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ABSTRACT

Lead halide perovskite nanocrystals (LHP NCs) have been developed since 2014. Due to their intrinsic ionic salts and lead-halogen composition, they have high molar absorbance coefficient, high defect tolerance, and ultra-fast carrier mobility, and their material structure and optical properties can be precisely controlled through ion exchange, which have aroused great research interest of scientific researchers as well as new thinking on the ion salt nanocrystal. Among LHP NCs family, CsPbBr₃ NCs are quite outstanding as they exhibit better luminescence properties, etc. They also demonstrate promising application prospects in the fields of optoelectronic devices, photovoltaics, and photocatalysis, occupying a central position in the current research of LHP NCs. However, their lack of stability to external elements, including light, humidity, and heat limits their use in practical applications. Heterostructure development is one of several approaches to overcome these limits. Combining two or more materials at the nanoscale results in new heteronanocrystals that outperform the pure material. To improve the stability of LHP NCs against environmental stress, core-shell NCs can be created by growing a shell on the surface of core NCs, drawing inspiration from chalcogenide semiconductor NCs. In this sense, there are multiple organic materials (e.g., phenylpropylammonium bromide and polymethyl methacrylate) and inorganic materials (such as NaBr, TiO₂, and metal chalcogenides, as well as perovskites, e.g., Cs₄PbBr₆, CsPb₂Br₅, and Rb₄PbBr₆) used for covering a perovskite core.

In this paper, the most promising approach involves coating perovskite NCs (PeNCs) with a crystalline perovskite shell by in situ synthesis, resulting in high-density NCs with a perovskite/perovskite core-shell configuration. This efficiently corrects the lattice mismatch between the core and shell. Because of its indirect band gap, photoluminescence (PL) intensity, water resistance, and minimum lattice mismatch with CsPbBr₃ NCs, 0D Cs₄PbBr₆ and 2D CsPb₂Br₅ perovskite materials are thought to be promising coating materials. The changes in luminescence properties and stability were studied and the application of the composite material in the field of anti-counterfeiting was studied. This paper describes the synthesis and characterisation of two core-shell structures based on CsPbBr₃ NCs, with a particular focus on enhancing their stability and physical properties. The research successfully achieved the in situ formation of a protective shell on the surface of CsPbBr₃ NCs using a simple room-temperature synthesis method, thereby overcoming lattice mismatch issues arising from stepwise synthesis. Research into this system not only aids in understanding interfacial chemistry but also provides

strategies for the low-cost synthesis of stable luminescent materials. This resolves the issue of the extremely complex fabrication process for core-shell structures, which is prone to generating interface defects and incomplete passivation, thereby leading to variations in their optical properties. Notably, in-situ spectroscopic and structural techniques were employed to investigate the exceptional performance of the synthesised core-shell structures under high-temperature and water immersion challenges. This demonstrates the critical role of the core-shell architecture in CsPbBr₃ NCs, effectively passivating the crystals while substantially enhancing environmental stability.

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List of Acronyms

LHPs	Lead halide perovskites
NCs	nanocrystals
PeNCs	perovskite NCs
MOFs	metal-organic frameworks
TiO₂	titanium oxide
ZrO₂	zirconium oxide
SiO₂	silicon oxide
MA⁺	methyl ammonium,
FA⁺	formamidinium
PL	Photoluminescence
PLQY	Photoluminescence quantum yields
FWHM	full width at half maximum
STEs	Self-trapped excitons
PeLEDs	Perovskite LEDs
CE	current efficiency
EQE	external quantum efficiency
PcLEDs	phosphor-converted LEDs
LED	Light-emitting diode
WLEDs	White Light-emitting diode
FF	fill factor
PCE	power conversion efficiency
3D	three-dimensional
2D	two-dimensional
1D	one-dimensional
0D	zero-dimensional
OA	Oleic acid
OLA	OLA
OLPA	oleylphosphonic acid
NMR	Nuclear Magnetic Resonance
DBSA	dodecylbenzene sulfonic acid
RH	Relative Humidity
OTAc	octanoic acid
QDs	Quantum Dots
DFT	Density functional theory
TRPL	time-resolved PL
DMF	dimethylformamide
TMOS	tetramethoxysilane
XRD	X-ray diffraction
SEM	Scanning electron microscope
TEM	Transmission electron microscopy
CCD	charge-coupled device
UV-Vis	Ultraviolet-Visible
GGA	generalized gradient approximation
PBE	Perdew-Burke-Ernzerhof
BFGS	Broyden-Fletcher-Goldfarb-Shannon
SCXRD	Single crystal X-ray diffraction
PXRD	Powder X-ray diffraction

EDS	energy-dispersive X-ray spectroscopy
RT	room temperature
TO	transverse optical
TE	lattice thermal expansion
EP	electron-phonon
DSC	differential scanning calorimetry
TGA	thermogravimetric
MCs	microcrystals
CW	continuous-wave
R²	correlation coefficient

Introduction & Thesis Outline

LHP NCs have received a lot of interest over the last five years because of their excellent optical properties, which make them prospective candidates for a variety of applications such as liquid crystal displays,¹ light emitting diodes,² solar cells³ and radiation detectors.⁴ LHP generally follow the chemical formula ABX_3 , known as 3D halide perovskites, where A ($A = Cs^+$, methyl ammonium(MA^+), formamidinium(FA^+)) and B ($B = Pb^{2+}$, Sn^{2+} , Ge^{2+}) represent two distinct cations, and X is an anion, typically a halogen ($X = Cl^-$, Br^- , and I^-).⁵ LHP NCs emit efficient PL due to their inherent defect tolerance.⁶⁻⁸ Despite structural characterisation results confirming the presence of numerous structural defects, its optoelectronic properties nevertheless exhibit an extremely low electron defect density. This indicates that the substantial structural defects present do not exhibit pronounced carrier quenching properties within the electronic structure of the PeNCs. It suggests that the energy levels of these defects are predominantly located not within the bandgap but within the conduction or valence bands, or that they occupy shallow positions (i.e., with small energy differences relative to the bottom of the conduction band or the top of the valence band) and exhibit strong coupling with conduction and valence band levels. Consequently, it exerts minimal influence on their photovoltaic performance even without extensive surface passivation treatment.

Among various LHPs, all-inorganic perovskites exhibit benefits over hybrid compositions. This is primarily because Cs exhibits exceptional chemical stability, which is largely attributable to its symmetrical charge distribution or the absence of a permanent dipole moment. All-inorganic (such as $CsPbX_3$; $X = Cl$, Br , or I) perovskites outperformed organic-inorganic hybrid lead halide perovskites ($MAPbX_3$ and $FAPbX_3$) due to higher thermal decomposition temperatures of inorganic cations. Besides, all-inorganic lead halide perovskites are highly effective in photovoltaic and optoelectronic applications, such as lasers, photodetectors, and photocatalysis.⁹ So, in various studies, the $CsPbX_3$ structured perovskite material was selected, and NCs were synthesized to achieve high absolute quantum efficiency, a wide emission wavelength range, and a narrow emission line width.^{10,11} At present, although the ionic nature of $CsPbX_3$ endows them with flexible ion exchange properties and high defect tolerance, their soft ionic lattice also renders their NCs less tolerant to external environments. They are prone to stability issues such as phase transitions, phase separation, or even crystal decomposition

under conditions including water, oxygen, polar solvents, irradiation, and elevated temperatures. So CsPbX₃ NCs are still far from large-scale practical application and commercialization. Research indicates that PeNCs synthesised under liquid-phase conditions harbour numerous non-radiative recombination defects both internally and on their surfaces. These include point defects (abundant Pb²⁺ or halide vacancies), interstitial defects, impurity defects, and interface defects, which diminish their PLQY and stability.¹² Therefore, controlling the microstructure and reducing defects within halide PeNCs is crucial for enhancing their stability and luminescent efficiency.

The aforementioned stability issues of CsPbX₃ NCs significantly impact the long-term photovoltaic performance stability during storage and utilisation, thereby constraining their practical application in photovoltaic fields. Extensive research efforts have consequently focused on enhancing perovskite stability, with numerous strategies demonstrating certain improvements. Firstly, the element doping strategy, including A-site and B-site doping, typically involves metal ion doping (e.g., Zn²⁺, Mn²⁺), optimization of surface ligands, and defect passivation. This approach enhances lattice stability by improving the tolerance factor and octahedral geometry of the perovskite crystal phase, thereby mitigating atomic size mismatch and lattice distortion. Widely employed in solar cell applications, the APbI₃ absorber layer frequently incorporates Cs⁺, MA⁺, FA⁺, and other atomic dopants at the A site, significantly extending the operational lifespan of solar cell devices. Encapsulation of PeNCs is another potential strategy for addressing the issue of stability. PeNCs can be protected from oxygen and moisture deterioration by using shells made of physically and chemically inert and/or stable materials such as oxides, metal-organic frameworks (MOFs), polymers, or other stable semiconductor NCs. PeNCs implanted in titanium oxide (TiO₂), zirconium oxide (ZrO₂), or silicon oxide (SiO₂) demonstrated increased oxidation and moisture resistance, as well as lower ion diffusion rates and better water dispersibility.¹³⁻¹⁵ Core-shell strategy can well maintain the properties of APbX₃ at the nanoscale, ideal for application in some special fields. Advanced techniques have been developed to control the thickness of the core-shell, from single-layer to multilayer core-shell structures, ultimately forming a core-shell structure with precisely controlled thickness between two perovskites. More importantly, since the NC surface is passivated, its optical and optoelectronic properties can be tuned.

This article describes the synthesis and characterization of various core-shell structures based on CsPbBr₃ NCs, with a focus on enhancing their stability and characterizing their physical

properties. Notably, this study explored the potential of core-shell structures synthesized during my PhD, aiming to demonstrate that the complementary properties of effectively passivating CsPbBr₃ NCs and improving environmental stability are crucial. This research provides the potential for improving the performance of CsPbBr₃ NCs in optoelectronic devices.

The material contained in this thesis is organized as follows.

[Chapter 1](#) introduces three primary research subjects: 0D Cs₄PbBr₆, 2D CsPb₂Br₅, and 3D CsPbBr₃. It discusses their structural characteristics and optoelectronic properties, along with the phase transitions they may undergo under certain environmental stimuli. Finally, it addresses issues concerning CsPbBr₃ NCs and outlines strategies currently developed to enhance stability. The main focus of this paper is the improvement in stability achieved through core-shell structures.

[Chapter 2](#) outlines the commonly employed techniques for perovskites, encompassing structural characterisation and spectroscopic methods. Regarding spectroscopic approaches, the configuration of the PL measurement apparatus is detailed, alongside the fundamental principles governing the determination of carrier lifetime and recombination rate constants under diverse conditions. These two chapters lay the groundwork for understanding the experimental results and discussions presented in the subsequent chapter.

[Chapter 3](#) reports on the novel results of the research conducted during this doctoral path, along with related discussions about CsPbBr₃@Cs₄PbBr₆. The chapter is divided into three main sections. [Section 3.2](#) and [Section 3.3](#) focus on the synthesis process and characterization methods as well as device parameter settings. The performance and characterization results of these devices are also discussed. This is intended to provide an initial understanding of CsPbBr₃@Cs₄PbBr₆ structure and optical properties. [Section 3.4](#) investigates the thermochromic phenomenon in CsPbBr₃@Cs₄PbBr₆, which was studied using *in situ* spectroscopic techniques. [Section 3.4.1](#) investigates the thermochromic phenomenon using *in situ* absorption spectra. The nature of thermochromism is often related to changes in the band gap, changes in the density of states, or the formation/disappearance of localized defect states. *In situ* absorption spectroscopy can monitor the shift of the absorption edge (red shift or blue shift) in real time during heating or cooling, thereby quantitatively analysing the evolution of the band gap with rising temperature. [Section 3.4.2](#) uses *in situ* Raman to observe the displacement, intensity change, or disappearance/appearance of vibrational peaks in real time, which directly corresponds to changes in chemical bonds and lattice dynamics. In [Section 3.4.3](#),

we conduct our analysis of electron-phonon coupling during the thermochromic process, temperature-dependent PL properties of $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$ are tested with a temperature range of 80 to 300 K. [Section 3.5](#) addresses the molecular structural changes of $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$. The single crystal XRD (SCXRD) and temperature-dependent powder XRD (PXRD) were carried out to study the changes in crystal parameters of $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$ under the influence of heat. Stability is a crucial characteristic in determining the long-term viability of perovskites for thermochromic applications as described in [Section 3.6](#). Based on these findings, [Section 3.7](#) explores the application of $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$. This approach aims to achieve anti-counterfeiting using a simple thermochromic phenomenon. Furthermore, a novel temperature-indicating label is introduced, which involves forming a polymer blend film to indicate high temperatures.

[Chapter 4](#) reports on replacing the shell Cs_4PbBr_6 in [Chapter 3](#) with CsPb_2Br_5 to form $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ and studying the optical properties and water stability of this core-shell structure. This chapter is divided into six parts (in the same order as the overview in Chapter 3). [Section 4.1](#) summarizes the research progress of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$. [Sections 4.2](#) and [4.3](#) obtain $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ by chemical precipitation method at room temperature. In addition, the basic structural and optical characterization results of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ are discussed. [Section 4.4](#) explores the exciton recombination dynamics of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ related to thermal effects. Some important physical parameters of semiconductor materials, such as exciton binding energy, exciton-phonon interaction, and band gap, can be estimated based on the temperature-dependent PL spectra. In [Section 4.5](#), to further investigate the intrinsic exciton recombination behavior, wavelength-dependent time-resolved PL (TRPL) measurements are employed to determine the lifetime (τ) of exciton recombination for $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$. Building on these findings, [Section 4.6](#) explores the stability of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ in water, demonstrating the significant improvement of the core-shell structure $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ compared with CsPbBr_3 NCs. The study highlights the high-yield synthesis of the highly water-resistant green luminescent $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ structure. It revealed that the small lattice mismatch between CsPbBr_3 and CsPb_2Br_5 accounts for the epitaxial crystallization at their interface.

[Chapter 5](#) contains concluding remarks and the outlook.

1 | Introduction

In this chapter, we will introduce the three core themes of the paper. First, the primary material categories under investigation will be introduced-the Cs-Pb-Br system-with a focus on 3D CsPbBr_3 , 2D CsPb_2Br_5 , and 0D Cs_4PbBr_6 . Next, the stability of LHP NCs will be discussed, including their stability under environmental factors such as light, heat, and water. Finally, the significant role of core-shell structures in enhancing the stability of the Cs-Pb-Br system will be reviewed.

1.1 Inorganic Halide Perovskites: The Cs-Pb-Br System

Since the first study on lead halide perovskite solar cells in 2009, the unique photosensitizer lead halide perovskite has gained more attention, and tremendous progress has been accomplished over the last ten years. The general formula for all 3D inorganic LHP is CsPbX_3 , where X refers to Cl, Br, I, and their mixtures. For the formula A_2BX_4 , the structure extends with larger A-site cations (usually aliphatic or aromatic alkylammonium ions), which forms 2D perovskite structure consisting of inorganic $[\text{BX}_6]^{4-}$ octahedron planes and organic ammonium layers. Further increasing the size or count of the organic spacers leads to A_3BX_5 and A_4BX_6 formulas, where the $[\text{BX}_6]^{4-}$ octahedra are separated into chains (1D structure) and isolated dots (0D structure), respectively.¹⁶

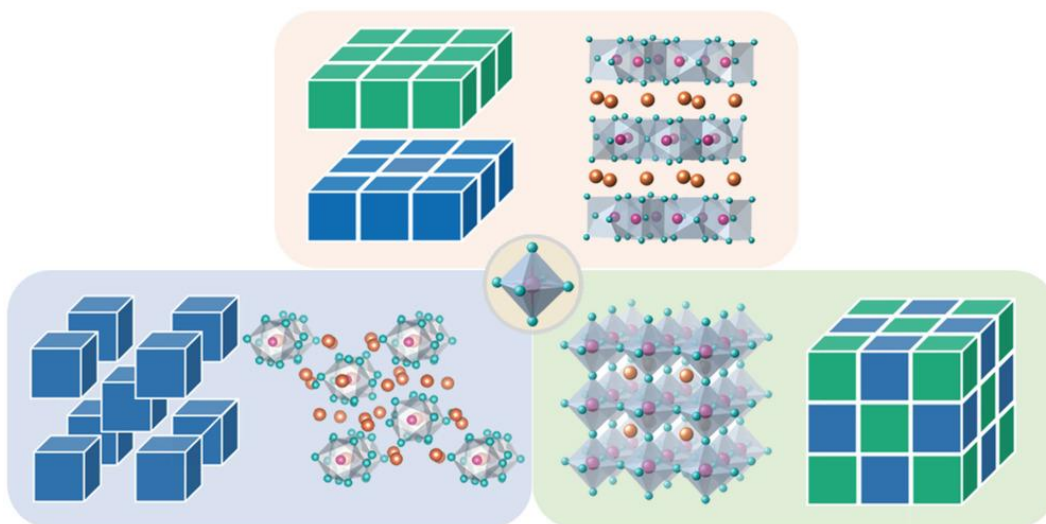


Figure 1. 1 Schematic illustration of 0D, 2D, and 3D cesium lead halide perovskites. Orange spheres: Cs^+ atoms, purple spheres: Pb^{2+} atoms, green spheres: halide atoms, grey octahedrons: $[\text{PbX}_6]^{4-}$ unit cells.

Cubes represent the building blocks $[\text{PbX}_6]^{4-}$ octahedrons. In CsPb_2Br_5 and CsPbBr_3 , two colored cubes are presented to better understand their 2D and 3D connectivity.¹⁷

The success of CsPbX_3 prompted the rapid development of its derivatives, Cs_4PbX_6 and CsPb_2X_5 , which share the same element compositions and $[\text{PbX}_6]^{4-}$ building cells. However, they differ significantly in terms of connectivity of $[\text{PbX}_6]^{4-}$ octahedra. CsPbX_3 is a 3D perovskite structure with corner-shared $[\text{PbX}_6]^{4-}$ octahedra along all three axes. In contrast, CsPb_2X_5 is a 2D phase with Cs^+ cations sandwiched between PbX_2 crystallographic planes. While in Cs_4PbX_6 , Cs^+ cations totally decouple unconnected $[\text{PbX}_6]^{4-}$ octahedra. Low-dimensional-networked cesium lead halide perovskites include CsPb_2X_5 and Cs_4PbX_6 , which have a network of less than three dimensions. These structures can be considered in terms of confinement, in addition to connectedness. CsPbX_3 is not restricted in any dimension, hence it can be called a 3D networked semiconductor. CsPb_2X_5 and Cs_4PbX_6 are referred to as 2D and 0D structures, respectively, due to their confinement in one and three dimensions.^{18, 19} Consequently, excitons in CsPb_2X_5 and Cs_4PbX_6 are limited to PbX_2 planes and individual $[\text{PbX}_6]^{4-}$ units, resulting in greater band gaps than the typical 3D ABX_3 phase. **Figure 1.1** shows three structures with different dimensions. Perovskite materials with different structures exhibit distinct optical and electrical properties, among which the zero-dimensional perovskite Cs_4PbBr_6 has garnered significant attention due to its exceptional luminescent characteristics.

There have been thorough descriptions of these Cs-Pb-Br system, the majority of recent studies have concentrated on CsPbBr_3 , which has outstanding optical characteristics and great promise for a range of applications. Since the pioneering work by the Kovalenko group in 2015, the preparation and application of CsPbBr_3 NCs have made significant strides in a remarkably short period. In addition to CsPbBr_3 NCs, other types of ternary Cs-Pb-Br materials, such as Cs_4PbBr_6 and CsPb_2Br_5 , have also been reported. Although its derivatives, CsPb_2Br_5 and Cs_4PbBr_6 , have made significant strides, they still lag far behind CsPbX_3 , including the core-shell structures they form. Numerous issues still severely restrict the quick development of these low-dimensional-networked perovskites, such as the controversy surrounding the source of their luminescence. These contradictory results may stem from the incorporation of trace amounts of CsPbBr_3 NCs within Cs_4PbBr_6 or CsPb_2Br_5 , as the different $\text{Cs}_x\text{Pb}_y\text{Br}_z$ phases readily interconvert to form mixed phases. We have reason to suspect that the presence of multiple compounds within the Cs-Pb-Br system may be linked to the unstable luminescent properties of CsPbBr_3 , which also constitutes a primary obstacle hindering progress in CsPbBr_3 research. The PL quantum yields

(PLQYs) of colloidal CsPbBr₃ exhibits a sharp decrease in luminescence quenching efficiency to below 20% when approximately 90% of the NCs are in the solid state (e.g., thin film state). Various mechanisms have been proposed to explain this luminescence quenching phenomenon, including nanocrystal aggregation leading to mass loss, removal of the surface passivation layer, and chemical decomposition of the material. Consequently, investigating the interconversion between the aforementioned Cs-Pb-Br compounds holds significant importance.

