneering research by Gao et al. [25], the development of environmentally friendly CsSnBr_3 HPs by Reyes-Pérez et al. [26], the insights into structure-engineered CsPbBr_3 by Stefan et al. [27], and the stability and efficiency enhancements achieved by Zhang et al. [28], collectively demonstrate the potential of HPs in addressing water pollution challenges. These studies have not only expanded the range of HP materials available for wastewater treatment but also provided valuable insights into the design, synthesis, and optimization of HP-based photocatalysts. Moving forward, continued research and innovation in this field will be crucial for developing practical and scalable solutions for addressing water pollution and advancing sustainable wastewater treatment practices [19].

5. Photocatalytic challenges of halide perovskites

Overall, the unique properties of HPs photocatalysts make them promising candidates for addressing critical challenges in industry and environmental sustainability, offering potential solutions for energy production and environmental remediation [19].

Researchers in the field of HPs photocatalysis face several key challenges, including:

- **Stability:** One of the primary challenges is the stability of halide perovskite materials, particularly in the context of photocatalytic applications. The instability of these materials in polar solvents can hinder their practical use in real-world applications.
- **Toxicity:** The high toxicity of lead-based halide perovskites is a significant concern for environmental and health safety, which may limit their widespread application.
- **Structural engineering and doping:** Improving device performance through structural engineering and doping is an ongoing challenge that requires innovative approaches to enhance the efficiency and stability of halide perovskite photocatalysts.
- **Development of Pb-free alternatives:** Given the toxicity concerns associated with lead-based perovskites, the development of lead-free halide perovskite materials for photocatalysis is an important area of research.

Addressing these challenges will require continued research and development efforts to enhance the stability, safety, and performance of halide perovskite photocatalysts for practical industrial and environmental applications [19].

6. Conclusion

The recent advancements in the design of high-performance photocatalysts based on (HPs) have demonstrated significant potential for a wide range of photocatalytic reactions, including CO₂ reduction, photodegradation of contaminants, photosynthesis of organic compounds, and the hydrogen evolution reaction (HER). Despite these promising developments, the practical application of HPs is hindered by their low stability and high toxicity. Addressing these challenges is crucial for unlocking the full potential of HP-based photocatalysts [19].

Moving forward, the future development of HP-based photocatalysts should prioritize three key aspects. Firstly, efforts should be directed towards enhancing device performance through structural engineering and strategic doping. This approach can lead to improvements in the overall efficiency and effectiveness of HP-based photocatalysts. Secondly, there is a need to focus on enhancing the stability of HPs by leveraging low-dimensional HPs that feature bulky hydrophobic organic cations and implementing surface passivation techniques. These strategies can contribute to mitigating the stability issues associated with HPs, thereby making them more viable for practical applications. Finally, the development of Pb-free HPs for photocatalysis represents a critical avenue for future research. This involves exploring alternative materials and compositions that can offer comparable or superior performance while addressing concerns related to the toxicity and environmental impact of lead [19].

Current research efforts are primarily concentrated on enhancing the photocatalytic activity of HPs by addressing challenges such as electron-hole recombination and reducing bandgap energy through innovative doping methods. Additionally, the utilization of electron- and hole-extracting and transporting materials has shown promise in

improving the overall performance of HP-based photocatalysts. Structural engineering plays a significant role in this process, as the modulation of HPs into nanodots, nanowires, and nanosheets, as well as the incorporation of metal catalysts, can lead to substantial improvements in their catalytic activity [19].

In parallel, the stability of HPs can be bolstered by incorporating bulky organic materials, embedding them in mesoporous scaffolds, or implementing surface passivation layers. These approaches offer potential solutions to the stability challenges associated with HPs, thereby enhancing their practical viability. Furthermore, the endeavor to develop Pb-free HPs presents an opportunity to create environmentally friendly catalysts. By exploring the replacement of lead with transition metals such as Sn, Sb, and Bi, researchers can work towards mitigating the environmental impact of HP-based photocatalysts. However, it is important to note that the stability of Pb-free HPs may pose challenges, and as such, the development of these catalysts must be accompanied by the implementation of stability-improving strategies [19].

In conclusion, the recent designs of high-performance photocatalysts based on halide perovskites hold significant promise for various photocatalytic reactions. However, the challenges related to stability and toxicity must be effectively addressed to realize their full potential. By focusing on enhancing device performance, improving stability, and developing Pb-free alternatives, researchers can pave the way for the practical application of HP-based photocatalysts in a wide range of fields, from environmental remediation to sustainable energy production. This concerted effort towards overcoming the current limitations will undoubtedly contribute to the advancement of photocatalysis and its potential impact on various industries and environmental sustainability [19].

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