



REVIEW

Recent Advances in the Stability and Photocatalytic Application in Organic Pollutant Degradation of CsPbX₃ (X = Cl, Br, I) Perovskites: A Review

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Over the past few decades, tremendous efforts have been invested in creating low-cost, non-toxic, stable, and potent photocatalysts. Cesium lead halides perovskites (CsPbX₃) have garnered significant attention in photocatalysis due to their excellent optoelectronic properties, like high absorptivity, distinctive defect tolerance and tunable bandgap. This class of materials has shown remarkable efficiency in facilitating solar-driven reactions, including organic pollutant degradation, water splitting, CO₂ reduction, and organic synthesis. The incorporation of cesium cations enhances the structural stability and optoelectronic properties of lead halide perovskites, leading to improved photocatalytic performance. Although cesium lead halides perovskites are more stable compared to organic-inorganic lead halides perovskites, CsPbX₃ are highly sensitive to environmental factors and can break down when they come into contact with air, light, humidity, and heat. In this mini-review, the crystal structure of CsPbX₃ perovskites, performance in photocatalytic organic pollutant degradation, and demonstrating the importance of stability through encapsulation, nanocomposite formation, doping, and heterostructure development are discussed. Some problems and outline prospects of CsPbX₃ in this field are also discussed. By delving into these aspects, this work aims to contribute to the ongoing efforts in developing robust photocatalytic systems that can effectively mitigate environmental pollution.

Keywords: CsPbX₃, Pollutant degradation, Encapsulation, Nanocomposite.

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1. INTRODUCTION

Hazardous waste, toxic pollutants, and contamination in environmental media are among the many environmental issues humans are facing. Aquatic media are crucial to the existence of organisms on earth, and although water is abundant, its composition varies across strata, which affects its suitability for both commercial and residential use [1]. Semiconductor photocatalytic technology is a convenient, effective, and environmentally beneficial way to solve energy and environmental issues by converting dangerous pollutants into harmless molecules without generating secondary pollution. Metal oxides, metal sulphides, and graphitic carbon like TiO₂, CdS, g-C₃N₄ semiconductors [10] have been reported to be effective photocatalysts over the past few years. However, their practical applications are hampered by their short carrier lifetime, high efficiency recombination process, and limited absorption of visible light. For a material to be a good photocatalyst it should be able to absorb large amounts of visible spectra (i.e, band gap energy should be small), efficient separation of holes and

electrons, high carrier mobility.

Recently, metal halide perovskite (MHP) semiconductors have gained prominence as optoelectronic materials with a variety of possible applications, ranging from efficient solar cells and LEDs to lasers and photodetectors. MHPs, which have the general chemical formula ABX₃, are ionic crystals because X is a halogen anion (Cl⁻, Br⁻, or I⁻), B is a divalent metal cation (Pb²⁺, Sn²⁺, or Cu²⁺), and A is a monovalent cation (MA: CH₃NH₃⁺, FA: CH(NH₂)₂⁺, and Cs⁺) [2]. Because of their exceptional photophysical properties, such as superior photoluminescence performance, prolonged carrier lifetime, high absorptivity, adjustable bandgap energy, and versatile chemical processability for photocatalytic applications. CsPbX₃ perovskite materials have been extensively researched in the past few years [3]. Most of the studies of CsPbX₃ mainly focus on the optoelectronic applications, light-emitting devices, inorganic solar cells, and so on. A remarkable power conversion efficiency of 21% was recently demonstrated by CsPbI₃ with an energy bandgap of 1.7 eV [4]. CsPbX₃ (X = Br, Cl, I) perovskite nanocrystalline is unstable due to two main factors: the

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weak adsorption of surface ligand and the intrinsic instability of Pb-X octahedral configuration. The surface ligand's poor binding causes it to slide off easily during the halide perovskite separation and purification procedure. These two factors contribute to its low stability, which significantly impedes the advancement of its real-world use. The surface halogen defects have a significant impact on the stability of CsPbX₃ (X = Br, Cl, I) perovskite nanocrystals, according to Xia et al. When the nanocrystalline surface is exposed to an electron beam, it breaks down into PbBr₂, which eventually turns into Pb atoms [5, 6]. Therefore, to improve the stability and charge recombination of CsPbX₃, researchers have developed composite, heterostructure, core-shell, and encapsulation materials with CsPbX₃. The crystal structure of CsPbX₃, photocatalysis organic degradation, critical stability factors, and modification of CsPbX₃ perovskite for enhancing the stability and photocatalytic activity are all covered in this review article. Additionally, some insights from the recent progress of CsPbX₃ based photocatalysts are provided. Lastly, the difficulties and prospects for the advancement of CsPbX₃ perovskite are highlighted.