1.1.1 Phase Engineering of 3D CsPbBr₃, 2D CsPb₂Br₅, and 0D Cs₄PbBr₆

Research into the dimensional definitions and composite phase correlations of CsPbBr₃, CsPb₂Br₅, and Cs₄PbBr₆ has been conducted, including applications of composite phases such as CsPbBr₃@CsPb₂Br₅ and CsPbBr₃@Cs₄PbBr₆ in fields like LEDs and X-ray detection. However, these studies have focused directly on dimensional aspects and explored related applications, without delving into the phase transitions between them. One of the primary drawbacks of these perovskite devices is their lack of long-term stability. When exposed to light, moisture, or thermal processing, phase transitions occur between different dimensions.²⁰ Research into the phase transitions between them is still in its infancy. To improve the optical and electronic properties and stability of metal halide perovskites, Cs-Pb-Br systems with different dimensional structures at the molecular level have been designed. Reversible phase transitions in 3D CsPbBr₃, 2D CsPb₂Br₅, and 0D Cs₄PbBr₆ have been studied and their mechanisms are illustrated in **Figure 1.2**. Owing to the ionic nature of the Cs-Pb-Br materials phase transitions of 3D CsPbBr₃, 2D CsPb₂Br₅, and 0D Cs₄PbBr₆ can be induced by external factors, such as ligands, laser beams, light, heating, excess Br, mechanochemical processes, and water.

The crystal structures of 3D CsPbBr₃, 2D CsPb₂Br₅, and 0D Cs₄PbBr₆ perovskites differ and can be influenced by AX and BX₂ species extraction or insertion. 3D CsPbBr₃ has a typical ABX₃ type perovskite structure similar to that of mineral CaTiO₃,²¹ in which [PbX₆]⁴⁻ octahedra are corner-shared along the three axes.²² In general, 3D CsPbBr₃ can have orthorhombic, tetragonal, and cubic configurations. CsPbBr₃ transitions from the orthogon phase (*Pbnm*) to the tetragonal phase (*P4/mbm*) at 88 °C, then to the cubic phase (*Pm3m*) at 130 °C.²³ After cooling to ambient temperature, the cubic phase transforms into the orthorhombic phase, which possesses a wide band gap of 2.3 eV and optical absorbance between 300-540 nm.²⁴ 3D CsPbBr₃ perovskites outperform other luminous Cs_xPb_yBr_z perovskites in terms of optical features, including high PLQYs, emission wavelength tunability, short irradiative lifetime, and narrowband emission.²⁵

CsPbBr₃ quantum dots (QDs) with an average size of 10 nm exhibit an absorption band at 450-530 nm, a full width at half maximum (FWHM) of 16 nm, and a band gap of 2.33 eV.²⁶ The high ionic internal structure and low formation energy of 3D CsPbBr₃ perovskites make them susceptible to environmental instability. Exposure to moisture, air, light, and heat significantly reduces their performance, limiting their use.²⁷ However, this also promotes reversible phase transitions within the Cs-Pb-Br system.

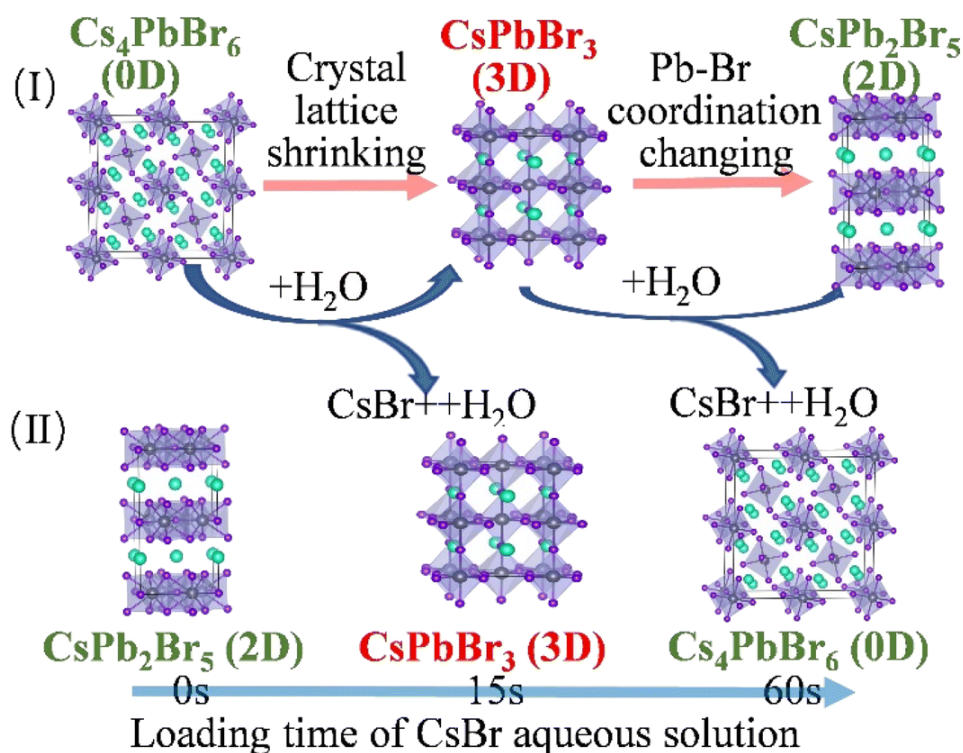


Figure 1.2 I: A schematic of the possible degradation mechanism of the Cs₄PbBr₆ crystal involving a water-triggered transition process.²⁸ II: The effect of the loading time of the CsBr aqueous solution on the phase transition of cesium lead bromide halide.²⁹

0D Cs₄PbBr₆ perovskite has a characteristic structure with isolated [PbBr₆]⁴⁻ octahedra surrounded by eight Cs⁺ cations and a relatively large band gap ($E_g \geq 3.1$ eV).³⁰ Due to the favourable photophysical characteristics of [PbBr₆]⁴⁻ clusters, where the [PbBr₆]⁴⁻ octahedra act as the common luminescence centers, it displays a strong quantum confinement effect and outstanding PLQY.³¹ 0D perovskites maintain the photophysical characteristics of individual metal halide octahedra or metal halide clusters without the creation of electronic couplings because of their crystal structure, which contains isolated metal halide octahedral anions or metal halide clusters. In other words, the optical characteristics are mostly determined by inorganic metal halide polyhedra or clusters. In addition, 0D Cs₄PbBr₆ perovskites exhibit higher moisture and heat stabilities than those of 3D CsPbBr₃. Good lattice matching between

0D Cs₄PbBr₆ and 3D CsPbBr₃ composites enhances the stability of 3D CsPbBr₃, including the development of core-shell structures.³² A layer of Cs-ions is sandwiched between the two neighbouring Br-Pb layers in 2D tetragonal CsPb₂Br₅ perovskites. 2D CsPb₂Br₅ is a semiconductor with a large indirect band gap of 2.98–3.87 eV and it may be PL inactive, which has been verified and scanned in many research studies.³³ Although these studies have reached consensus on the structure and composition, there remains significant divergence in the interpretation of its intrinsic optical properties, a topic that remains contentious to this day. For instance, research on CsPb₂Br₅ nanosheets and microplates indicates that the material exhibits intense green luminescence and green laser properties. Consequently, there is an urgent need to resolve the controversies arising from differing interpretations of optical properties and to advance the field towards the targeted regulation of key material characteristics. The reversible phase transitions of 3D CsPbBr₃, 2D CsPb₂Br₅, and 0D Cs₄PbBr₆ can be realized by the extraction or insertion of CsBr species owing to the high solubility of CsBr in water²⁸ or continuous loading of a CsBr solution.³⁴ The phase transition from 0D Cs₄PbBr₆ to 2D CsPb₂Br₅ can be realized through the intermediate 3D CsPbBr₃ phase. For example, minimal water interactions with all-inorganic perovskites typically result in phase transformations from 0D Cs₄PbBr₆ to 3D CsPbBr₃ and eventually 2D CsPb₂Br₅, with continual stripping of CsBr.³⁵ The phase transition from 0D Cs₄PbBr₆ to 3D CsPbBr₃ also occurs through the PbBr₂-insertion mechanism. Consequently, the insertion or extraction of CsBr or PbBr₂ encourages the reversible phase transitions of 3D CsPbBr₃, 2D CsPb₂Br₅, and 0D Cs₄PbBr₆ perovskites together with crystal structure modification, taking into account the reactive character of various perovskite formulations. For example, CsPb₂Br₅ is often obtained as a secondary product during the syntheses of CsPbBr₃ perovskites, Cs₄PbBr₆ perovskite-related structure, and/or as a converted product from CsPbBr₃ NCs. All the phase transitions must be induced by water and ligands and cannot be converted automatically.

1.1.2 Recent Progress in Applications of Cs-Pb-Br Perovskites

The preceding discussion outlined multiple interconversions within the Cs-Pb-Br system. As these transitions require external environmental influences to occur, such phase transformations aim to enhance the stability of these materials in aqueous and thermal environments while optimizing the luminescent properties of perovskites. Compared to single-phase CsPbBr₃ perovskites, Cs-Pb-Br perovskite composites featuring core-shell structures and mixed phases are emerging as novel materials. Their exceptional optical and electronic

properties enable applications across numerous fields, including electro-optical, optoelectronic, and all-optical conversion devices. Solid-state lighting and displays prepared using representative Cs-Pb-Br perovskite composite materials as emitters especially make full use of their high PLQY, high emission color purity, fast carrier mobility, low-cost solution preparation, and narrow emission linewidth.^{28, 36} The CsPbBr₃ NCs in Cs₄PbBr₆ crystals exhibit superior luminous performance as compared with that of CsPbBr₃ SCs with weak exciton binding. For example, for perovskite LEDs (PeLEDs) with CsPbBr₃ SCs as the emission layer, the maximum current efficiency (CE) is $3.33 \times 10^{-3} \text{ cd A}^{-1}$ and the maximum external quantum efficiency (EQE) is 3.5×10^{-7} . But the PeLEDs made of CsPbBr₃ NCs in a Cs₄PbBr₆ matrix, the CE and EQE values are 0.30 cd A^{-1} and 2.4×10^{-5} , respectively.³⁷ The fabricated LED emitted strong green light when powered on, with an emission spectrum located at 525 nm and a FWHM of 17 nm. Even after 116 hours of operation, the LED performance remained stable, retaining 55% of its original intensity.³⁵ Compared with phosphor-converted LEDs (PcLEDs) made of single-phase perovskites, PcLEDs containing Cs-Pb-Br composites (such as dual-phase CsPbBr₃/Cs₄PbBr₆NCs or CsPbBr₃/CsPb₂Br₅ NCs) exhibit high stability and high PLQY, making them alternative candidates for future LEDs and WLEDs.

In addition to the LEDs, solar cells based on Cs-Pb-Br perovskite composites are widely studied for photoelectric conversion due to their compelling optoelectronic properties, including high absorption coefficients, long charge carrier diffusion length. While stability remains a challenge, creating composite structures is a key approach to mitigating degradation from moisture, light and heat. Cs-Pb-Br perovskite composites can improve photovoltaic performance by acting as both an absorbing and photoconversion layer. CsPbX₃ NCs with a wide band gap can be effective photon energy converters due to their tunable PL outputs, high PLQYs, and large Stokes shift, which reduces self-reabsorption losses and converts ultraviolet photons into visible photons.^{38, 39} Liu *et al.* stated that by precisely adjusting the loading time (*t*) of a CsBr aqueous solution on the PbBr₂ film surface, a maximum power conversion efficiency (PCE) of 9.14% was reached. In addition, a high fill factor (FF) of 0.84 with a PCE of 9.02% was attained.²⁹ Duan *et al.* optimized the phase transitions of 3D CsPbBr₃, 2D CsPb₂Br₅, and 0D Cs₄PbBr₆ to achieve a PCE of 9.72% during standard solar illumination.⁴⁰ An optimal CsPbBr₃-CsPb₂Br₅ composite film was grown as the absorbing layer of a solar cell by digital inkjet printing technology, and the fabricated device exhibited a high efficiency of 6.81% with long-term stability as shown in **Figure 1.3**.⁴¹ Tong *et al.* used CsPbBr₃-CsPb₂Br₅ thin films to create

a flexible photodetector with high responsivity and detectivity (0.375 AW^{-1} and 10^{11} Jones, respectively) and excellent air stability (more than 65 days without encapsulation).⁴² These highlight the potential of Cs-Pb-Br perovskite composites with mixed phases.

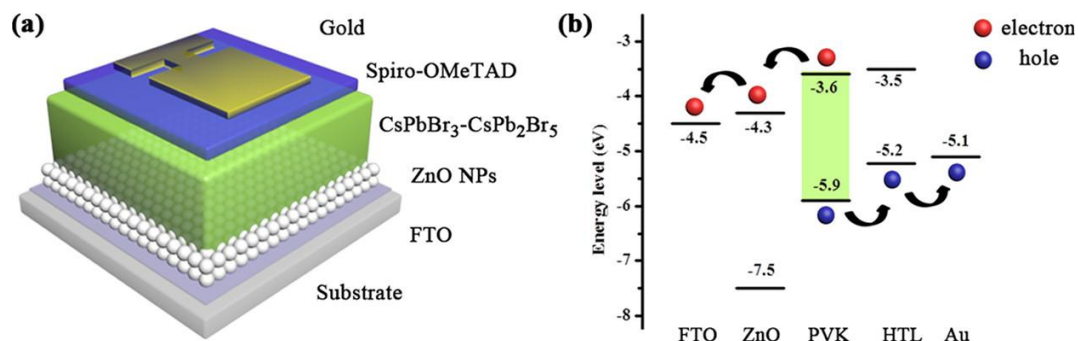


Figure 1.3 (a) Schematic structure of the device. (b) Energy level diagram which exhibits the collection process of the photogenerated charge carriers.⁴³

Under appropriate external conditions, Cs-Pb-Br perovskite systems can easily undergo phase transitions, leading to improved optical properties. CsPbBr₃'s weak stability against heat, light, and moisture continues to be a major hurdle to practical usage. Controlling the phase transition results in all-inorganic lead halide perovskites with 3D CsPbBr₃ NCs embedded in 0D Cs₄PbX₆, which are environmentally insensitive and highly luminous. These materials can be used in stable and bright electroluminescent devices. This is primarily because the CsPbBr₃ lattice perfectly matches that of Cs₄PbBr₆, eliminating lattice mismatch. This enhances passivation while avoiding additional strain.^{44, 45} The device performance of CsPbBr₃ containing CsPb₂Br₅ is significantly improved compared with that of CsPbBr₃ tailored solar cells alone, due to the indirect band gap of CsPb₂Br₅ that suppresses electron-hole recombination.^{46 47} As a result of a better understanding of the multiphase transformation of Cs-Pb-Br derivatives, precise phase control of Cs-Pb-Br derivatives from 3D CsPbBr₃ to 0D Cs₄PbBr₆ or 2D CsPb₂Br₅ is critical for significantly improving the photovoltaic performance of all-inorganic CsPbBr₃ perovskites. Especially this combination of composite Cs-Pb-Br phase compounds, which shows better application prospects.

1.2 Origins of Instability in LHP NCs

The low stability of LHP has long been one of the most significant obstacles encountered in the commercialisation of LHP. Halide perovskites are particularly susceptible to external factors such as light, heat, oxygen, and water. Among these, the thermal stability of PeNCs has attracted

considerable attention, with numerous research groups undertaking extensive work in this area. PeNCs, as ionic crystal compounds, derive their instability from the combined effects of their high specific surface area at the nanoscale and their crystalline properties. This instability can be broadly categorised into two main types: intrinsic factors and environmental stability. The intrinsic factors include the transformation of the perovskite crystal structure, surface ligand detachment, and halide vacancy. Methods for evaluating the tolerance factor and octahedral geometry factor of perovskite crystals, where the calculated values conform to the conditions for forming stable cubic perovskite crystal phases, also reflect to a certain extent the structural stability of the corresponding perovskite crystals. In LHP NCs structures, the corner-sharing $[BX_6]^{4-}$ octahedra are crucial to the optoelectronic properties of the material. Distortion and deformation of the $[BX_6]^{4-}$ octahedra can lead to a severe loss of optoelectronic properties.⁴⁸ As shown in **Figure 1.4 (a)**, perovskite crystal structure of $CsPbI_3$ in (cubic) α -, (tetragonal) β -, and (orthorhombic) γ -phase (photoactive phases) could transform into (orthorhombic) non-perovskite δ -phase at room temperature, in which $[PbI_6]^{4-}$ octahedra are not corner-shared due to big octahedral distortion.⁴⁸ Since non-perovskite δ - $CsPbI_3$ does not have the optoelectronic properties of a semiconductor, this instability hinders the application of $CsPbI_3$. At room temperature, $CsPbBr_3$ NCs transform from a cubic phase to an orthorhombic phase, and the $[PbBr_6]^{4-}$ octahedrons sharing vertices maintain a perovskite structure, but the octahedrons are slightly tilted, which contrasts sharply with the formation of non-perovskite δ - $CsPbI_3$ (**Figure 1.4 (b)**). Furthermore, the surface ligands of NCs affect many of their properties, including shape, size, PLQY, and colloidal stability. By varying the hydrocarbon chain lengths of the amine and carboxylic acid ligands, PeNCs of various shapes and sizes can be obtained, such as 0D spherical NCs, 1D nanorods, 2D nanosheets, and 3D nanocubes. Dimensionality here refers to the regulation of morphology.^{49, 50} Previous studies have found that surface ligand desorption and halide vacancies lead to the increase of surface trap states, aggregation, and degradation of PeNCs.⁵¹ It is generally accepted that the detachment of ligands on the nanocrystal surface, which is thought to be one of the primary causes of the instability of PeNCs, can be caused by external stimuli. These external stimuli can also significantly impair the intrinsic factors of PeNCs, lowering their colloidal stability. Dynamic binding modes,⁵² binding energies,⁵³ and activation energies⁵⁴ are only a few of the numerous variables that affect ligand desorption. Oleic acid (OA) and OLA (OLA), the two most widely utilized ligands, have been shown to exhibit dynamic binding modes. In short, OA and OLA undergo proton transfer to become oleate anions and OLA cations, respectively, which then interact with the

surface of the nanocrystal.⁵⁵ Binding mode and energy are currently the most commonly used factors to explain the instability of lead halide PeNCs induced by heat and/or light,⁵⁶ but few studies have explored ligand detachment upon exposure to polar solvents. DuBose *et al.* compared the changes in surface activation energy when CsPbBr₃ nanoplatelets (NPLs) are transformed into larger structures in the presence and absence of polar solvents.⁵⁴

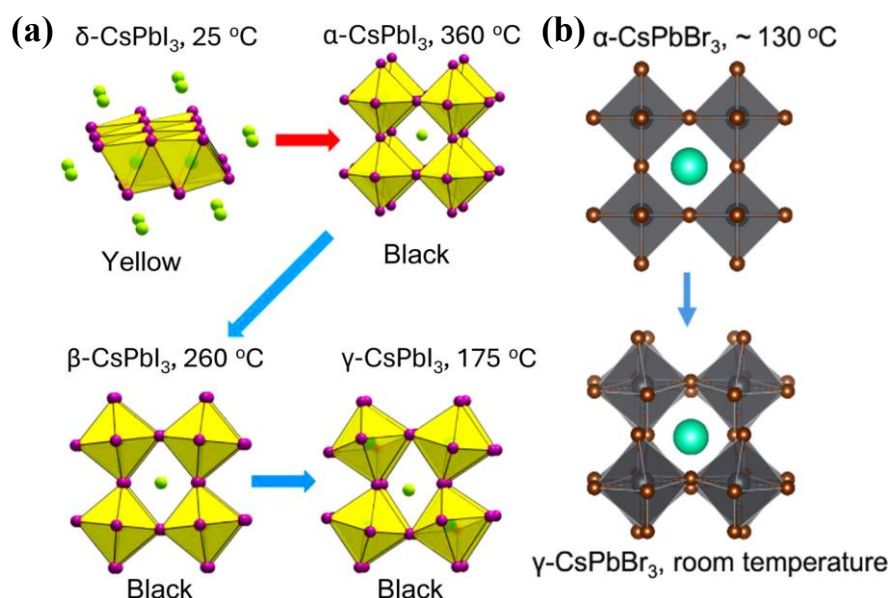


Figure 1. 4 Schematic illustration of phase transition of (a) CsPbI₃ and (b) CsPbBr₃ NCs.^{57, 58}

Various environmental conditions can induce phase transitions, decomposition or spontaneous growth in PeNCs. When environmental factors cause the desorption of surface ligands, the PeNCs will continue to degrade, resulting in the formation of a large number of surface halide vacancies, which will lead to a decrease in the stability and PLQY of the perovskite nanocrystal.^{51, 59} Moreover, PeNCs typically undergo prolonged, high-intensity laser irradiation during practical applications, particularly in display technologies such as light-emitting diodes(LEDs), backlight displays, and laser light sources. Consequently, their ability to withstand optical irradiation is of paramount importance. The photostability of perovskites directly determines the practical value of devices. In current perovskite-based LED devices, significant progress has been made in the performance and lifetime of red and green LEDs, whereas blue LED performance remains unsatisfactory. Li *et al.* discovered that under high-intensity blue light irradiation in atmospheric conditions, the fluorescence of CsPbBr₃ NCs quenches rapidly;⁶⁰ whereas in an inert gas environment, agglomeration phenomena are significantly reduced. The primary reason lies in the combined effects of light, moisture, and

oxygen, which cause NCs to agglomerate and undergo spontaneous growth. This ultimately results in the formation of larger NCs with a high surface defect density, leading to a sharp decline in quantum efficiency. Brief exposure to water can cause degradation of the perovskite surface, reducing surface defects. For all-inorganic perovskites, trace water causes phase transformation, turning 3D CsPbBr₃ perovskites into 2D perovskite-related CsPb₂Br₅.³⁵ When a modest amount of water is introduced, the previously non-luminescent spherical Cs₄PbBr₆ NCs can be converted into green-emitting cubic CsPbBr₃.⁶¹ Under high-temperature conditions, the fully inorganic perovskite CsPbX₃ undergoes [PbX₆]⁴⁻ octahedral collapse at temperatures exceeding 500 °C.⁶² Furthermore, elevated temperatures accelerate the degradation reactions of perovskite under conditions of humidity, oxygen exposure, and illumination. Huang *et al.* studied the effects of light, humidity, oxygen and temperature on the optical properties of CsPbBr₃ NC films. In view of moisture, 80% relative humidity (RH) also results in a larger PL loss of 95.6% compared to 89.4% with 60% RH.⁶⁰ However, compared with organic MAPbBr₃, CsPbBr₃ showed better thermal stability. After two weeks of continuous light ageing, the prepared solar cells still had good stability.⁶³ Further studies, which calls for systematic studies to unravel the interplay between intrinsic and extrinsic degradation mechanisms, on these observations are necessary to fully understand the degradation mechanism of PeNCs, which calls for systematic studies to unravel the interplay between intrinsic and extrinsic degradation mechanisms.

1.3 Strategies to Improve the Structural Stability and Optical Properties

The instability problem caused by the internal easy phase transition, high concentration defects, as well as high sensitivity of PeNCs to external conditions such as moisture, oxygen, heat, and light, deserves attention in practical applications. A great effort has been devoted to stabilizing PeNCs. Within several years, as listed in **Figure 1.5** numerous strategies have been developed. These strategies can be divided into two categories: post-synthesis modification and encapsulation.

1.3.1 Engineering of Ligands

Surface ligand engineering has a vital role in controlling the stability of NCs. The ligands on the surface of PeNCs are all weakly bound and undergo dynamic motion. The Kovalenko group⁵²

demonstrated that organic ligands adsorbed onto the surface of NCs can detach from the surface, whilst externally free ligands can re-adsorb, maintaining a dynamic equilibrium between the two. When protonated OLA ligands detach from the nanocrystal surface, they carry away surface halide anions (X^- acids) to maintain electrical neutrality. This exposes the perovskite directly, facilitating aggregation with neighbouring NCs and reducing stability. Conversely, the absence of surface ligands allows surface ions to diffuse, triggering recrystallisation between smaller NCs. This leads to the formation of larger NCs, resulting in significant alterations to emission peak positions and PLQY. Therefore, surface modification during the synthesis of PeNCs, aimed at increasing the interaction between the NCs surface and surface ligands because the weakly bound ligands can also detach easily during purification with antisolvent or when exposed to ambient conditions during storage, accelerating structural degradation. It can have a major impact on the overall stability of the perovskite devices. To overcome this issue, researchers have explored alternative ligands that have a strong binding affinity to the NC surface.

To overcome these limitations, researchers have explored alternative ligands with stronger binding affinities. Phosphorus-based ligands have shown promise as alternative capping ligands for perovskites. When oleylphosphonic acid (OLPA) was employed in the synthesis of CsPbBr_3 NCs, nuclear magnetic resonance (NMR) spectroscopy verified effective surface passivation through multiple binding modes. Upon exposure to ambient air, water molecules present in the atmosphere could protonate the OLPA ligands, thereby inducing their partial detachment from the NCs surface into the surrounding solution. Importantly, these released ligands remain available and were able to dynamically rebind to the NCs, therefore establishing a reversible binding-unbinding equilibrium, which in turn contributed to improved structural integrity and enhanced stability under air exposure.⁶⁴ Y.S. Tian *et al.* discovered that compared to OA and OLA—the most commonly used ligands in synthesising halide perovskite materials—the use of octylphosphonic acid as a ligand significantly enhances both thermal and environmental stability.⁶⁵ This improvement stems from the relatively strong interaction between octylphosphonic acid and lead ions. Furthermore, octylphosphonic acid was found to provide superior protective effects for CsPbX_3 NCs.

In addition to phosphorus-based ligands, organic sulfate ligands have also attracted attention due to their strong binding affinity to Pb^{2+} surface ions. Organic sulfate ligands have been shown to have superior performance in improving the colloidal stability and PLQY of PeNCs.

Didodecyldimethylammonium bromide (DDAB), a short-chain ligand, was used to replace OLA and oleic acid ligands in CsPbX_3 NCs via a ligand-exchange method. This resulted in PeNCs film with improved stability and LED performance due to the stability of the DDAB passivate surface defects and prevent aggregation.⁶⁶ Long-chain sulfonic acid ligands, such as dodecylbenzene sulfonic acid (DBSA), were used to synthesize CsPbI_3 and CsPbBr_3 NCs due to their high acidity and strong ability to adsorb electrons. The enhanced optical properties are attributed to the reduction of bromine vacancies, which can act as bromide ions, and the strong interaction between the ligand and the nanocrystal surface.^{67,68}

Overall, replacing weakly bound native ligands with strongly coordinating alternatives such as phosphonic acids, sulfates, and sulfonic acids provides an effective strategy to enhance the structural robustness, colloidal stability, and optoelectronic performance of PeNCs.

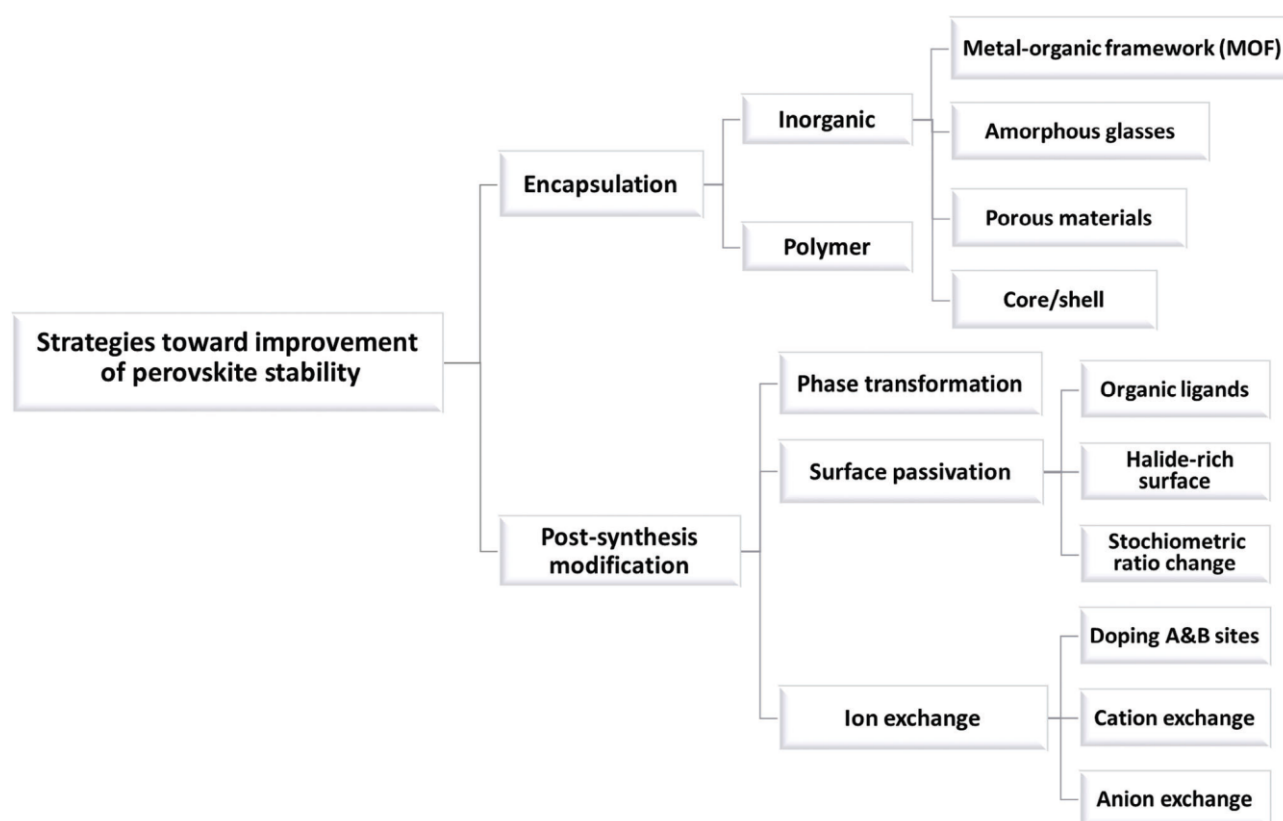


Figure 1. 5 Different strategies toward the improvement of perovskite stability by encapsulation and post-synthesis modification.⁶⁹

1.3.2 Halide Passivation

The stability of PeNCs is largely determined by the halide vacancies. These vacant sites on the surface are easy prey for moisture or oxygen, causing NCs deterioration. This explains why

removing faults improves both PLQY and stability. The vacancies also have a negative impact on the performance of devices that use mixed halide NCs due to defect hopping, which results in anion diffusion and halide segregation.⁷⁰ Developing mixed-halide perovskites that resist halide segregation under operational conditions is a significant challenge and this is also one of the ways to improve the stability of perovskite. To improve the PLQY of blue-emitting CsPbBr₃ NPLs, a PbBr₂ solution was utilized instead of methylammonium halides to passivate uncoordinated surface atoms with Pb and Br vacancies.⁷¹ Li *et al.* reported a facile ZnX₂/hexane post-treatment that simultaneously increased PLQY and stability of CsPbX₃ QDs; XPS analysis showed Br 3d signals that could be deconvoluted into inner and surface components (pristine: 68.2 / 69.1 eV; treated: 68.4 / 69.3 eV), consistent with reduced surface defects after treatment.⁷² Moreover, it was found that the post-treatment of capping ligands can achieve distributed control of the crystallization process of perovskites, thereby further improving their luminescence properties and stability.⁷³ Zhang *et al.* introduced 3-phenyl-2-propen-1-amine into CsPbBr₃ QDs through a two-step surface ligand engineering process and obtained QDs with a near-perfect crystalline quality and excellent luminance.⁷⁴ The fluoride anion occupied bromide vacancies, suppressing nonradiative recombination. Research indicates that using halide-rich salts, either during or after synthesis, can effectively decrease halide vacancies. This technique is less likely to cause problems, unlike ligand exchange procedures. In addition to halide-rich salts, pseudo-halogens are effective ways to enhance optical performance by fill in halogen vacancies in PeNCs. For example, the thiocyanate treatment is capable of minimizing the nonradiative pathways present in untreated samples. In CsPbBr₃ NCs, the surface passivation by sodium thiocyanate improves the quantum yield of both freshly synthesized (PLQY $\approx$ 90%) and aged NCs (PLQY $\approx$ 70%).⁷⁵

1.3.3 Elements Substitution and Doping

Metal cations doping and substitution have the potential to influence the optical, electrical, and magnetic properties of semiconductor NCs. This doping approach improves NC characteristics by suppressing defects. Substituents should be chosen to maintain appropriate charge balance and ionic size so that the Goldschmidt tolerance and octahedral factors remain within ranges that support the perovskite framework.⁷⁶ Over the years, several reports have focused on improving the stability of the PeNCs via A- and B-site substituting or alloying with metal cations like Na⁺, Ag⁺, Mn²⁺, Zn²⁺, Sr²⁺, and Ni²⁺.^{77,78} The inherently low lattice formation energy of PeNCs

contributes to their poor thermal stability, whereas substitution and doping also increases the lattice formation energy and thus improves stability.

Among all inorganic PeNCs, inorganic CsPbBr_3 materials consistently exhibit markedly superior thermal stability. As emitters within LED chips, they demonstrate reduced decomposition under heat-induced conditions, alongside enhanced environmental stability compared to hybrid perovskite materials. A work described $\text{Rb}_x\text{Cs}_{1-x}\text{PbX}_3$ QDs with tunable fluorescence and high PLQYs up to 60%.⁷⁹ Following incorporation of Rb^+ ions, the structural integrity of $\text{Rb}_x\text{Cs}_{1-x}\text{PbX}_3$ QDs remains intact. Although both the particle size distribution and average edge length of the nanoparticles exhibit a decreasing trend with increasing Rb^+ content, the stability test revealed that the mixed Rb/Cs bromide NCs present a non-shift in absorption in the first week compared with CsPbX_3 nanoparticles. Similarly, the incorporation of K^+ into CsPbBr_3 QDs brings in the improvement of PLQYs to 83% from 65%.⁸⁰ Further photostability testing revealed that after 45 hours of irradiation, the luminous intensity of the CsPbBr_3 thin films had diminished to 50% of its original value, whereas the $\text{K}_x\text{Cs}_{1-x}\text{PbBr}_3$ thin films maintained 100% luminous intensity even after 153 hours of exposure.

In addition to suppressing defects in B-site doping, doping alters the B-X bond length due to changes in the radius of the dopant elements. Doping CsPbBr_3 NCs with smaller size of Cu^{2+} ions leads to a more stable lattice and improves thermal stability. Density functional theory (DFT) calculations show that Cu^{2+} doped CsPbBr_3 have higher formation energies than CsPbBr_3 , indicating they are more stable than CsPbBr_3 nano NCs crystals.⁸¹ It should be noted that, although the doping of divalent ions has no significant effect on the PLQY of CsPbBr_3 NCs compared to CsPbI_3 NCs, trivalent ions reduce the luminescence efficiency of the host NCs as the doping concentration increases except for Ce^{3+} .^{82,83} When Ce^{3+} is doped, the luminescence efficiency of the host CsPbBr_3 NCs can be improved to 89%. This is because the doped Ce^{3+} provides new energy levels near the conduction band edge, which facilitates the radiative recombination of excitons, while other trivalent cations such as Bi^{3+} introduce deep energy level traps,⁸⁴ promoting non-radiative recombination. Therefore, metal ion doping may not be the correct strategy for enhancing the PL of CsPbBr_3 NCs, but it can be used for other purposes, such as optical tuning. Doping at both A and B sites can affect the band gap, emission wavelength, and electrical characteristics of PeNCs.⁸⁵

1.3.4 Core-Shell Structures: Thin and Thick Shells

Another strategy to safeguard and improve the stability of PeNCs is to encapsulate them in organic polymer films or inorganic compound powders with strong chemical stability as the matrix. By passivating dangling bonds and removing surface defects from different QDs, this technique enhances their photophysical characteristics. It is especially appropriate for the field of LEDs because it is also compatible with traditional LED encapsulation procedures. Oxides, MOFs, polymers, or other stable semiconductor NCs are frequently selected as shells. Such core-shell structures can effectively shield the crystal core serve as a protective barrier against external perturbations. Among potential isolation materials, transparent SiO_2 with stable chemical properties is an ideal coating layer for light-emitting units.⁸⁶ Several studies have also reported SiO_2 -coated NCs with improved stability in water.^{87,88} To prevent the ion diffusion and ion exchange commonly observed in mixed halide polysilicon NCs, growing polysilicon NCs within porous materials can enhance their stability.²⁷ Furthermore, the NCs can be effectively protected from the hazardous environment by inorganic salts, which have a higher heat resistance than the majority of organic compounds. The stability of CsPbX_3 NCs was improved when Eychmuller's group⁸⁹ demonstrated that adding CsPbX_3 NCs via solid-state anion exchange processes to ionic matrices of potassium halide salts (KCl, KBr, and KI) did not alter their original photoluminescence quantum efficiency. In addition to the single-matrix encapsulation strategy described above, PeNCs may also be stabilised through multiple encapsulation approaches or by first passivating the surface with ligands before encapsulation. It is generally accepted that the shell thickness affects the degree of defect state passivation, the structure of the energy band, the dynamics of carriers, and so on. Li *et al.* incorporated a toluene solution of CsPbBr_3 NCs into SiO_2 and TiO_2 precursors.⁹⁰ Under humid conditions, solvent evaporation triggered a sol-gel hydrolysis reaction, yielding CsPbBr_3 NCs encapsulated within a $\text{SiO}_2/\text{TiO}_2$ composite. The composite material achieved a PLQY of 90% and exhibited reduced susceptibility to QDs aggregation. We will discuss the specifics in **Section 1.4 Core-shell structure of Perovskites**.

1.4 Core-Shell Structure of Perovskites

1.4.1 Styles of Core-Shell Structure

The shell material must be carefully chosen to engineer the core-shell structure and achieve favourable band alignment before the shell layer grows on PeNCs. Depending on the relative

positions of the conduction and valence band edges of the core and shell components, different types of heterostructures can be formed. These band configurations not only determine the spatial distribution of charge carriers but also dictate the optical and electronic characteristics of the resulting NCs. Broadly, perovskite core-shell heterostructures can be categorized into Type-I and Type-II architectures as shown in **Figure 1.6**, each exhibiting unique advantages for specific applications ranging from LEDs to photovoltaics and photocatalysis.

In a Type-I core-shell structure, the band gap of the shell material exceeds that of the core material. Consequently, the conduction and valence band edges of the core material lie within the shell's band gap, confining electrons and holes to the core region. The band gap energy of the heterostructure is determined by the core material's band gap, whilst the shell passivates surface defects and restricts electrons and holes within the core region. Hence, these structures are considered as suitable luminescent phosphors for applications in lighting, displays, ink-jet printing, etc. A number of perovskite structures were successfully demonstrated, for example, Cs_4PbX_6 as the shell material was proposed and demonstrated by Kaur *et al.* Higher exciton binding energy for the Cs_4PbBr_6 shell phase can be probable reasons accounting for the reduced PL lifetime in as-synthesized $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ core-shell NCs.⁹¹ The structure was evidently proven to effectively confine electrons and holes of CsPbBr_3 NCs for the obvious improvement of the radiative recombination efficiency. Cao *et al.* constructed a $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ heterojunction to enhance the performances of PeLEDs by adding trace water with strong polarity⁹² and the as-fabricated PeLEDs exhibit a maximum current efficiency of 43.62 cd A^{-1} and a peak EQE of 11.31%.

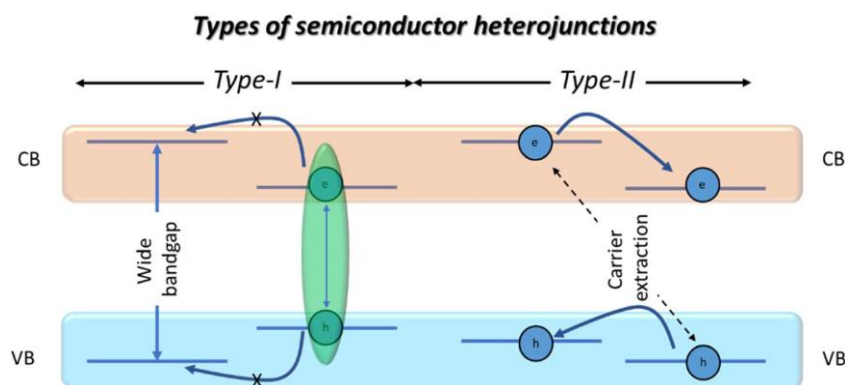


Figure 1. 6 A schematic representation of type-I and type-II heterojunctions in typical core-shell nanostructures.⁹³

In contrast, the Type-II structure has a staggered band structure because the energy levels of the core material's valence band and conduction band borders are either higher or lower than those of the shell material. The Type-II structure's band gap is determined by the energy differential between the two semiconductors' valence and conduction band edges. Charge carriers are spatially segregated within this structure, which may be advantageous for applications like photovoltaics and photocatalysis.^{94, 95} The successful synthesis of well-dispersed CsPbBr₃@TiO₂ heterostructure NCs is a typical II core-shell structure.⁹⁶ The TRPL showed that CsPbBr₃ NCs exhibited a much longer carrier lifetime ($\tau = 15.5$ ns), which is more than 9 times that of CsPbBr₃@TiO₂ NCs ($\tau = 1.51$ ns). The TPRL results further demonstrated the rapid transfer of electrons from the excited states of CsPbBr₃ NCs to TiO₂. As a consequence, the CsPbBr₃@TiO₂ NCs showed greater water stability than did the pristine TOP-modified CsPbBr₃ NCs, and their PLQY gradually decreased after more than 1 week. Kong *et al.*⁹⁷ also showed that the PL intensity of the CsPbBr₃/zeolite core-shell structure decreases once the shell layer forms, mainly because radiative recombination processes are suppressed due to a staggered band structure. The study also suggested that the photogenerated electron transfer efficiency is greatly increased with increasing loading amounts of CsPbBr₃ NCs onto zeolite, giving these NCs substantial advantages for applications like photocatalytic carbon dioxide reduction. Besides, Chen *et al.* reported a CsPbBr₃/ZnS type-II structure,⁹⁸ ZnBr₂ is introduced on the surface of bromine-vacancy-rich CsPbBr₃ NCs. The PLQY of CsPbBr₃/ZnS core-shell NCs is improved to 85%, which is 5 times higher than that of CsPbBr₃ NCs (17%). That is to say, the substantial bromine vacancies in the CsPbBr₃ NCs are well-passivated after the growth of the ZnS shell layer.