2. CRYSTAL STRUCTURE OF CSPBX₃

ABX₃ is the typical chemical formula for all-inorganic perovskites. Cubic Crystal structure of CsPbX₃ has been shown in Fig. 1. All-inorganic perovskite structures have monovalent Cs⁺ at the A-site and show minimal bandgap tunability, divalent Pb²⁺ at the B-site, and I⁻ and/or Br⁻ at the X-site. These octahedra structures can share vertices to create a three-dimensional network structure, and the octahedra space is filled with A atoms. Using the octahedra factor (μ) and the Goldschmidt tolerance factor (t), one may computationally anticipate the formation and geometric stability of the CsPbX₃ perovskite structure, where R_A, R_B, and R_X stand for the ionic radii of the A, B, and X-sites, respectively [10]. The equation is shown below:

$$t = \frac{R_A + R_B}{\sqrt{2}(R_B + R_X)} \quad (1)$$

$$\mu = \frac{R_B}{R_X} \quad (2)$$

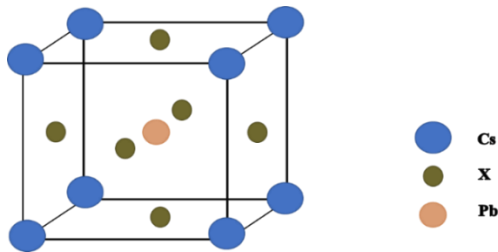
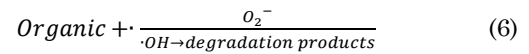
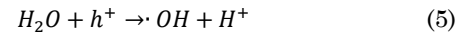
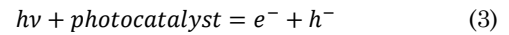


Fig. 1 – Cubic Crystal structure of CsPbX₃ here (Cs – cesium, Pb – lead, X = Cl, Br, I)

At room temperature, the cubic phase of inorganic perovskites is not always stable. All-inorganic perovskites can typically form orthorhombic (γ -phase), tetragonal (β -phase), cubic (α -phase), and non-perovskite (δ -phase) structures based on the ambient temperature [7].

3. ORGANIC POLLUTANT DEGRADATION

Environmentally hazardous pollutants, which get emitted from the textiles industry, are dissipated into the soil and water bodies, and these pollutants include Eosin B, Rhodamine B (RhB), Methyl Orange (MO), 2-mercaptobenzothiazole (MBT), Sudan red III, etc. This leads to unidentified environmental issues. To solve this issue, photocatalysis technology has been considered the most effective and economical method. Photocatalysis mechanisms refer to Fig. 2 generally follow three separate processes: (i) Generation of electron and hole pairs by the absorption of light by a photocatalyst. (ii) Separated electrons and holes move to the reaction sites on the photocatalyst surface. (iii) Oxidation and reduction chemical reactions at the surface are mediated by the photogenerated holes and electrons, respectively [8] The equation can be written below:



In 2017, Gao et al. used halide perovskite for photocatalytic degradation of methyl orange via hydroxyl and superoxide radical formation. They demonstrated that CsPbCl₃ outperformed TiO₂ and ZnO in the decomposition of methyl orange in water [9].

4. MODIFICATION OF CSPBX₃

4.1 Encapsulation

The CsPbX₃ perovskite is extremely sensitive to environmental factors and breaks down readily in the presence of heat, humidity, light, and air. Their practical application and future development were severely constrained by the unstable state. CsPbX₃ perovskite encapsulation in materials with shell structures prevents CsPbX₃ from coming into contact with water, preserves the CsPbX₃ perovskite's original surface states, and promotes the spatial separation of charges, participate in the chemical events occurring on the surface, and increase the stability over the long run [10].