1.4.2 Synthesis of Core-Shell Structure

Based on the unique properties, core-shell structural styles and formation mechanisms of NCs, various methods have been developed for synthesizing core-shell structures, which can fall into four categories: sol-gel synthesis, template-assisted methods, physical techniques, and microencapsulation. Typically, some common synthesis methods involve adding template substances to precursors, enabling NCs to undergo rapid, transient nucleation followed by a relatively slow growth phase. Other approaches employ techniques such as thermal injection or ligand-mediated precipitation to grow new shell layers or multilayer structures onto the surfaces of pre-synthesized NCs.

Among these methods, the sol-gel and microencapsulation strategies are two widely explored approaches. The sol-gel method is a wet-chemical process that creates bulk solid materials from precursors, which are tiny molecules. This technique has recently been expanded to successfully create a number of protective layers for NCs: inorganic ceramic polymers, binary oxides of $\text{SiO}_2/\text{Al}_2\text{O}_3$, and monoacidic oxides of SiO_2 and TiO_2 . For instance, monodisperse $\text{CsPbX}_3/\text{SiO}_2$ and $\text{CsPbBr}_3/\text{Ta}_2\text{O}_5$ Janus nanoparticles were successfully prepared by combining a water-triggered transformation process and a sol-gel method.⁹⁹ In a typical procedure, the tantalum (V) ethoxide and acetylacetone were added to Cs_4PbBr_6 NCs/hexane solution, and then water was injected quickly into the mixture under vigorous oscillation using a vortexer for 2 mins. In an attempt to avoid random encapsulation of the SiO_2 shells and in the meantime surpass the hydrophilicity and the microporosity of SiO_2 shells. A double-shell strategy to establish a new core-shell/shell architecture $\text{CsPbBr}_3/\text{SiO}_2/\text{Al}_2\text{O}_3$, sol-gel is equally applicable.⁹⁰ Furthermore, zhong *et al.* reported $\text{CsPbBr}_3/\text{SiO}_2$ with a single CsPbBr_3 NCs using the one-pot synthesis method.¹⁰⁰ In the synthesis process, a mixture of CsBr , PbBr_2 , OA, oleylamine, dimethylformamide (DMF), and ammonia solution into a toluene containing tetramethoxysilane (TMOS) was injected. $\text{CsPbBr}_3/\text{SiO}_2$ exhibits remarkable long-term stability even when exposed to the synergistic effects of water, oxygen, and light. Z.C. Li *et al.*⁹⁰ employed a straightforward sol-gel reaction to react an aluminium-silicon precursor with CsPbBr_3 NCs in a toluene solution, successfully incorporating CsPbBr_3 NCs into silica/alumina zeolite. This approach not only endowed the CsPbBr_3 NCs with high photostability but also conferred superior thermal stability, rendering them highly suitable for applications within the LED sector.

In contrast to sol-gel synthesis, the term "microencapsulation strategy" primarily describes the macroscale, self-organization process that forms a protective coating atop NCs. NCs are closely shielded from heat, oxygen, and water by the matrix that forms a cohesive barrier layer. Usually, this strategy relies on a unique physical process-such as the swelling-deswelling of a polymer or the self-crystallization of glass in a high-temperature reaction-to achieve microencapsulation. Glass works well for encasing NCs since it is a more stable and tighter material. Microencapsulation within glass can be achieved by creating the right glass composition. NCs self-crystallization combined with a traditional melting-quenching method is also an effective approach. In this process, the raw materials in precise molar proportions were melted in an alumina crucible over time at a steady temperature, then the molten glass is cast

onto a copper block and compressed to form a plate with the appropriate thickness.¹⁰¹ For example, Yuan *et al.* embedded CsPbBr₃ QDs within a low-melting-point TeO₂-based glass matrix. X-ray diffraction (XRD) characterisation confirmed the coexistence of the glass's amorphous structure with the pure cubic phase of CsPbBr₃ in the prepared CsPbBr₃@glass composite.¹⁰² Transmission electron microscopy (TEM) images clearly reveal the uniform distribution of CsPbBr₃ QDs (6–10 nm) within the glass matrix. Concurrently, high-resolution TEM micrographs confirm the single-crystal nature of these NCs, exhibiting a highly compact crystalline structure with clearly discernible lattice fringes.

1.4.3 Enhanced Properties from Core-Shell Structures

Within the core-shell structure, the influence of the shell layer on NCs' surface defect states and electronic structure affects the optical properties of the core. It has been demonstrated that the shell layer can eliminate the detrimental effects of surface defect states—these defect states act both as traps for photo-generated carriers and provide non-radiative recombination sites, thereby diminishing the PL intensity. Core-shell PeNCs primarily exert influence through contact configuration, hybridisation, and interaction-induced band gap states.¹⁰³ For the previously discussed Type-I heterostructures, electrons and holes exist within the core region, while the shell enhances radiative recombination efficiency by passivating surface traps and maintains long-lived excited states to delay phosphorescence decay processes.^{15, 104, 105} The quantum confinement effect of photogenerated carriers induced by the shell layer is equally crucial for enhancing the optical properties of the perovskite core.¹⁵ Enhancement of the PLQY was also observed in other type-I core-shell structures in CsPbBr₃/Cs₄PbBr₆.¹⁰⁶ The quantum efficiency could be improved from 31.41% to 45.87% via silica-coated method and crystal phase transition in low-temperature synthesis. The increase of average lifetime for CsPbBr₃/ZnS core-shell NCs to 102.6 ns, which is about 15 times longer than pure CsPbBr₃ NCs.¹⁰⁷ It can be explained by the formation of pseudo type-II band alignment at the core-shell interface, where the photoexcited electrons are confined inside the core while the holes are delocalized.

Compared with the single system of PeNCs, perovskite core-shell structured NCs can significantly change the carrier dynamics of PeNCs core.¹⁰⁸ This is because carrier dynamics are intrinsically linked to radiative and non-radiative recombination processes, as well as charge extraction mechanisms. In solar cells, short charge separation distances and rapid charge

extraction represent the ideal state. The short separation distance enables photoexcited carriers to be collected rapidly and efficiently at the core-shell interface. Consequently, the core-shell structure influences carrier dynamics by passivating surface defects within the NCs. For type-I core-shell perovskite nanomaterials, where the band gap of colloidal QDs is smaller than that of perovskite nanomaterials, both electrons and holes are confined within the core, increasing the probability of direct radiative recombination. For type-II core-shell PeNCs, the band gap of traditional QDs is larger than that of PeNCs, effectively separating electrons and holes spatially and increasing the probability of radiative recombination. Taking CdS-coated CsPbBr₃ QDs as an example,¹⁰⁹ the spontaneous emission efficiency of the coated CsPbBr₃ NCs is significantly improved compared with that of pure CsPbBr₃ NCs. This is due to the reduced competition between stimulated emission and the suppression of non-radiative biexciton Auger recombination. In addition, researchers have also studied the carrier dynamics in the core-shell structure of carbon-based QDs and perovskites¹¹⁰ and the core-shell structure of black phosphorus and perovskites.¹¹¹

A number of studies focused on assessments of stability and shelf life of core-shell perovskite structures. PeNCs must be environmentally stable and have a long shelf life before being used in industry. Encapsulating PeNCs in an inert protecting shell are commonly used to improve stability in many situations, including polar solvents, high temperatures, and moisture. In conclusion, the construction of core-shell architectures presents a comprehensive and powerful strategy for advancing PeNCs technology. By precisely tailoring the shell material and structure, it is possible to simultaneously enhance optical performance through defect passivation, quantum confinement, and controlled carrier dynamics and achieve the exceptional environmental stability required for commercial applications. This synergistic improvement in both functionality and robustness underscores the great potential of core-shell PeNCs in next-generation optoelectronic devices.

2|Characterisation Techniques

In this chapter, the experimental characterization techniques employed in this study will be described, including XRD, PL spectroscopy, Raman spectroscopy, and Ultraviolet–Visible (UV–Vis) spectroscopy. The stability experiments of the core-shell structure and the theoretical calculations will also be introduced afterward.

2.1 XRD

In the study of all-inorganic perovskite materials, understanding the crystal structure is essential for elucidating their physical and chemical properties as well as their optoelectronic performance. Since the structural characteristics of perovskites—such as phase composition, crystallinity, and lattice parameters—are closely related to their stability and functionality, it is necessary to perform a thorough structural characterization. XRD is a widely used and reliable technique for this purpose, providing detailed information on the phase structure, crystal symmetry, and preferred orientation of the material. Introducing XRD characterization not only confirms the successful synthesis and purity of the all-inorganic perovskite but also enables the analysis of structural evolution under different preparation or treatment conditions, thereby offering crucial insights for subsequent performance optimization.¹¹²

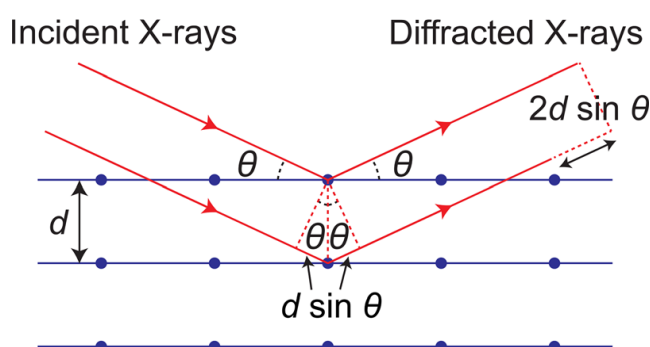


Figure 2. 1 Schematic diagram showing the Bragg diffraction of x rays from atomic planes of the crystalline material with the interplanar distance of d .¹¹³

Bragg's law lays the foundation of XRD, which relates the location of a peak in a diffraction pattern to the distance between planes of atoms in the material. For crystalline material that has an ordered arrangement of atoms in three dimensions, the periodic repetition of these

planes of atoms results in the constructive and destructive interference of X-rays resulting in diffraction features. A diffraction peak corresponding to the constructive interference of X-rays forms when X-rays with a wavelength comparable to atomic spacings are incident on a crystalline material satisfying Bragg's law (**Figure 2.1**).

$$2d \sin \theta = n\lambda \quad (\text{Eq. 2.1})$$

Where d is the distance between atomic planes, θ is the angle of the incident X-rays with respect to the atomic plane (also referred to as the Bragg angle), n is the order of reflection, and λ is the X-ray wavelength. A typical XRD pattern is collected by recording the intensity of diffracted X-rays as a function of 2θ .

XRD patterns are the structural fingerprints of materials. The position and intensity of each diffraction peak in an XRD pattern encodes information about the crystal structure: peak positions reflect interplanar spacings, peak intensities correlate with crystallographic orientation and relative abundance, while peak widths are closely related to grain size and lattice strain. The comprehensive interpretation of this information renders XRD a window through which structure becomes visible. When X-rays interact with the electron cloud in a material and undergo diffraction, any change in the spatial distribution of electron density in the material will alter the diffraction pattern. Therefore, XRD patterns are highly sensitive to the types of atoms (elements) in a sample and their spatial arrangement. The position of the peaks seen for a particular sample reflects the geometry and dimensions of the unit cell, with the relative intensities of the peaks influenced by the position of the atoms/molecules within the unit cell. Therefore, the XRD pattern can be used for identifying the crystal phase of chemically similar materials. Various crystal phases may exist in a perovskite film depending on the film fabrication process. While there is generally a desired photoactive perovskite phase, other non-photoactive non-perovskite phases, precursor phases, and solvent-coordinated intermediate phases can co-exist. These phases exhibit unique diffraction patterns that can be identified using XRD techniques. The reference diffraction patterns used for such phase identification primarily originate from single-crystal SC-XRD analysis. While the PXRD techniques described above are ideal for characterizing polycrystalline thin films, SC-XRD requires a high-quality, isolated single crystal. It works by collecting a three-dimensional diffraction pattern, from which the precise atomic coordinates within the unit cell—including bond lengths, bond angles, and octahedral tilting—can be solved. This provides the definitive crystal structure model that serves as the foundation for interpreting PXRD patterns. For

instance, the precise crystal structures of the cubic, tetragonal, and orthorhombic phases of MAPbI_3 were all determined through SC-XRD. In the early stage of photovoltaic perovskite research, the main perovskite composition of interest was MAPbI_3 . The phase transition behavior of this perovskite composition was of particular interest as it undergoes a cubic-to-tetragonal phase transition at temperatures which can be reached during solar cell device operation.¹¹⁴

2.2 Scanning Electron Microscope

Scanning electron microscopy (SEM) is a microscopic technique that uses the interaction of an electron beam with a sample surface to produce high-resolution images. SEM is characterized by its ability to provide information about the microstructure of a sample's surface, typically with resolution down to the nanometer level. Unlike ordinary optical microscopes, SEM controls magnification by controlling the size of the scanning area. If a higher magnification is required, only a smaller area needs to be scanned. Therefore, the lens in the SEM has nothing to do with magnification. When a high-energy electron beam is focused and scanned across a sample's surface, it generates signals such as secondary electrons, backscattered electrons, and X-rays. These signals are received by detectors and converted into images or other forms of information. An electron beam is generated by an electron gun (such as a thermal emission gun or a field emission gun). The electron beam is then focused onto the sample surface by a lens system and scanned along a specific path. The interaction between the electron beam and the sample generates signals (such as secondary electrons), which are captured by detectors. The electron beam actually acts not only on the surface atoms of the sample, but also on the sample atoms within a certain thick range, so there is an action volume. After processing, these signals are converted into images showing the microscopic structure of the sample's surface.

2.3 PL Spectroscopy

Halide perovskite solar cells have reached power conversion efficiencies exceeding 25%, that is, more than any other thin film technology except for GaAs. In order to better understand the recombination process and quantify losses in solar cells and at different interfaces, PL spectroscopy technology has become one of the key experimental methods. PL is a type of cold luminescence, referring to the process by which a substance re-radiates photons (or electromagnetic waves) after absorbing photons (or electromagnetic waves). From the perspective of quantum mechanics, this process can be described as a process in which a substance absorbs a photon, transitions to an excited state at a higher energy level, then returns

to a lower energy state while emitting a photon. It generally proceeds through three main stages: absorption, energy transfer, and light emission. Both light absorption and emission occur through transitions between energy levels and require passing through an excited state. Energy transfer is due to the movement of the excited state. UV radiation, visible light, and infrared radiation can all cause PL. PL spectroscopy is a widely used non-destructive optical technique to investigate the band structure, defect states, and carrier dynamics of semiconductors. When the sample absorbs high-energy photons (typically from a laser or xenon lamp), electrons are excited from the valence band to the conduction band, creating electron-hole pairs. Some of these carriers relax and recombine radiatively, emitting photons in the process. The steady-state PL spectra technology, for example, has been used to identify the limiting interfaces and/or components of the complete cell.¹¹⁵⁻¹¹⁷ Temperature-dependent PL spectra have been used to identify the distribution of trap states at low temperatures, phase transitions, and different perovskite crystal structures.¹¹⁸ Steady-state PL spectra have been used to study the movement of different ionic species, which may quench or enhance the PL over long timescales (>s). In contrast, TRPL, which is based on the time-correlated single photon counting technique, was used to investigate the quick radiation process (femtosecond-second timescale to seconds) of the emission. Measuring the TRPL kinetics of a material by altering its ambient temperature provides information about the exciton recombination process. A general sketch of a typical setup is shown in **Figure 2.2(a)**.

Usually, various experimental setups can be used to measure PL spectra in thin film semiconductors and also in complete solar cell layer stacks. The major components of a PL spectroscopy system are shown in **Figure 2.2(b)**. Samples being studied are excited by a light source with the right amount of energy and power. Confocal optics may focus the stimulated region onto a micrometer-size spot or make it uniform over a wide area (cm to mm). A sensitive detector then picks up the scattered light after the PL signal is sent into a spectrograph. Before the detected optical signal is shown on a screen, electronic components transform it into an electrical signal. A typical setup for steady-state PL can be almost identical to the setup used in TRPL but often employs a charge-coupled device (CCD) as a detector behind the monochromator, thus enabling to capture of a full spectrum at once. The most common excitation sources used in modern instruments are solid-state pulse laser diodes, which are available at various wavelengths, repetition-rate adjustable and a wide range of powers. Excitation and detection can be performed in a confocal arrangement or with separate beam paths.

Recently, many studies have been devoted to revealing the carrier recombination mechanism behind these properties.¹¹⁹ Such electron–phonon interactions matter, because they set a fundamental intrinsic limit to charge-carrier mobilities in the absence of extrinsic scattering off impurities or interfaces. In addition, electron-phonon coupling has been shown to cause uniform emission line broadening in mixed lead iodide perovskites at room temperature, making them suitable as gain media for short-pulse lasers. Therefore, temperature-dependent PL spectra would be a powerful tool for studying electron-phonon coupling.¹²⁰ Analysis of temperature-dependent emission broadening has long been used to assess the mechanisms of electron–phonon coupling in a wide range of inorganic semiconductors.¹²¹ In parallel, TRPL measurements have been extensively employed to probe carrier dynamics, offering critical insights into recombination pathways, defect-mediated processes, and exciton behavior.

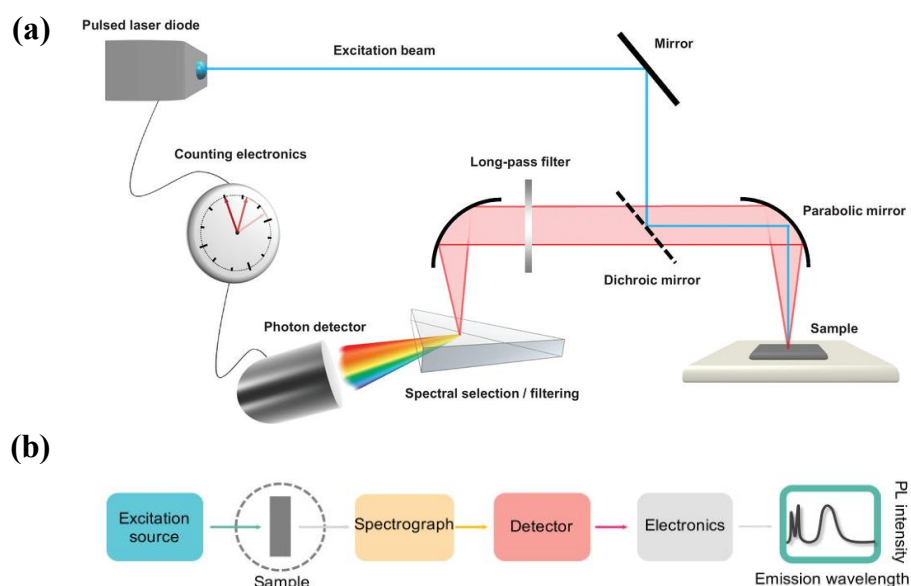


Figure 2.2 (a) Setup, typically used to measure transient PL decays.¹²² (b) Experimental setups of PL spectroscopy systems.¹²³

2.4 UV-Vis Spectroscopy

UV-Vis spectroscopy refers to passing UV, visible, and infrared beams through a single light sheet and then hitting the sample. UV-Vis spectroscopy is collected by comparing the intensity of transmitted light in the sample with that of reference light. The wavelengths of light absorbed by the components depend on the intrinsic properties of the material under study, such as the type of ions or molecules that compose it, as well as the system's unique photoelectron configuration. Therefore, absorption spectroscopy provides broad and in-depth insights into

electron-phonon-ion dynamics, while also serving as a key complement to fluorescence spectroscopy and scattering spectroscopy.¹²⁴

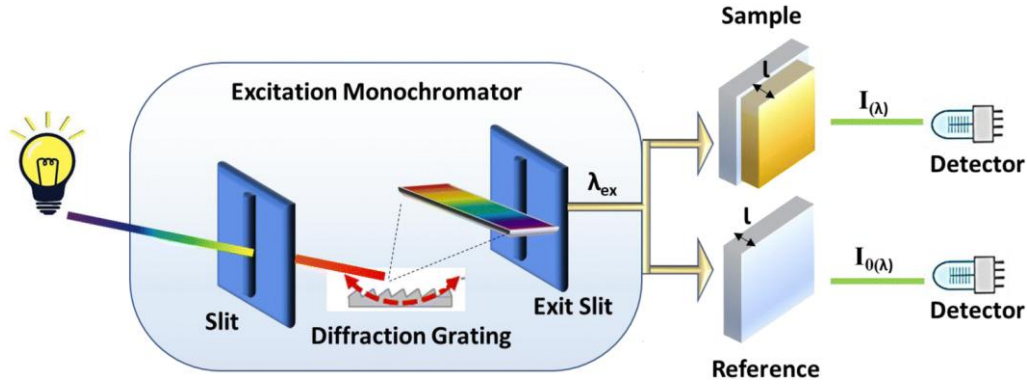


Figure 2.3 Schematic of the measurement of absorption spectra in a spectrophotometer.¹²⁵

Figure 2.3 illustrates the fundamental components of an absorption spectrophotometer, including a light source, a collimator, a monochromator, and a wavelength selector. The light source produces light at the desired wavelength. Then a collimator (lens) transmits a straight beam of this light that passes through the monochromator to select a single wavelength component. A slit is used as a wavelength selector to transmit only a limited range of wavelengths at a time. Once this wavelength light passes through the sample, the photodetector measures the intensity of the transmitted light. The signals collected by the photodetectors are analysed to measure the transmittance and the absorption of the sample.

The absorption coefficient quantifies the distance that light of a specific wavelength can penetrate a sample before being absorbed, indicating the intensity reduction of the transmitted light. A higher absorption coefficient $\alpha_{(\lambda)}$ results in a shorter penetration depth. In crystalline semiconductors, the absorption coefficient is utilized to determine the band gap energy of the material using the Tauc-plot method, expressed through the following equation:¹²⁶

$$(\alpha_{(\lambda)} h\nu)^{1/n} = B(h\nu - E_{gap}) \quad (\text{Eq. 2.2})$$

Where E_{gap} is the semiconductor optical band gap, B is a constant, and $h\nu$ is the incident photon energy; $\alpha_{(\lambda)}$ is the absorption coefficient defined by the Beer-Lambert law. n is a factor, which depends on the electron transition properties of the material. The value of n is $1/2$ and 2 for direct and indirect band gap transitions, respectively. Therefore, E_{gap} of a semiconductor can be calculated by knowing the absorbance and thickness of the absorbing layer.

2.5 Raman Spectroscopy

Raman spectroscopy is one of the key techniques used to study structural dynamics in materials. It can be performed under ambient conditions-room temperature and atmospheric pressure-without requiring elaborate sample preparation, making it highly accessible and non-destructive. Raman scattering involves illuminating a material with a focused monochromatic laser beam. While most photons are elastically scattered (Rayleigh scattering), a small fraction undergoes inelastic scattering, known as Raman scattering, resulting in an energy shift (Stokes or anti-Stokes) corresponding to the vibrational modes of the lattice or molecular bonds.

Each vibrational mode arises from a distinct combination of atomic displacements within the material and is characterized by a unique energy, which appears as a peak in the Raman spectroscopy. These vibrational signatures are sensitive to the material's structural state and can reveal detailed information about phase transitions, lattice strain, polarization, defect states, and dopant incorporation. Variations in peak position, FWHM, and intensity can be systematically analyzed to infer these properties.

Due to these advantages, Raman spectroscopy has become an essential tool in the crystallographic and molecular characterization of a wide range of materials, from semiconductors to polymers, especially for materials with the low-dimensional nanostructures. However, lead halide perovskites pose a particular challenge for Raman analysis due to their intrinsically soft lattice, dynamic disorder, and the presence of both organic and inorganic components. These factors often lead to broad and weak Raman signals that can overlap with PL background or suffer from laser-induced degradation. Nevertheless, with proper experimental conditions, such as low excitation power, temperature control, and polarized Raman configurations, valuable vibrational information can still be extracted to probe structural dynamics, electron-phonon interactions, and phase stability in perovskite systems.

2.6 Molecular Dynamics Performed by Material Studio

DFT calculations have become a powerful theoretical tool for studying the electronic and optical properties of perovskite systems, including the electronic band structures and optical absorption,¹²⁷ the defect properties like formation energies and charge transition levels, the assignments for the emission states, the dimensionality effect on the optical response, the interactions between ligands and NCs surfaces, the doping effect on the PL enhancement/decay and other unique features like molecular behavior. Recent advancements in molecular dynamics have played a pivotal role in this process by enabling the direct and fast prediction of

material properties from vast datasets, significantly reducing the computational cost of DFT calculations, allowing researchers to explore a larger chemical space in less time.¹²⁸

In this paper, the DFT calculations related to Cs_4PbBr_6 structures are completed by the pseudopotential plane waves based CASTEP module encapsulated in Materials Studio software.^{129, 130} Cs_4PbBr_6 structures are obtained from the Materials Project database directly and undergo precise geometric optimization prior to the molecular dynamic calculations.¹³¹ The self-consistent field iterations with a density-mixing electronic minimizer are applied to get suitable electronic distribution. In detail, we use generalized gradient approximation with the Perdew-Burke-Ernzerhof functional to deal with the exchange-correlation terms and apply Broyden-Fletcher-Goldfarb-Shannon algorithm to proceed with the structure relaxation.^{132, 133} To treat the geometry optimization calculations, the norm conserving pseudopotential is selected and the cutoff energy is set as 910 eV¹³⁴. Convergence tolerance parameters are set strictly as energy 5×10^{-6} eV/atom, force 1×10^{-2} eV/Å, stress 2×10^{-2} GPa, and displacement 5×10^{-4} Å. Monkhorst-Pack grid parameters are set as Gamma-only during the task¹³⁵. In addition, to quantify the lattice structure variations of Cs_4PbBr_6 structures at room temperature and high temperature, molecular dynamics simulations based on the constant-pressure, constant-temperature (NPT) ensemble were performed for these structures at 300 K and 500 K, respectively. The total simulation time is 1 ps, with a time step of 1 fs.

3 | Temperature-Dependent Crystal Properties of CsPbBr₃@Cs₄PbBr₆

In this chapter, we have synthesized CsPbBr₃@Cs₄PbBr₆ crystals based on the 3D@0D core-shell structure with excellent green fluorescence. Through temperature-dependent PXRD and UV-vis absorption spectra, it was verified that the mechanism behind this thermochromism in the CsPbBr₃@Cs₄PbBr₆ is the result of a change in the optical band gap, which is determined by the competition between lattice thermal expansion and electron-phonon coupling. The CsPbBr₃@Cs₄PbBr₆ crystal shows reversible thermochromism, making it suitable for designing anti-counterfeiting and temperature indication labels. Crucially, our findings complement previous explanations of the thermochromic mechanism and further raise the urgency of the great potential of dual-phase perovskite thermochromic materials for applications.

3.1 Introduction

In recent years, all-inorganic perovskites showed improved thermal stability due to the intrinsically high thermal decomposition temperature of the inorganic cations.¹³⁶ Furthermore, the low formation energy¹³⁷ and soft crystalline nature¹³⁸ of all-inorganic perovskites provide additional degrees of dynamic structural ‘switch ability’. As a result, Chameleon-inspired stimuli-responsive all-inorganic perovskites can reversibly change their colors or other physical properties when exposed to external stimuli such as light, temperature, pressure, electricity, and chemical environment. This reversible stimulus-response pattern is applicable in a range of technologies, such as smart windows and mirrors,¹³⁹ anti-glare glasses,¹⁴⁰ memory devices,¹⁴¹ data encryption¹⁴² and sensors.¹⁴³ All-inorganic perovskites’ distinct stimulus response allows them to display a variety of crystal colors and emission wavelengths, offering new technical support for sophisticated encryption and decryption techniques and anti-counterfeiting measures. Among the family of all-inorganic perovskites, the 0D perovskite Cs₄PbBr₆ has attracted considerable interest from researchers because of its exceptional PLQY in solid form, distinctive crystal structure, and optoelectronic properties.

Cs_4PbBr_6 is the first 0D all-inorganic metal halide to be discovered when Wells investigated the perovskite in 1891.¹⁴⁴ The 0D trigonal Cs_4PbBr_6 structure features isolated $[\text{PbBr}_6]^{4-}$ octahedra surrounded by eight Cs^+ cations compared with the 3D crystal structure. This unique structure gives Cs_4PbBr_6 different photophysical properties compared to CsPbBr_3 . Due to the bonding and antibonding state splitting, Cs_4PbBr_6 with isolated octahedra demonstrates a much larger band gap, which is inherited from its individual $[\text{PbBr}_6]^{4-}$ units.¹⁷ Therefore, it is not surprising that the early reported pure Cs_4PbBr_6 exhibited no PL properties due to its unsuitable band structure.¹⁴⁵ There are now two primary explanations put out by the growing number of studies in the literature that attempt to resolve the contentious PL origin of Cs_4PbBr_6 crystal: (1) emission caused by CsPbBr_3 impurities or inclusions, and (2) emission caused by defect states. Manna *et al.* compared the PL properties of the pure Cs_4PbBr_6 phase and CsPbBr_3 -doped Cs_4PbBr_6 phase in order to investigate the impurity phase-induced PL mechanism.¹⁷ They also found that a small amount of CsPbBr_3 impurities did not appear in the XRD pattern. In 2020, novel analysis by using high-resolution TEM supported the existence of embedded nanoscale CsPbBr_3 domains within Cs_4PbBr_6 ,¹⁴⁶ which indicates the strong luminescence originates from CsPbBr_3 NCs. Due to this interesting luminescence mechanism, this study is based on the $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals and tries to get a deep understanding of more optical properties.

3.2 Sample Preparation

Synthesis and Preparation: For the growth of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$, 1.2 mmol of cesium bromide (ALFA AESAR, CsBr , 99%) and 0.3 mmol of lead (II) bromide (ALDRICH, PbBr_2 , 99.99%) were simultaneously dissolved into 6 mL methyl sulfoxide (ALDRICH, $\text{C}_2\text{H}_6\text{OS}$, DMSO, 99.99%) solution at 90 °C with magnetic stirring until no precipitation can be observed. To eliminate the influence of impurities, the precursor solution was filtered with hydrophobic paper, and a clear precursor solution was prepared and then 3 mL hydrobromic acid (ALDRICH, HBr , 33wt % in acetic acid) was added into the precursor solution. The final solution was stored in the oven at 90 °C and the temperature was decreased with a certain cooling rate of 2 °C/hour. After the solution was cooled down to room temperature, the $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ single crystals were collected from the cultivation by washing with N,N-Dimethylformamide (MERCK, $\text{C}_3\text{H}_7\text{NO}$, DMF, 99.9%) and Dichloromethane with amylene (ACROS, CH_2Cl_2 , DCM, Dichloromethane, water <50 ppm, extra dry over mol. sieve, 99.8%). The final yellow-green crystals were dried under vacuum for 3 hours at 60 °C. The detailed process for growing the $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ single crystals is shown schematically in **Figure 3.1 (a)**, which illustrates the cell diagram of the 0D Cs_4PbBr_6 in its rhombohedral phase along. In the 0D Cs_4PbBr_6 crystal structure, where

$[\text{PbBr}_6]^{4-}$ octahedra are surrounded and isolated by Cs^+ cations, and in the 3D CsPbBr_3 structure, $[\text{PbBr}_6]^{4-}$ octahedra corner-share each Br^- anion between two octahedra. The absence of PbBr_2 in the Cs_4PbBr_6 structure results in large voids that can accommodate large compressions and distortions.¹⁴⁷ This also provides the possibility that Cs_4PbBr_6 can exhibit different optical properties in a stimulus-responsive environment. The resulting crystals exhibit a pale green color under ambient light, but when exposed to 365 nm lamp irradiation, they emit bright green light as shown in **Figure 3.1 (b)**.

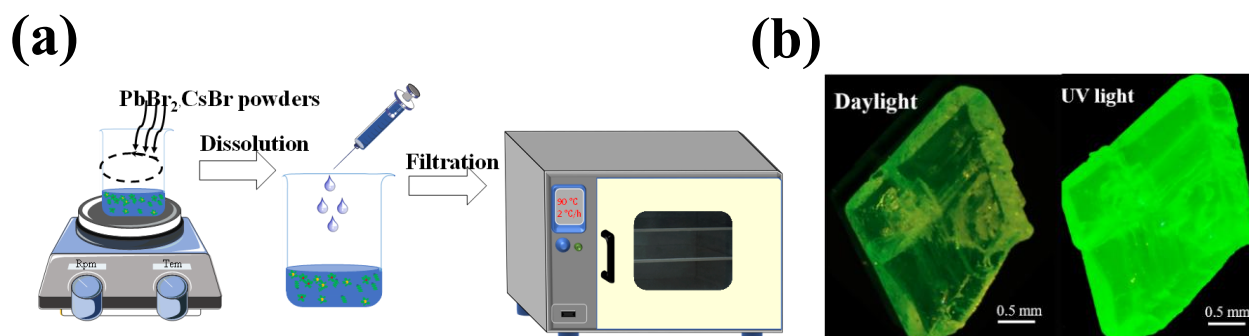


Figure 3. 1 (a) Schematic illustration of the process to grow $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$ crystals. (b) Resulting $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$ crystals are under daylight and 365 nm UV light.

3.3 Sample Characterization

3.3.1 Experimental Setup and Measurement Methods

PLQY: A FLS980 fluorescence spectrometer with Direct & Indirect Excitation mode at 400 nm was used to detect PLQY. The spectrometer's built-in Xenon Lamp served as the excitation source. Powders, bulk materials, and film samples that are more likely to exhibit anisotropic emissions are frequently excited using this method. A calibrated integrating sphere was used to record the PLQY values from powders of $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$.

XRD: SCXRD data were collected on a Rigaku Synergy S Diffractometer with a microsource tube with a Mo anode and a nitrogen cryogenic system (Oxford Cryosystems 800+). The final structure was solved and refined by the crystallographic programs SHELXT, using Olex2 software. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were located and refined geometrically. Temperature-dependent PXRD patterns within 295 and 495 K were obtained using a Bruker D8 Advance diffractometer equipped with a temperature controller and $\text{Cu K}\alpha$ radiation source, and the incident angle was kept at 0.5° during the measurement.

PL and Raman spectra: Temperature-dependent Raman spectra were collected using a 671 nm laser. Steady-state PL and Raman spectra were obtained with a spectrometer (IHR550, Horiba) and a CCD (Synapse, Jobin Yvon). When performing temperature-dependent PL spectroscopy, the laser beam passes through an attenuator and then converges onto the sample through a lens. The sample is then placed in a cryostat, which can slowly raise the temperature of the sample's environment from liquid nitrogen (80 K) to 300 K. Upon exposure to the laser, the sample emits fluorescence, and the PL spectrum data at the corresponding temperature is collected using a fluorescence spectrometer. To eliminate interference from oxygen and water vapor in the air during the experiment, the sample chamber in the cryostat is evacuated before cooling. Furthermore, because instrument vibration significantly affects the measured PL intensity, all experimental instruments must be placed stably before spectral measurements to prevent vibration from altering the spectral results. In general, the only variable during the experiment is temperature.

3.3.2 Characterization Results

Physical characterization would give basic knowledge of the crystal. SEM images of $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$ single crystals exhibit irregular morphology and small microcrystals (MCs) on the surface at submicron scale size as shown in **Figure 3.2**. The fundamental elemental molar ratio of Cs:Pb:Br, as determined by energy-dispersive X-ray spectroscopy (EDS), is 3.5:1.0:5.4, as seen in **Figure 3.3 (a)**. This value does not strictly correspond to the elemental distribution ratio of the Cs_4PbBr_6 molecular formula. This is because millimetre-scale Cs_4PbBr_6 crystals do not exclusively contain the Cs_4PbBr_6 crystal structure; they also incorporate CsPbBr_3 . The absorption and PL spectra show in **Figure 3.3 (b)** that the assumption that a type-I junction forms and optical excitations diffuse from the large-gap Cs_4PbBr_6 matrix to the small-gap CsPbBr_3 NCs is confirmed by the PL peak energy of $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$ being approximately 2.34 eV with FWHM of 116.0 meV. The position of the absorption peak typically makes it easy to differentiate between CsPbBr_3 and Cs_4PbBr_6 . Strong absorption peaks at roughly 310 nm (~ 4.0 eV) and another absorption edge at roughly 520 nm (~ 2.4 eV) are visible in the absorption spectra, and they are ascribed to the absorption of Cs_4PbBr_6 and CsPbBr_3 , respectively.^{148, 149} These results are consistent with the aforementioned Cs_4PbBr_6 microcrystals, further demonstrating that the luminescence of Cs_4PbBr_6 originates from CsPbBr_3 . The crystal field splitting caused by the $\text{Pb}^{2+}(\text{Br}^-)_6$ clusters' violation of the O_h symmetry can account for the absorption's split at 300 nm into two peaks at about 307 and 325

nm. The ICSD 25124 database and the XRD pattern displayed in **Figure 3.3 (c)** match well, indicating that most of the as-prepared crystals are 0D Cs_4PbBr_6 . Within the Cs_4PbBr_6 matrix, no clear diffraction peaks corresponding to CsPbBr_3 are seen. According to earlier observations, trace amounts of 3D perovskite phases may occur in small crystallites or in low concentrations; therefore, their presence cannot be totally ruled out.¹⁵⁰

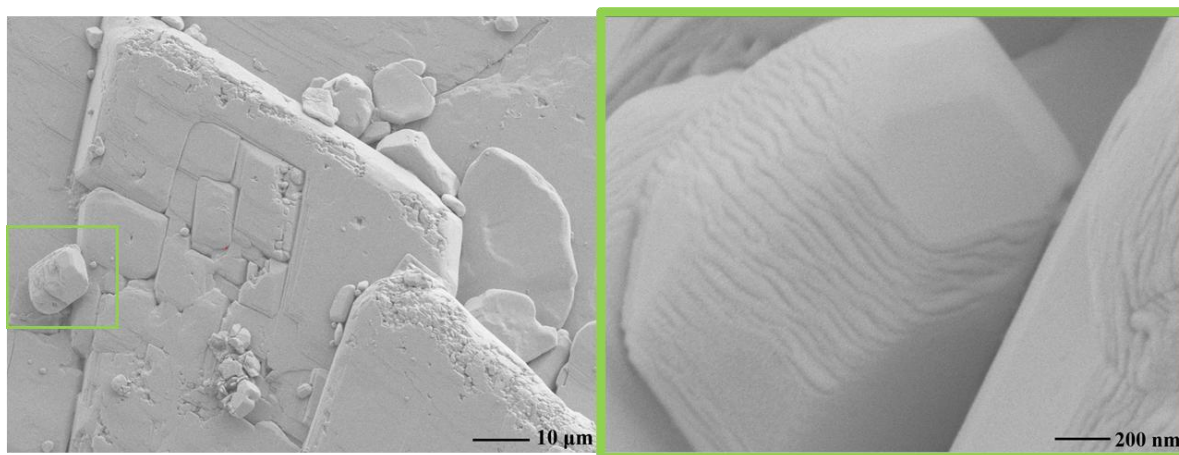


Figure 3. 2 SEM image on 10 μm and 200 nm scale.