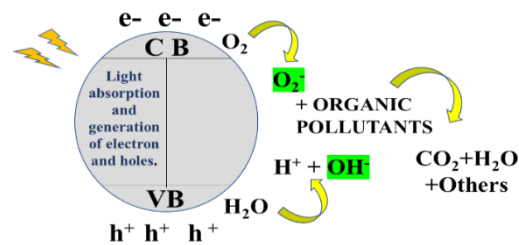


Fig. 2 – Photocatalysis process for organic pollutants

In addition to shielding the CsPbX_3 perovskite from the environment, TiO_2 with a shell structure speeds up the rate of electron transmission. Zheng et al. created $\text{CsPbBr}_3/\text{TiO}_2$ core/shell NCs. These NCs demonstrated exceptional stability in water over three months, maintaining their identical morphology, structure, size, and optical characteristics while also demonstrating enhanced photoelectric activity in water [16]. Hot pot injection was used to create CsPbX_3 , which has a cubic shape and stable optical characteristics. SiO_2 core shells with an average thickness of 2 to 6 nm are added to protect the CsPbX_3 from contact with the outside world, and surface passivation lowers the defect density, which increases the stability of the CsPbX_3 . The SiO_2 shell successfully guarantees the long-term stability of $\text{CsPbCl}_3/\text{SiO}_2$ and $\text{CsPbBr}_3/\text{SiO}_2$ quantum dots in ethanol and water environments while maintaining the morphology and crystal structure of CsPbCl_3 and CsPbBr_3 quantum dots. Additionally, the fluorescence lifetime, quantum efficiency, and PL stability have all been greatly enhanced [17].

4.2 Nanocomposites

The photocatalytic degradation of organic pollutants is accomplished by the preparation of $\text{CsPbBr}_3/\text{CN}$ type I and $\text{CsPbCl}_3/\text{CN}$ type II heterojunctions composites, which greatly increase the photocatalytic activity and

stability of CsPbX_3 . Both CsPbX_3/CN heterostructures could aid in the separation of electron-hole pairs (e^-h^+) and demonstrate exceptional photocatalytic activity for penicillin 6-aminopenicillanic acid (6-APA) degradation under visible light as shown in Fig. 3. The higher light-harvesting capability, the effective charge separation capability, the promising adsorb-ability, and the synergistic effects of CsPbX_3 NCs and CN could all be responsible for the CsPbX_3/CN heterostructures' increased photocatalytic activity [13].

4.3 Heterostructure

Gull et al., 2022 synthesized the $\text{CsPbX}_3/\text{ZnO}$ heterostructure by using the traditional hot injection method. They also demonstrated the photocatalytic test and observed 52% efficiency for heavy metal removal, which is higher than the degradation efficiency of CsPbI_3 . Because of the synergistic photogenerated charge carrier $\text{CsPbX}_3/\text{ZnO}$ catalyst has outstanding oxidation/reduction characteristics and ionic conductivity. The electrical conductivity is confirmed by the CV and EIS measurements, which also reveal excellent resistance to electron transport and high oxidation and reduction properties. As a result, this synthesized heterostructure material could be employed as a catalyst for water cleansing and heavy metal degradation [18].

Table 1 – Summary of the reported photocatalytic organic pollutants degradation of CsPbX_3 under various illumination conditions

Sl. No.	Photocatalyst material	Organic pollutants	Efficiency	Light illumination	Limitations
1.	CsPbI_3 [11]	Methyl violet	81.7 %	Visible light	Fast charge recombination, low utilization of visible light, low migration of electrons-holes.
2.	$\text{CsPbBr}_3/\text{TiO}_2$ [12]	Degrade methylene blue Detoxifies methylene blue	78 % > 99 %	Sunlight	–
3.	CsPbX_3/CN [13]	Penicillin 6-aminopenicillanic acid (6-APA)	81.31 %	Visible light	Inadequate stability, inefficient photocatalytic and rapid recombination of electrons and holes.
4.	CsPbCl_3 [14]	Eosin-B	–	Visible light	–
5.	$\text{CsPbBr}_3/\text{TiO}_2$ [15]	Rhodamine B (RhB)	97.7 %	Visible light	High electron and hole recombination, thereby constructing heterojunction/homojunction, suppresses electron and hole recombination, and increases better efficiency in photocatalytic compared to pure CsPbBr_3 and TiO_2 .

4.4 Doping

Doping CsPbX_3 enhances photocatalytic efficiency, which includes charge separation, stability, and removes toxicity of the material. The integration of transition metals and non-toxic elements has been investigated to improve the photocatalytic performances. The incorporation of Sn to CsPbX_3 reduces the toxicity of lead,

and improves photocatalytic efficiency, the ideal $\text{CsPb}_{0.5}\text{Sn}_{0.5}\text{Br}_3$ excel pure CsPbBr_3 and CsSnBr_3 by 79% in 60 minutes of tetracycline hydrochloride degradation [19].

5. CHALLENGES AND FUTURE DIRECTIONS

Cs_2PbX_3 (X = Cl, Br, I) perovskites have shown enormous potential in photocatalysis due to their

exceptional optoelectronic performance, strong light-harvesting ability and adjustable bandgaps. Fortunately, several challenges hinder their practical application.

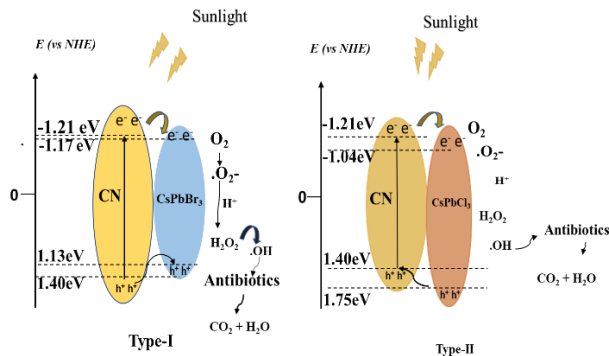


Fig. 3 – Photocatalytic mechanism of Heterojunction composites

1) Stability: The intrinsic structural stability of CsPbX_3 still needs to improve, although many researchers have developed several techniques like encapsulation, semiconductor composite, and heterostructure to improve the stability of perovskite against polar solvents, air, high temperature, and light. And also, the related decomposition mechanisms are not yet completely understood, and the water stability of CsPbX_3 perovskite is still poor.

2) Toxicity: CsPbX_3 contains lead, which poses a threat to environmental and human health because of its toxicity. Therefore, introducing lead-free with ABX_3 perovskite structure. Although there have been a few reported on CsPbX_3 in photocatalysis organic degradation, researchers should explore and develop more CsPbX_3 -based photocatalysts that can absorb light in the visible spectrum, electron-hole pair separation efficiency, and improve oxidation/reduction reaction.

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3) Scalability and reproducibility: At the moment, the majority of CsPbX_3 perovskites can only be produced on small-scale synthesis techniques. One of the biggest challenges in large-scale production is maintaining uniformity and reproducibility. Additionally, the high cost of lead and cesium precursors may hinder the economic feasibility of large-scale production.

To overcome these challenges, future studies should concentrate on improving stability through structural alterations, encapsulating techniques, or surface passivation. Environmentally friendly substitutes may be provided via the creation of lead-free halide perovskites (such as Cs_2SnX_3 or Cs_2BiX_6). Additionally, charge separation and photocatalytic efficacy may be improved via heterostructure engineering using co-catalysts or other semiconductor materials.

6. CONCLUSION

CsPbX_3 perovskites exhibit excellent photocatalytic properties for organic pollutant degradation, making them a suitable candidate for environmental remediation. However, overcoming stability and toxicity challenges is important for their practical applications. With ongoing advancements in material engineering and composite development, perovskite based photocatalysis holds great promise for environmental protection and optoelectronic applications.

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Останні досягнення в галузі стабільності та фотокаталітичного застосування в деградації перовскітів CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$): огляд

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Протягом останніх кількох десятиліть величезні зусилля були вкладені у створення недорогих, нетоксичних, стабільних та потужних фотокаталізаторів. Перовскіти галогенідів свинцю цезію (CsPbX_3) привернули значну увагу у фотокаталізі завдяки своїм чудовим оптикоелектронним властивостям, таким як висока поглинальна здатність, відмінна толерантність до дефектів та регульована ширина забороненої зони. Цей клас матеріалів продемонстрував чудову ефективність у сприянні реакціям, що протікають під дією сонячного випромінювання, включаючи деградацію органічних забруднювачів, розщеплення води, відновлення CO_2 та органічний синтез. Включення катіонів цезію підвищує структурну стабільність та оптикоелектронні властивості перовскітів галогенідів свинцю, що призводить до покращення фотокаталітичної продуктивності. Хоча перовскіти галогенідів свинцю є більш стабільними порівняно з перовскітами органічно-неорганічних галогенідів свинцю, CsPbX_3 дуже чутливий до факторів навколишнього середовища та може руйнуватися при контакті з повітрям, світлом, вологістю та теплом. У цьому міні-огляді обговорюються кристалічна структура перовскітів CsPbX_3 , їх ефективність у фотокаталітичному розкладанні органічних забруднювачів, а також демонстрація важливості стабільності шляхом інкапсуляції, формування нанокompозитів, легування та розвитку гетероструктур. Також обговорюються деякі проблеми та загальні перспективи CsPbX_3 у цій галузі. Заглиблюючись у ці аспекти, ця робота має на меті зробити внесок у постійні зусилля щодо розробки надійних фотокаталітичних систем, які можуть ефективно зменшити забруднення навколишнього середовища.

Ключові слова: CsPbX_3 , Деградація забруднюючих речовин, Інкапсуляція, Нанокompозит.