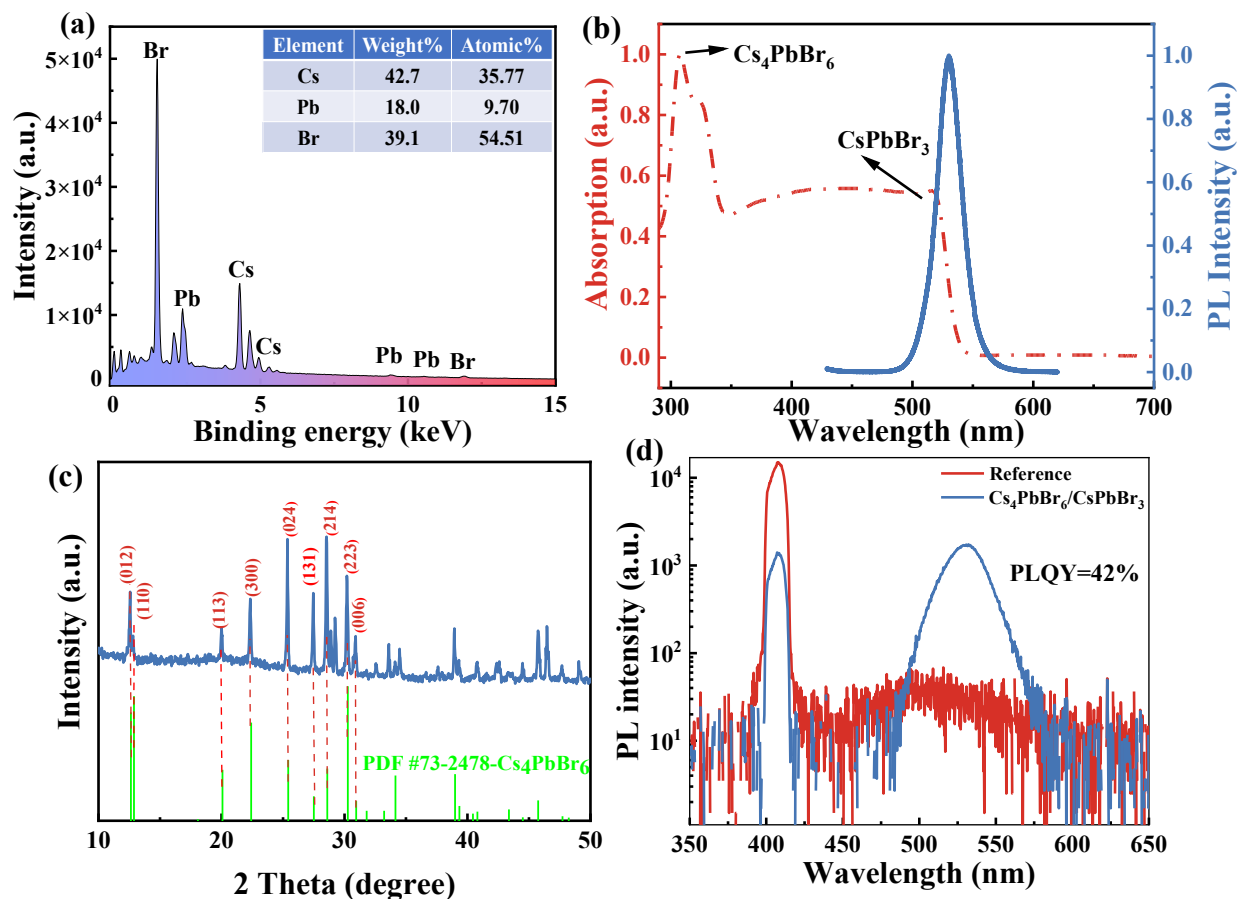


Figure 3.3 (a) EDS spectrum and extracted composition. (b) The normalized absorption and PL spectra of $\text{CsPbBr}_3@/\text{Cs}_4\text{PbBr}_6$ crystals. (c) PXRD profile of $\text{CsPbBr}_3@/\text{Cs}_4\text{PbBr}_6$ crystals. (d) The measured PLQY of $\text{CsPbBr}_3@/\text{Cs}_4\text{PbBr}_6$ crystals.

The $\text{CsPbBr}_3@/\text{Cs}_4\text{PbBr}_6$ exhibit high PLQY in the crystal form (PLQY: 42%) as shown in **Figure 3.3 (d)**, close to the 45 % reported in the previous literature.¹⁵¹ Compared to other solid forms of lower-dimensional metal halide perovskite derivatives and PeNCs, the PLQY of Cs_4PbBr_6 is significantly higher. This represents a relatively high luminescence efficiency among bulk materials, thereby holding certain research significance. For example, the PLQY of 2D lead bromide-based perovskite solids was reported to be around 9%.¹⁵²

3.4 In Situ Spectral Analysis of $\text{CsPbBr}_3@/\text{Cs}_4\text{PbBr}_6$ Thermochromic Phenomenon

We investigate the changes of the optical properties of $\text{CsPbBr}_3@/\text{Cs}_4\text{PbBr}_6$ crystals from room temperature (RT) to 495 K and show the optical images at different temperatures in **Figure 3.4**. Under high temperatures, it is clearly seen that the thermochromic phenomenon in the samples:

the crystals' color shifts from yellowish green to orange as the temperature rises from RT to 495 K. After cooling, the crystals regain their original color, demonstrating the complete reversibility of the $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$ crystals' thermochromic activity.

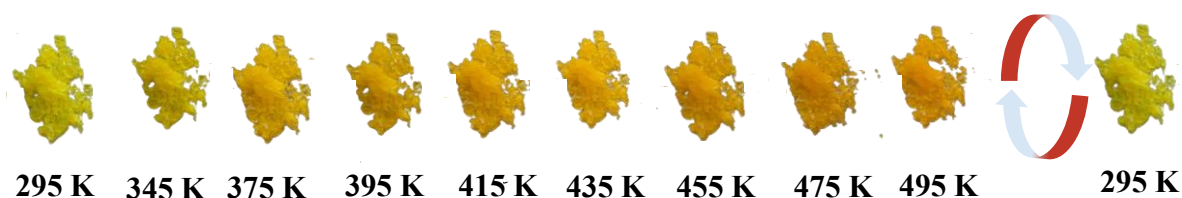


Figure 3. 4 Optical images of $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$ crystals under different temperatures.

To investigate the thermochromic behavior of $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$ crystals, temperature-dependent PL, UV-vis absorption, and Raman spectra were employed. Absorption spectra complement this by revealing temperature-dependent variations in the optical band gap and electronic structure. Raman spectra offer structural information at the molecular level, allowing the identification of temperature-induced lattice dynamics and vibrational mode shifts. The combination of these techniques allows for a comprehensive understanding of the interplay between the optical and structural properties of $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$ crystals during thermal modulation. Meanwhile, Temperature-dependent PL spectra enable direct observation of changes in emission intensity and peak position as a function of temperature, providing insights into phase transitions and excitonic behavior.

3.4.1 Temperature-Dependent Absorption Spectra

To determine the temperature dependence of the optical properties of $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$ crystals, the optical band gap was obtained by fitting from the Tauc plots that were extracted from the temperature-dependent UV-Vis absorption spectra. The plots at 295 and 495 K are displayed in **Figure 3.5**, respectively. In the investigated range, the band gap of CsPbBr_3 NCs very slightly varies with temperature (it drops from 2.24 eV to 2.22 eV as the temperature rises from 295 to 495 K). This is due to the fact that Cs_4PbBr_6 can improve thermal stability through passivating the grain boundaries and generating a host-guest system with CsPbBr_3 crystallites. On the other hand, as the temperature rises from 295 K to 495 K, the band gap of Cs_4PbBr_6 progressively shrinks from 3.63 to 3.53 eV. A negative thermo-optic coefficient results from this band gap lowering, which is the opposite of what is seen in traditional inorganic semiconductors. The interaction between electron-phonon interactions and lattice thermal expansion is responsible for the lowering of the band gap.¹⁵³ Notably, as the temperature rises, so does the divergence trend of the two absorption peaks that belong to Cs_4PbBr_6 . While the

overall broadband absorption stays constant, the absorption peak experiences a striking red shift from its initial value of 325 nm to its final value of 340 nm when the temperature rises to 495 K. The creation of these two absorption peaks is probably related to the distortion of $[\text{PbBr}_6]^{4-}$ octahedra, since the nature of the octahedra has a major effect on the absorption profile of perovskites. When $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals are heated, the $[\text{PbBr}_6]^{4-}$ octahedra tilt and spin considerably, exhibiting an incoherent and disorderly deviation from their initial orientation.

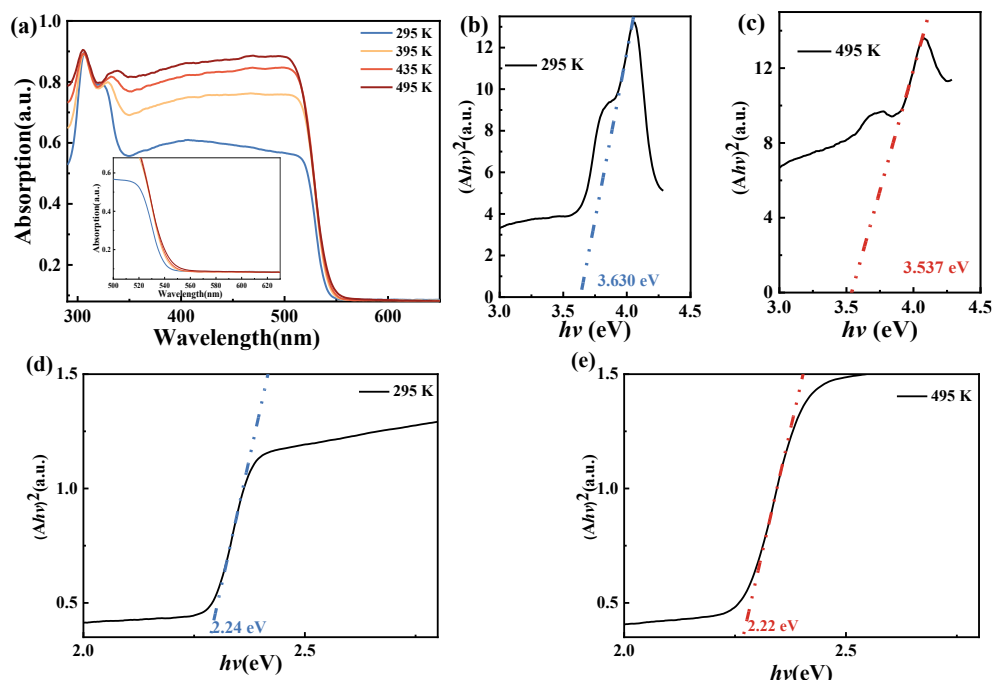


Figure 3. 5 (a) UV-vis absorption spectra at different temperatures. Tauc plot of $(\alpha h\nu)^2$ versus $h\nu$ for (b, c) Cs_4PbBr_6 and (d, e) CsPbBr_3 at 295 K and 495 K.

3.4.2 Temperature-Dependent Raman Spectra

According to the Lyddane-Sachs-Teller relation,^{154, 155} three doubly degenerate transverse optical (TO) phonon modes, designated as $(\text{TO}_i, i=1-3)$, are present in the highly symmetric perovskite-type structure. The $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals' Raman spectra were recorded under excitation with a 671 nm laser in order to uncover details including structural characteristics and the function of atomic interactions, as shown in **Figure 3.6 (a)**. Three optical phonon modes (TO_1 , TO_2 , TO_3) of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals are observed at around 77, 88 and 116 cm^{-1} , respectively. The TO_2 mode is assigned to the vibrational mode of the $[\text{PbBr}_6]^{4-}$ octahedron, while both TO_1 and TO_3 modes have important implications for the motion of Cs^+ cations. To gain insight into the overall thermochromic process of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$, reversible temperature-dependent Raman measurements were performed in a temperature range from 295 to 495 K, as shown in **Figure 3.6 (b)**. It is evident that the TO_1

and TO₃ signals gradually disappear with the increase of temperature from 295 K to 495 K, and the TO₂ signal shows a comparable but less pronounced reduction in Raman peak intensity.

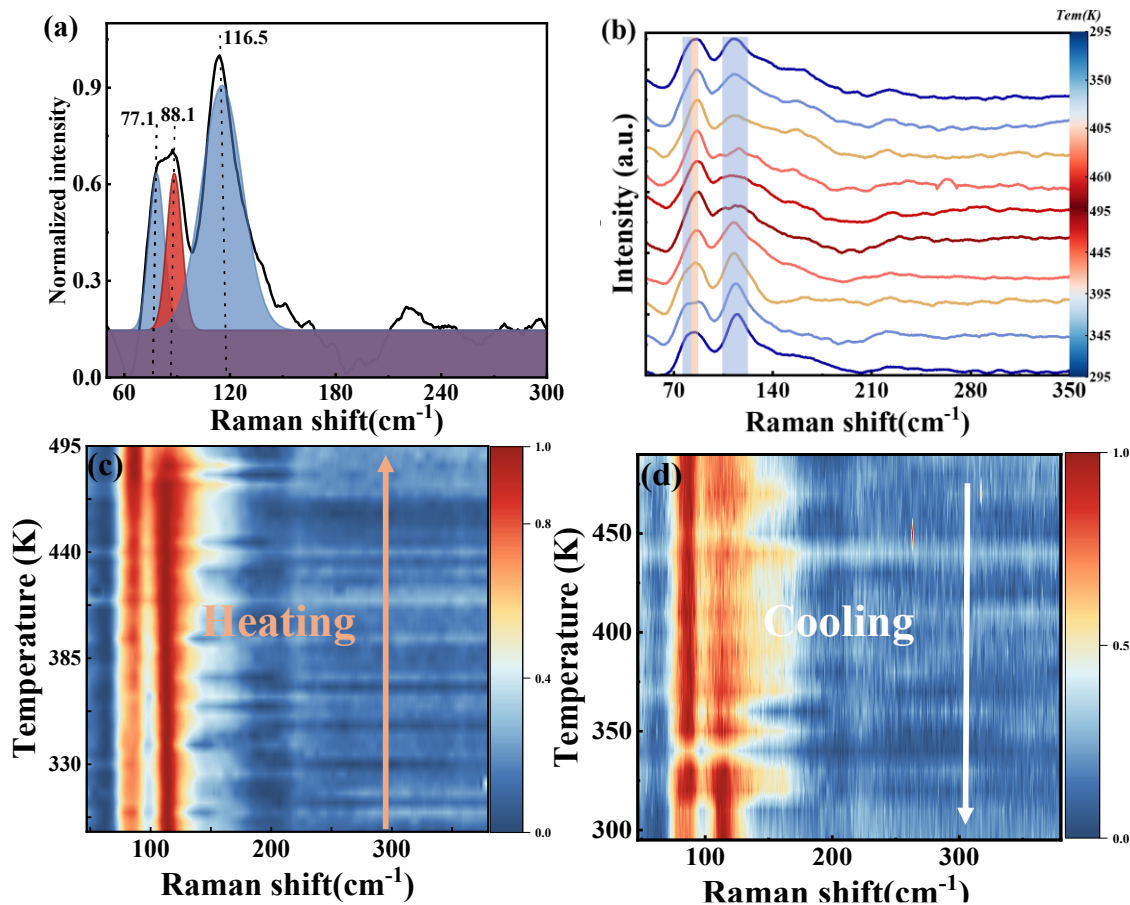


Figure 3. 6 (a) Raman spectra of the CsPbBr₃@Cs₄PbBr₆ crystals under 671 nm excitation at RT. (b) Temperature-dependent Raman spectra (295 K-495 K). 2D color maps of the normalized Raman intensity spectra (c) heating process, (d) cooling process.

These results imply that the distortion of the Cs⁺ cations during the heating and cooling process is at least as significant as the function of [PbBr₆]⁴⁻ octahedron. It shows that lead moves more rigidly than cesium, most likely because Pb-X bonds have a higher covalency degree than Cs-X bonds.¹⁵⁶ Furthermore, it is noteworthy that as the temperature drops down to RT, the TO₁, TO₂, and TO₃ signals progressively return to their initial Raman intensities, indicating the high reversibility of the thermochromic process in CsPbBr₃@Cs₄PbBr₆ crystals. For the second-order phonon mode of the octahedron, no CsPbBr₃ signals are observed during the whole cooling and heating operation at roughly 300 cm⁻¹. This suggests that as the temperature varies, Cs₄PbBr₆ does not experience a large-scale phase transition to CsPbBr₃. The corresponding 2D color maps are shown in **Figure 3.6 (c) and (d)**. In accordance with the above discussion, the thermochromic process in CsPbBr₃@Cs₄PbBr₆ crystals is related to the motion of Cs⁺ cation and

the distortion of the $[\text{PbBr}_6]^{4-}$ octahedron induced by thermal energy, rather than phase transition.

3.4.3 Temperature-Dependent PL Spectra

To further corroborate the Raman results and explore the role of electron–phonon coupling in thermochromism, the temperature-dependent PL properties were investigated. Few studies have taken into account the impact of electron-phonon coupling, while many of the processes described in the literature to explain thermochromism in halide perovskites exclusively use phase transition or lattice expansion for modulation.¹⁵⁷ To conduct analysis of electron-phonon coupling during the thermochromic process, temperature-dependent PL properties of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ are tested with temperature range of 80 to 300 K. The corresponding 2D color map in **Figure 3.7 (a)** does not exhibit abrupt shifts in PL peak energies at various temperatures that associated with phase transition commonly found in MAPbBr_3 and FAPbI_3 .¹⁵⁸ In $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$, it is evident that the PL intensity decreases. Generally speaking, as temperature increases, electron-phonon interactions intensify, thereby enhancing the non-radiative recombination probability during electron transitions and consequently diminishing the photoluminescence intensity. The PL peak continuously moves towards higher energy as the temperature rises, in addition to the well-known temperature trends. This general trend is in contrast to that of typical semiconductors, for which the band gap decreases with temperature as a result of lattice dilation.¹⁵⁹ The corresponding temperature-dependent integrated PL intensity is shown in **Figure 3.7 (a)**, which can be fitted by the Arrhenius equation with exciton binding energy E_b :¹⁶⁰

$$I(T) = I_0/[1 + A\exp(-E_b/K_B T)] \quad (\text{Eq. 3.1})$$

here, $I(T)$ and I_0 are the PL intensities at temperature T and 0 K, respectively, A is the fitting parameter, E_b is the exciton binding energy, and K_B is the Boltzmann constant. The blue solid curve represents the exciton binding energy of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals, which is 176.89 meV based on the fitting results in **Figure 3.7 (b)**. It is much greater than that of the conventional 3D CsPbBr_3 perovskite (~ 40 meV). This is because, although both CsPbBr_3 NCs are luminescent, the CsPbBr_3 in $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals is passivated by Cs_4PbBr_6 . During heating, the shedding of ligands and quenching due to agglomeration are suppressed, thereby relatively enhancing the exciton binding energy. This also demonstrates that DP-CPB exhibits relatively superior thermal stability. These firmly bound excitons are confined to a single unit cell and are unlikely to disperse throughout the crystal lattice.¹⁶¹ As mentioned above,

millimetre-scale Cs_4PbBr_6 crystals contain two crystalline structures: Cs_4PbBr_6 and CsPbBr_3 . When the Cs_4PbBr_6 content is high, the CsPbBr_3 domains become significantly smaller. Due to spatial confinement, the excited charge carriers experience stronger Coulombic interactions, leading to a substantial increase in the exciton binding energy. This provides a fundamental explanation for the elevated PLQY observed in millimetre-scale Cs_4PbBr_6 crystals. This phenomenon is similarly present in Cs_4PbBr_6 thin-film materials.

Temperature not only affects the PL intensity of fluorescent materials but also exerts a significant influence on the FWHM. The temperature response of PL linewidth is also commonly employed to investigate phonon scattering within semiconductor materials. The analysis of temperature-dependent emission broadening has long been used to assess the mechanisms of electron-phonon coupling in a wide range of perovskites.¹⁶² The PL spectral data from the experiment can be fitted using a Gaussian function to yield corresponding FWHM values. As temperature increases, phonon broadening within the material manifests as a corresponding widening of the FWHM in the PL spectrum. This phonon broadening primarily originates from acoustic and optical phonons. Based on the results of temperature-dependent PL, the relationship between the FWHM of the emission peak and temperature is obtained, as shown in **Figure 3.7 (c)**. Previous research indicates that the expansion of the linewidth with temperature is caused by electron-phonon interactions, primarily Fröhlich coupling with longitudinal optical phonon scattering, with acoustic phonon or impurity scattering playing a less significant role.¹⁶³ Therefore, in the following discussion of the temperature dependence of the FWHM, Fröhlich coupling with longitudinal optical phonon scattering is primarily taken into consideration, with scattering off acoustic phonons being unimportant. The temperature dependence line widths $[\Gamma(T)]$ are fitted by the following equation:¹⁶⁴

$$\Gamma(T) = \Gamma_0 + \sigma T + \Gamma_{LO} \left[\exp\left(\frac{E_{LO}}{k_B T}\right) - 1 \right]^{-1} \quad (\text{Eq. 3.2})$$

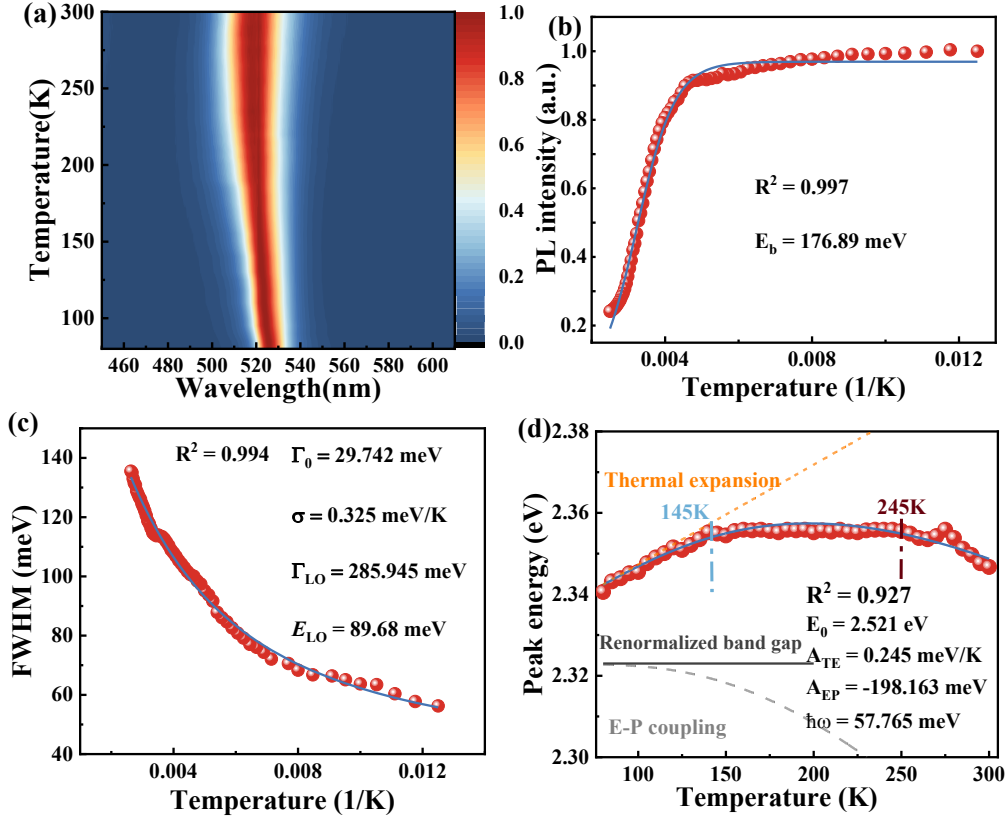


Figure 3. 7 (a) Temperature-dependent 2D color map of the normalized PL spectra. (b) The normalized PL intensity as a function of temperature. (c) Relationship between the FWHM and temperature, along with its fitting curve. (d) PL peak energy with various temperatures of CsPbBr₃@Cs₄PbBr₆ crystals. The orange and gray dashed lines respectively represent the contribution curves of lattice thermal expansion and electron-phonon coupling with temperature.

where the first term (Γ_0) is the temperature-independent inhomogeneous broadening, which depends on several factors such as size, shape, and compositional inhomogeneities in the crystals. σT is the homogeneous broadening term which is due to acoustic phonon scattering through the deformation potential with a charge carrier-acoustic phonon coupling strength σ . The exciton-optical phonon parameter Γ_{LO} quantifies the interaction between excitons and optical phonons, and E_{LO} is the longitudinal optical phonon energy. With the FWHM at various temperatures being fitted by this model, the fitting results of $\Gamma_0 = 29.7$ meV, $\sigma = 0.325$ meV/K, $\Gamma_{LO} = 285.9$ meV and an electron-phonon coupling strength of $E_{LO} = 89.6$ meV as temperature increases from 80 to 300 K. The results imply that the exciton-optical phonon Γ_{LO} is the dominant factor to broaden the FWHM, the E_{LO} is much higher than that of pure CsPbBr₃ NCs¹⁶⁵. This further supports the theory on how electron-phonon coupling affects CsPbBr₃@Cs₄PbBr₆ crystals thermochromism, and a higher E_{LO} value suggests that fewer phonons are generated, which would act as scattering sites for nonradiative decay of excitons.¹⁶³ This further explains why Cs₄PbBr₆ exhibits significantly superior luminescence

properties compared to CsPbBr₃, while also demonstrating that the passivation effect of Cs₄PbBr₆ on CsPbBr₃ positively influences the luminescence of the latter compound.

To further understand the PL behavior in CsPbBr₃@Cs₄PbBr₆ crystals, the temperature-dependent optical band gap change of the material was fitted with the following model:¹⁶⁶

$$E_g = E_0 + A_{TE}T + A_{EP} \left[\frac{2}{\exp(\hbar\omega/K_B T) - 1} + 1 \right] \quad (\text{Eq. 3.3})$$

where E_0 is the unrenormalized band gap, A_{TE} and A_{EP} are the weight of the lattice thermal expansion (TE) and electron-phonon (EP) interaction, respectively, and $\hbar\omega$ is the average optical energy. Due to the quantum factor in the phonon distribution function, there is an energy correction of the band gap even at 0 K, i.e. $E_g(T = 0) = E_0 + A_{EP}$. The trends of these two effects with temperature fluctuation were assessed using A_{TE} and A_{EP} in order to demonstrate the relevance of the TE and EP interaction. The dominance of TE, represented by the orange dotted curve, at a relatively low temperature can be used to explain the linear growth of the PL peak, whilst the EP interaction is inconsequential because of the sparsely populated optical phonon modes. In contrast to typical semiconductors, the PL peaks exhibit a linear blue-shift with increasing temperatures below 145 K. Similarly, CsPbBr₃ nanowires¹⁶⁷ show a blue shift. It clearly shows that the linear-increased PL peak can be derived from the domination of TE below 145 K. At low temperatures, excitons are known to occupy lower discrete energy levels below the conduction band. Thermal activation causes electrons to fill up to higher energy states as the temperature rises, which causes the emission band to shift blue.¹⁶⁸ The PL peaks exhibit about consistent values for 145K–245K because TE and EP play roles that are evenly matched. But, as the grey dashed dotted line illustrates, optical phonon modes are heavily populated at temperatures above 245 K because the optical phonons have more energy than the acoustic phonons, which results in an increasingly negative contribution in **Figure 3.7 (d)**. Fitting the temperature-dependent PL peak with Eq. (3.2) leads to the solid curve in **Figure 3.7 (d)**, and the parameters are obtained from the fitting, i.e. $E_g(T = 0) = 2.521$ eV, $A_{TE} = 0.245$ meV/K, $A_{EP} = -198.163$ meV, $\hbar\omega = 57.765$ meV, it demonstrates that the shift in the optical band gap of CsPbBr₃@Cs₄PbBr₆ is primarily influenced by the EP interaction. The fitted average phonon energy $\hbar\omega$ value is similar to that of CsPbBr₃, a similarity also reported in the literature. The specific reasons for this require further investigation.¹⁶⁹ The electron-phonon interactions intensify at temperatures above 300 K, leading to non-radiative recombination and a shorter PL lifespan for carrier decay in CsPbBr₃@Cs₄PbBr₆, according to temperature-dependent time-resolved PL decay,¹⁷⁰ commonly known as thermal quenching. This explains the physical

process behind the extraordinary thermochromism of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$, which is different from phase transition induced thermochromism.

3.5 The $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ Crystals Properties

When excited, the inorganic lattice structures are readily distorted because of the high sensitivity of Cs_4PbBr_6 formations. The chemical valence of counter ions and the volume of anions. While variations in bond angle can also affect the molecule's structure and characteristics, variations in bond length can cause molecular structural deformation.¹⁷¹ Thus, it can be inferred that the molecular structural changes may be attributed to variations in bond length and bond angle. Furthermore, these changes in structures can significantly affect the optical characteristics of materials, resulting in the enhancement of PLQYs. Hence, controlling the molecular structures is very important for the adjustment of material properties. Therefore, we used SCXRD and temperature-dependent PXRD to study the changes in crystal parameters of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ under the influence of heat, which is of great significance for exploring the mechanism of thermochromic phenomena and fills the gap in the thermochromic phenomena caused by simple bond lengths and bond angles.

3.5.1 Temperature-Dependent *in-Situ* XRD

To gain further insight into the crystalline nature of the $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals, we investigated the SCXRD of their structure at RT. Based on the SCXRD results (**Table 3.1**), the cell parameters and volumes of Cs_4PbBr_6 crystals at room temperature were extracted. SCXRD data confirmed that Cs_4PbBr_6 crystallizes in the trigonal space group with $R-3c$ symmetry. The unit cell dimensions are $a = b = 13.72 \text{ \AA}$, and $c = 17.30 \text{ \AA}$. We then analyzed the change in bond length as a function of temperature to gain a better understanding of the importance of each component of the crystal structure.

Table 3. 1 Crystallographic data and refinement parameters for Cs_4PbBr_6 SCs at 297 K.

Compound	Cs_4PbBr_6
Temperature (K)	297.4(4)
Wavelength	0.71073
Formula	Cs_4PbBr_6
Formula Weight	1218.29
Space Group	$R-3c$
Crystal System	trigonal
a ($\text{\AA}$)	13.72

b (Å)	13.72
c (Å)	17.30
α (°)	90
β (°)	90
γ (°)	120
V (Å³)	2825.87(9)
Z	6
ρ (g·cm⁻¹)	4.295
F (000)	3072
θ range for data collection (°)	3.517-30.315
Index ranges	$-19 \leq h \leq 18, -18 \leq k \leq 19, -24 \leq l \leq 22$
Rint (%)	5.77
Goodness of fit on F2	1.251
R₁, WR₂ (%)	1.96, 4.28

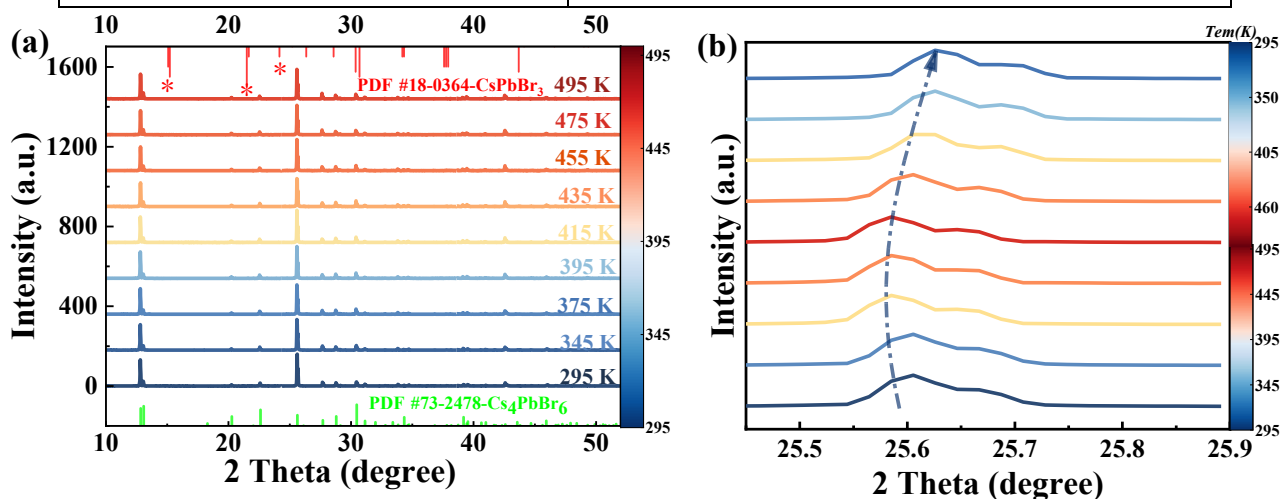


Figure 3. 8 (a) Temperature-dependent (295 K-495 K) XRD spectra of the CsPbBr₃@Cs₄PbBr₆ powder. (b) Magnified view of the (024) diffraction peak in the temperature-dependent XRD spectra.

Based on the similar composition of 0D Cs₄PbBr₆ and 3D CsPbBr₃, 0D Cs₄PbBr₆ can be transformed into 3D CsPbBr₃ under the influence of external factors, such as temperature, water¹⁷² and ligands.¹⁷³ Vacuum annealing at 150 °C causes the pure transparent Cs₄PbBr₆ crystal to exhibit pale yellow and intense green luminescence, which is attributed to the formation of the CsPbBr₃ phase in the Cs₄PbBr₆ crystal; such conversion is irreversible.¹⁷⁴ Therefore, temperature-dependent PXRD experiments were carried out in powder state to examine the change of crystal structure with temperature variation in order to obtain additional insight into the nature of thermochromic behavior in CsPbBr₃@Cs₄PbBr₆ crystals, as shown in **Figure 3.8 (a)**. The absence of phase transitions during the whole thermochromic

process is suggested by the PXRD spectra of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals, which do not exhibit any drop or rise in diffraction peaks associated with the CsPbBr_3 phase, in contrast to the phase transition induced thermochromism.

Interestingly, zooming in on the (024) diffraction peaks shown in **Figure 3.8 (b)**, due to the lattice's thermal expansion with rising temperatures and its gradual recovery upon cooling to room temperature, it is evident that the (024) diffraction peaks gradually shift to lower angles. An increase in the distance between the electron clouds of two interacting atoms is associated with the lattice expansion, which suggests a rise in the lattice constant value. Valence electrons and their parent atoms have less binding force as a result. The valence electrons must be moved into the conduction band with a minimum of energy equal to the band gap since they are bound. A decrease in the binding energy indicates that less energy is required to transport them into the conduction band, resulting in a smaller band gap. On the other hand, the cooling of the $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals leads to lattice compression, which pulls the electron cloud closer and increases the attraction between the atoms.¹⁷⁵ Thus, we initially attribute the color shift of the crystals to thermally induced lattice expansion. We also used Material Studio to simulate the changes in the unit cell during temperature changes, which also verified the XRD results.

3.5.2 Molecular Dynamics Simulation

The Pb-Br, Cs-Br, Cs-Pb bond length changes at 300 and 500 K have been further analyzed as shown in **Figure 3.9 (a)**, by running a series of Material Studio simulations using the experimentally determined lattice parameters. Such lattice expansion also triggers the thermochromic process as shown in **Figure 3.9 (b)**. It is obvious that when the temperature rises, the lattice volume increases as a result, a phenomenon known as thermal expansion. It is noted that the Pb-Br₄, Cs1-Br₃, Cs3-Pb bond lengths are significantly different at 300 K than at 500 K as shown in **Figure 3.9 (c)**. The bond lengths of Pb-Br₄, Cs1-Br₃, and Cs3-Pb all marginally lengthen as the temperature rises. However, compared to the slight shift in Pb-Br₄, the variations in the bond lengths of Cs1-Br₃ and Cs3-Pb are more noticeable and significant. A number of factors can be used to explain this discrepancy in the bond-lengths' temperature progression. The Pb-Br link is fundamentally covalent and far stronger than the Cs1-Br₃ and Cs3-Pb bonds, which are ionic in nature. Therefore, elongating the weaker Cs1-Br₃ and Cs3-Pb bonds is the main way that lattice expansion takes place. In addition, the bulk modulus of $B_0 = 12.1$ GPa for Cs_4PbBr_6 was obtained by fitting to the third-order Birch-Murnaghan equation-of-state,¹⁷⁶ which suggests 0D Cs_4PbBr_6 is much softer than 3D CsPbBr_3 ($B_0 = 21.5$ GPa).¹⁷⁷ By calculating the thermal variation of the mean-square displacement factor with temperature, it

can be concluded that the lower value of the Debye temperature for Cs⁺ cations.¹⁷⁸ Conversely, Pb-Br bonds have a greater electron density (29.6×10^{-3}) than Cs-Br bonds ($6.4\text{--}10.8 \times 10^{-3}$). This finding supports the earlier hypothesis that Pb is more constrained at its position, whereas the Cs atom has greater mobility.

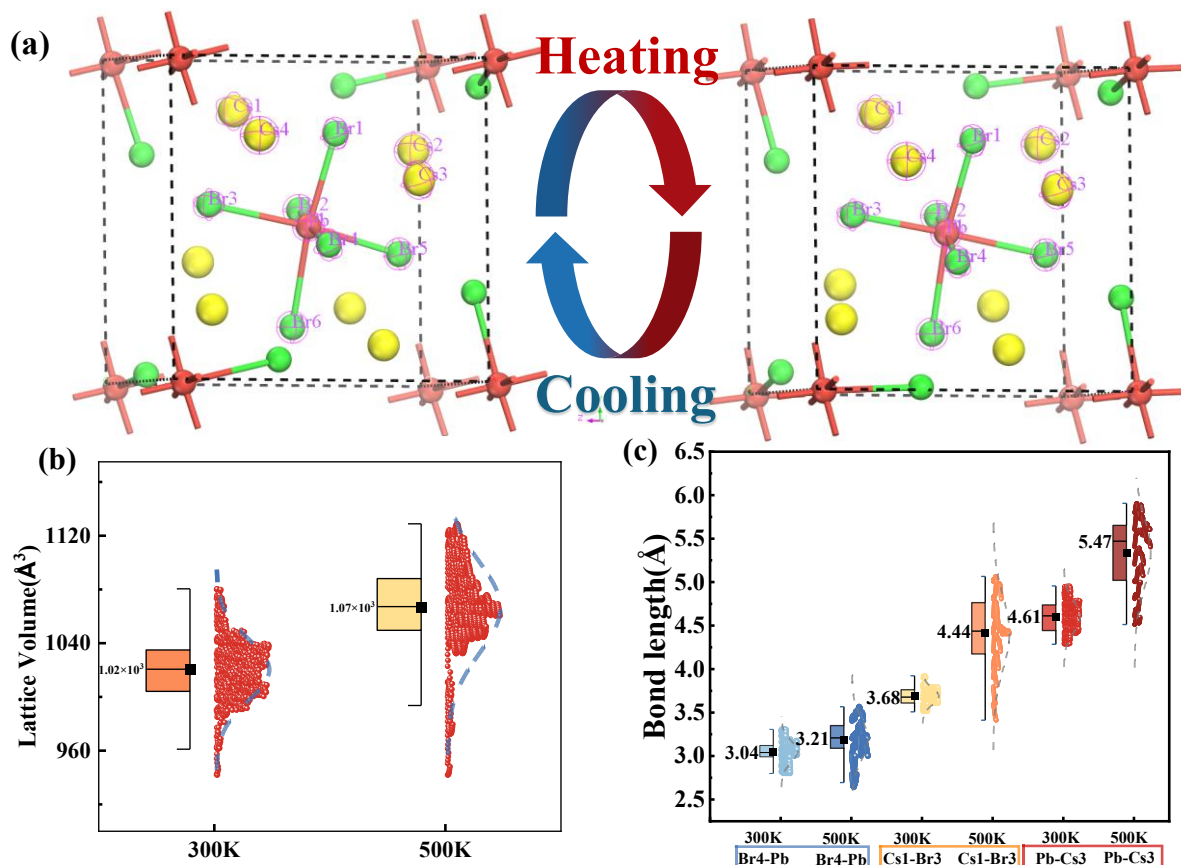


Figure 3. 9 (a) Schematic representation of a supercell containing three pristine cells of CsPbBr₃@Cs₄PbBr₆ crystals at 300K, 500 K. Relationship between lattice parameters and temperature (b) Lattice volume. (c) Bond length of Pb-Br₄, Pb-Cs₃, Cs₁-Br₃.

3.6 Stability Measurements

Perovskite materials are unstable due to their decomposition in water, oxygen, high temperature, and ultraviolet light, a major issue that has hindered their commercial application. The thermal stability of the PL of perovskite materials is a pressing issue, especially in the lighting field, where long-term operation of lighting devices inevitably leads to heat generation. When solving the thermal stability problem of perovskite materials, most research groups generally passivate the perovskite materials by changing the ligands or using materials with good thermal stability, such as SiO₂, AlO_x, etc., or directly use polymers to coat the perovskite materials to improve the stability of the perovskite materials. During the preparation, only the proportions of the raw materials have been altered, thereby regulating the perovskite materials

with different structures, namely Cs_4PbBr_6 and CsPbBr_3 . To further confirm that the thermochromism is not due to the phase change as shown in **Figure 3.10 (a)**, the differential scanning calorimetry (DSC) did not exhibit any endothermic or exothermic peaks associated with phase transitions within 295 to 495 K, suggesting that no sudden change of the entropy associated with the orientation disorder of the constituent atoms took place. The outcomes of these measurements can demonstrate that the crystals experienced lattice expansion without undergoing any phase change. The environmental and thermal stability of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals has been investigated using time-dependent PXRD and thermogravimetric (TGA) measurements. The crystals show no weight loss up to 495 K, indicating excellent thermal stability compared to perovskite materials commonly employed in photovoltaic devices. The sudden decrease around 795 K is related to the phase transition from solid melting followed by evaporation, which can be clearly seen in the TGA plot.¹⁵⁵ **Figure 3.10 (b)** shows the time-dependent PXRD, demonstrating its excellent environmental stability as indicated by the negligible degradation of the sample after 150 days of storage in the air (unsealed, 23°C, 45% RH). A synergistic aging experiment of 365 nm UV lamp exposure and humidity was performed, and the data is shown in **Figure 3.10 (c)**. The PL peak from the sample remains identical, with good stability (reduction of PL within 5%) observed after 12h of exposure to the air. These proved that the core-shell structure plays an important role in improving the stability of PeNCs

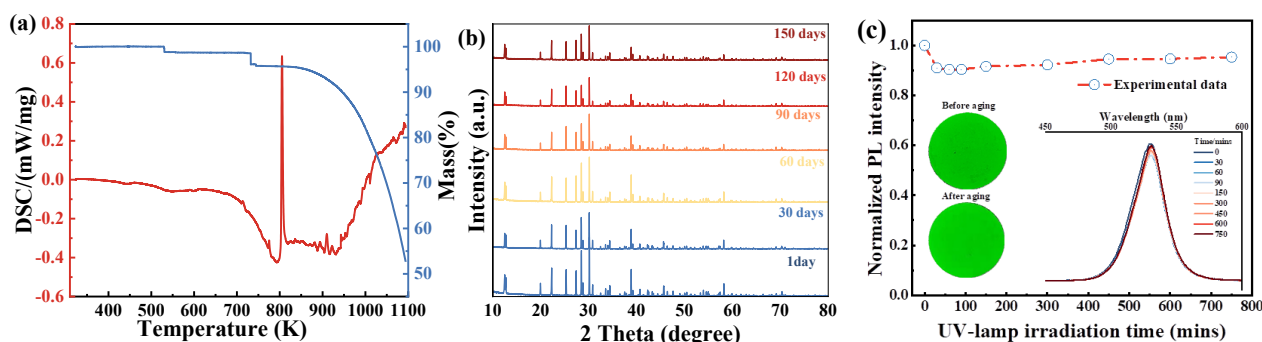


Figure 3. 10 (a) DSC spectra and TGA analysis of the $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals with a heating rate of 5 K/min. (b) Time-dependent PXRD patterns of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ powder after exposure to ambient atmosphere. (c) Normalized PL intensity of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystal during aging test. The images are the sample under 365 nm UV illuminations before and after aging.

3.7 Applications

It makes the $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ crystals a good application potential due to their good thermal behavior. Thermochromic perovskites are perfect for energy-efficient smart windows because of their steep absorption edge and high absorption coefficients. Applications might also be

expanded to temperature indicator labels or anti-counterfeiting labels. An efficient anti-counterfeiting method is the finding of thermochromism, which occurs when $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals change color when heated. To demonstrate its potential for anti-counterfeiting and information encryption, we ground the $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ composite and $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (YAG:Ce) into powder and filled it into openwork molds displaying the letters "UNICA" and the artistic Chinese word "electricity". YAG:Ce yellow phosphor was used as reference. As shown in **Figure 3.11**, we can easily obtain the information on the image, but the correct information can only be obtained after decoding. **Figure 3.11 (a)** displays patterns of Chinese characters and letters that can be used as surface-level information about the image. In the cold state, when there is no heating, these patterns are entirely yellow-green. However, some areas of the Chinese characters and letters will turn orange if the designs are just heat-treated (hot state). It is observed that multiple cycles of heating-cooling treatments, which are essential for attaining reproducible anti-counterfeiting, can restore the color of the patterns. This suggests that thermochromic technology has a lot of promise for creating secure and dependable encrypted data in anti-counterfeiting applications. A unique chemical compound that is integrated into the temperature indication label undergoes a chemical reaction when heated, changing its color. By watching the color change, one may determine the temperature of an object's surface because, in theory, the degree of color change is proportionate to the quantity of heat received. Simple temperature indication labels have been developed to increase the thermochromic properties of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals' potential applications. To create a film, we ground $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ crystals. Then, we combined the $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ composites with polymethyl methacrylate, rotated the mixture, and applied it to the cup's outside. When hot boiling water is poured into the cup, the color of the film turns orange, which effectively prevents burn caused by high temperature environment, as shown in **Figure 3.11 (b)**.

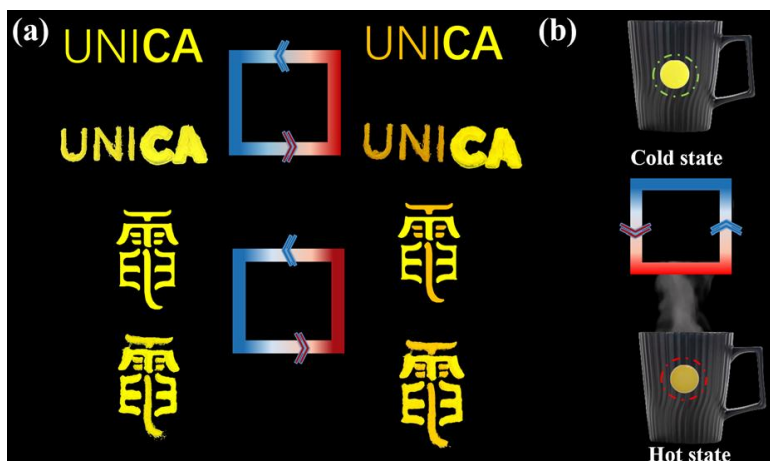


Figure 3. 11 (a) Illustration of the digital information encryption - decryption processes under thermal treatment of the $\text{CsPbBr}_3@/\text{Cs}_4\text{PbBr}_6$ crystals. (b) The $\text{CsPbBr}_3@/\text{Cs}_4\text{PbBr}_6$ crystals-based temperature indication label when hot water is poured into the cup.

3.8 Conclusion

In summary, we have synthesized original $\text{CsPbBr}_3@/\text{Cs}_4\text{PbBr}_6$ crystals with excellent green fluorescence using the PTGC method. By using temperature-dependent PXRD and UV-vis absorption spectra, it was verified that the mechanism behind this thermochromism in the perovskite $\text{CsPbBr}_3@/\text{Cs}_4\text{PbBr}_6$ is the result of a change in the optical band gap, which is determined by the competition between lattice thermal expansion and electron-phonon coupling. Through reversible temperature-dependent Raman spectra, as the temperature increases, the Raman peaks of the TO_1 and TO_3 modes (related to Cs^+ cations) gradually disappear and then both modes return when the temperature returns to room temperature. Compared to the obvious changes in the TO_1 and TO_3 modes, the changes in the TO_2 mode (related to $[\text{PbBr}_6]^{4-}$ octahedra) are relatively soft, suggesting that the movement of Cs^+ ions is more intense due to the unique Bergerhoff-Schmitz-Dumont-type crystal structure throughout the thermochromic process. In order to get an insight into the whole mechanism of thermochromism, we simulated the crystal change information of $\text{CsPbBr}_3@/\text{Cs}_4\text{PbBr}_6$ crystals with Materials Studio at 300 K, 500 K. A marked change is the Pb-Cs, Cs-Br bond length, which is more affected by thermal than Pb-Br in the $[\text{PbBr}_6]^{4-}$ octahedra, and this mechanism differs from the previously proposed change of bond lengths based solely on octahedral distortions. In the presence of heating, the $\text{CsPbBr}_3@/\text{Cs}_4\text{PbBr}_6$ crystal shows reversible thermochromism, making it suitable for designing anti-counterfeiting and temperature indication labels. Crucially, our findings complement previous explanations of the thermochromic mechanism and further highlight the great potential of 0D perovskites thermochromic materials for applications.

Furthermore, the thermal response of $\text{CsPbBr}_3@ \text{Cs}_4\text{PbBr}_6$ underscores the crucial role of its core-shell-like structure in enabling such reversible behavior.

4 | Temperature-Dependent PL Properties of CsPbBr₃@CsPb₂Br₅

In this chapter, we have replaced the 0D Cs₄PbBr₆ shell from [Chapter 3](#) with a 2D CsPb₂Br₅ perovskite. The CsPbBr₃@CsPb₂Br₅ core-shell structure has been prepared as powder by the chemical precipitation conducted at room temperature. The structural and optical properties of the CsPbBr₃@CsPb₂Br₅ MCs were characterized using PXRD, UV-vis absorption spectra, and PL spectra. Two distinct absorption peaks at 307 nm and 515 nm are attributed to the CsPb₂Br₅ matrix and the CsPbBr₃ NCs, respectively. The MCs exhibit a PL peak at 518 nm with a FWHM of 86.1 meV at room temperature. Temperature-dependent steady-state PL measurements, conducted from 80 to 320 K, reveal an exciton binding energy of approximately 84.1 meV, which is higher than that of the pure CsPbBr₃ NCs. These experimental results demonstrate that the CsPbBr₃@CsPb₂Br₅ MCs possess excellent stability against thermal stress, water exposure, and light irradiation, making them promising candidates for commercial applications in lasing and display technologies.

4.1 Introduction

Perovskites offer many advantages, but their practical uses are severely limited by their instability when exposed to heat or moisture. This restricts the device applications of self-assembly crystalline organic-inorganic hybrid perovskites and is especially significant for them. Due to their superior stability and luminescence characteristics, the all-inorganic CsPbX₃ (X = Cl, Br, and I), and their NCs have sparked a lot of attention. CsPbBr₃ is all-inorganic lead halide perovskites with high PLQY and narrow FWHM. However, their environmental stability remains a challenge.¹⁷⁹ Research is focusing on improving the stability of lead halide perovskite materials and enhancing their efficiency and environmental compatibility through doping,^{106, 180} or forming core-shell structures.¹⁸¹ Adding shell material to core NCs to create core-shell structures is an efficient method to enhance stability. The shell layer enhances chemical stability by isolating the environment and preventing surface traps, while also optimizing optoelectronic performance.¹⁸² Researchers have studied the development of core-shell structures with core PeNCs using oxides,^{13, 183} metal chalcogenides,¹⁰⁹ and other perovskite materials.¹⁸⁴ And their findings have greatly improved the stability and device performance of

PeNCs. Creating "perfect" morphology-tunable perovskite core-shell NCs remains challenging, as the shell layer must completely encapsulate the core NCs and maintain its block shape with well-defined edges.¹⁸⁵

Basic CsPbX_3 derivatives, such as CsPb_2X_5 , exhibit distinct layer stacking when Br and Pb ions form octahedral structures of $[\text{PbBr}_6]^{4-}$, which might improve chemical and physical properties.¹⁸⁶ CsPb_2Br_5 displays stronger stability against water compared with traditional organic–inorganic hybrid perovskites and orthorhombic phase counterparts of CsPbBr_3 . The 2D CsPb_2Br_5 perovskite material has been considered a good candidate as a coating material due to its indirect band gap (2.979 eV) PL inactivity, water resistance properties, and minimal lattice mismatch with CsPbBr_3 NCs. The small mismatch between both favored the epitaxial crystallization interphase. The previous study has also confirmed that the synthesized millimeter-sized CsPbBr_3 crystals contained a small amount of CsPb_2Br_5 (~10%) as the byproduct.¹⁸⁷ Similar to Cs_4PbBr_6 , this has also led to the photoluminescence mechanism of CsPb_2Br_5 remaining unclear. There exists inconsistency between theoretical simulations and experimental results. In certain theoretical calculations, CsPb_2Br_5 is non-luminous. No photoluminescence was indeed observed in the pure CsPb_2Br_5 sample. However, in numerous research reports, CsPb_2Br_5 samples continue to exhibit intense green PL. Different mechanisms have been proposed to explain the observed PL emission: CsPbBr_3 impurities or crystal defects.

These unique perovskite-derivative $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs with effective luminescence and anti-water stability have been discovered,¹⁸⁸ which can be easily precipitated and have prospective uses in LED and photodetector systems. Furthermore, the presence of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ core-shell structure in the composite did not only enhance the current efficiency, but it also (i) reduced the trap density in the band gap, (ii) increased the ionic conductivity, and (iii) improved the PL lifetime of the CsPbBr_3 NCs. Performance optimization has ensured that the $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs core-shell structure remains constantly under the scrutiny of researchers.

4.2 Sample preparation

Materials and chemicals: Cesium acetate ($\text{C}_2\text{H}_3\text{CsO}_2$ 99.9%, Macklin), Lead bromide (PbBr_2 99.0%, Macklin), Ethanol Absolute ($\text{C}_2\text{H}_6\text{O}$ 99.5%, Fuyu Shiji), Deionized Water, all of these chemicals are used without any further purification.

Synthesis of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs: $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs is synthesized by chemical precipitation conducted at RT.¹⁸⁹ Firstly, deionized water and ethanol are mixed to obtain the

solvent mixture (total volume = 2.25 ml, $V_{H_2O}:V_{EtOH} = 1:3$). The mole ratio of Cs^+/Pb^{2+} in mixed solution is adjusted to 1/1 and 1/2.5. $C_2H_3CsO_2$ (1 mmol) is added into the above solution until completely dissolved. $PbBr_2$ (2.5 mmol) is added into $C_2H_3CsO_2$ solution and mixed mechanically which results in the formation of $CsPb_2Br_5$ as a precipitate at the bottom of the solution. The $CsPbBr_3$ can be obtained when $PbBr_2$ (1 mmol) is added into $C_2H_3CsO_2$ (1 mmol) solution. The obtained products are dried for 12 h and are washed by deionized water three times to remove surface impurities.

4.3 Sample characterization

4.3.1 Experimental Setup and Measurement Methods

UV-vis absorption spectrum is collected using a Hitachi-U2001 spectrophotometer with the reflectance mode. The image of SEM is measured by scanning electron microscope (Sigma 300, Zeiss) at 15 kV. The PXRD is measured on a Panalytical X'Pert pro powder X-ray diffractometer equipped with $Cu\ K\alpha$ radiation. The temperature-dependent PL measurements of $CsPbBr_3@CsPb_2Br_5$ MCs are measured based on a home-built setup. A continuous-wave (CW) laser (UV-FN-405-200 mW, CNI) at 405 nm is used as an excitation light source for steady-state excitation. The steady-state PL spectra are collected by a spectrometer (HR4000CG-UV-NIR, Ocean Optics). The temperature-dependent PL measurements are performed using a vacuum liquid-nitrogen cryostat (Cryo-77, Oriental Koji) with the temperature variation from 80 to 320 K. TRPL decays were recorded using a time-correlated single-photon counting system. The sample was excited by a 372 nm pulsed laser diode (HORIBA, DD-375L), controlled by a Deltadiode (HORIBA) driver and DeltaHub (HORIBA) controller. The resulting emission was detected by a hybrid photomultiplier tube (PMT), achieving a temporal resolution of up to 25 ps.

4.3.2 Structural and Optical Characterization

Figure 4.1 (a) and (b) illustrates the crystal structures of orthorhombic $CsPbBr_3$ and tetragonal $CsPb_2Br_5$ perovskites. From various angles, the $CsPb_2Br_5$ perovskite has two layers of $[Pb_2Br_5]^-$ sandwiched by a layer of Cs^+ ions. Through nonstoichiometric material transfer or structural rearrangement of its 3D analog, $CsPb_2Br_5$ is a secondary metastable material¹⁹⁰. The inherent symmetry of crystal structure affects how crystals form. Consequently, the optoelectronic characteristics of $CsPbBr_3$ and $CsPb_2Br_5$ exhibit different crystal structures. The PL emission spectrum of $CsPbBr_3@CsPb_2Br_5$ MCs exhibit a peak at 518 nm with a narrow FWHM of 22 nm, which is similar to $CsPbBr_3$ exhibits a peak at 514 nm. The $CsPbBr_3@CsPb_2Br_5$

MCs PL spectra peak position has a 4 nm red shift relative to the CsPbBr_3 according to **Figure 4.1 (c) and (d)**. The illustration in **Figure 4.1(c)** shows photographs of CsPbBr_3 powder under UV light and daylight. This is because the CsPbBr_3 powder particles, after scattering/absorbing visible light, exhibit an orange-tinged ‘body color’ (the inherent colour of the powder under normal illumination) when viewed by the naked eye. As shown in **Figure 4.1(d)**, a white powder of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ can be observed. CsPb_2Br_5 is a wide-bandgap insulator that does not absorb visible light, appearing close to white or colourless. When used as a shell layer, it “dilutes” the orange body colour of CsPbBr_3 , so the overall powder appears whitish. The green light primarily originates from the luminescence of the CsPbBr_3 core within the shell layer. CsPb_2Br_5 itself does not emit light, but it serves a passivation function, reducing non-radiative recombination and thereby stabilizing the green fluorescence of CsPbBr_3 .

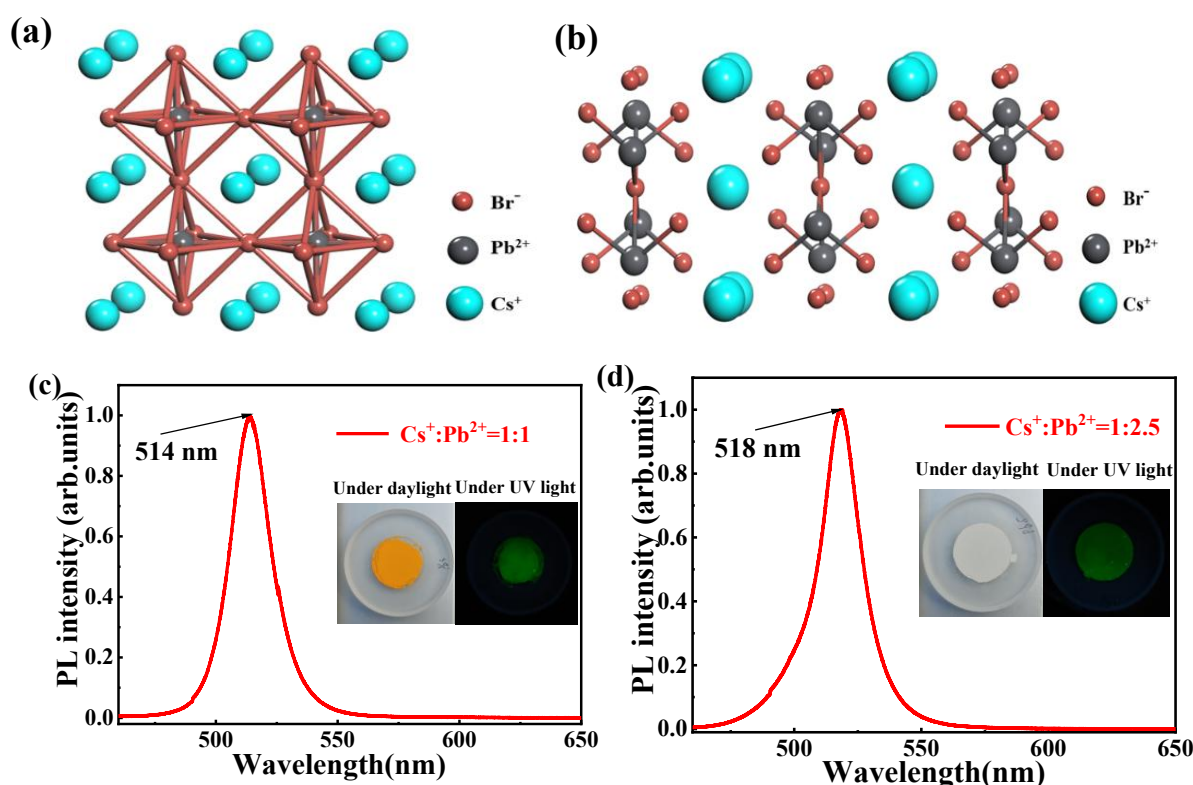


Figure 4. 1 The crystal structure of (a) CsPbBr_3 and (b) CsPb_2Br_5 . PL Spectra with $\text{Cs}^+/\text{Pb}^{2+}$ mole ratio of (a) 1/1 and (b) 1/ 2.5. And the inset is pictures of CsPbBr_3 and $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$.

The images in **Figure 4.2 (a)** depict $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ in daylight, where it is plainly visible as white powder, and under a UV lamp (365 nm), where there is a discernible green emission in the atmosphere. As can be seen in **Figure 4.2 (b)**, the PXRD diffraction peak perfectly matches the standard tetragonal CsPb_2Br_5 (PDF#25-0211); the XRD pattern of the original sample film exhibited strong peaks at 2θ of 11.6° , 23.4° , 35.4° , 47.6° , and 47.8° , corresponding

to the (002), (210), (312), (413), and (420) planes of the tetragonal CsPb_2Br_5 phase, respectively. Hydrated derivatives like CsPbBr_3 and PbBr_2 do not exhibit any discernible purity signals. It should be noted that because of their small mass and measurement limit, no equivalent diffraction peaks of CsPbBr_3 can be observed.¹⁹¹ **Figure 4.2 (c)** shows the absorption and PL spectrum of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs. The dual-phase $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ exhibits a strong green emission at 518 nm with a narrow FWHM of 15 nm (86.1 meV), close to CsPbBr_3 's peak at ~ 520 nm.¹⁹² Two absorption peaks can be seen around 300-400 nm, one at 345 nm, which is consistent with prior results¹⁹³. The shoulder at 345 nm was attributed to the bandgap transition. So far there has been no consensus on the assignment of the broad band absorption from 350 to 500 nm, which was assigned to the exciton absorption in CsPb_2Br_5 . In the enlarged region, a few weak peaks were observed at 14.9° , which could be ascribed to the (101) planes of the orthorhombic CsPbBr_3 phase. According to the plots of $(\alpha h\nu)^{0.5}$ vs. photon energy in **Figure 4.2 (d)**, an indirect band gap of 3.01 eV is calculated, which is in accordance with the reported results.^{194, 195}

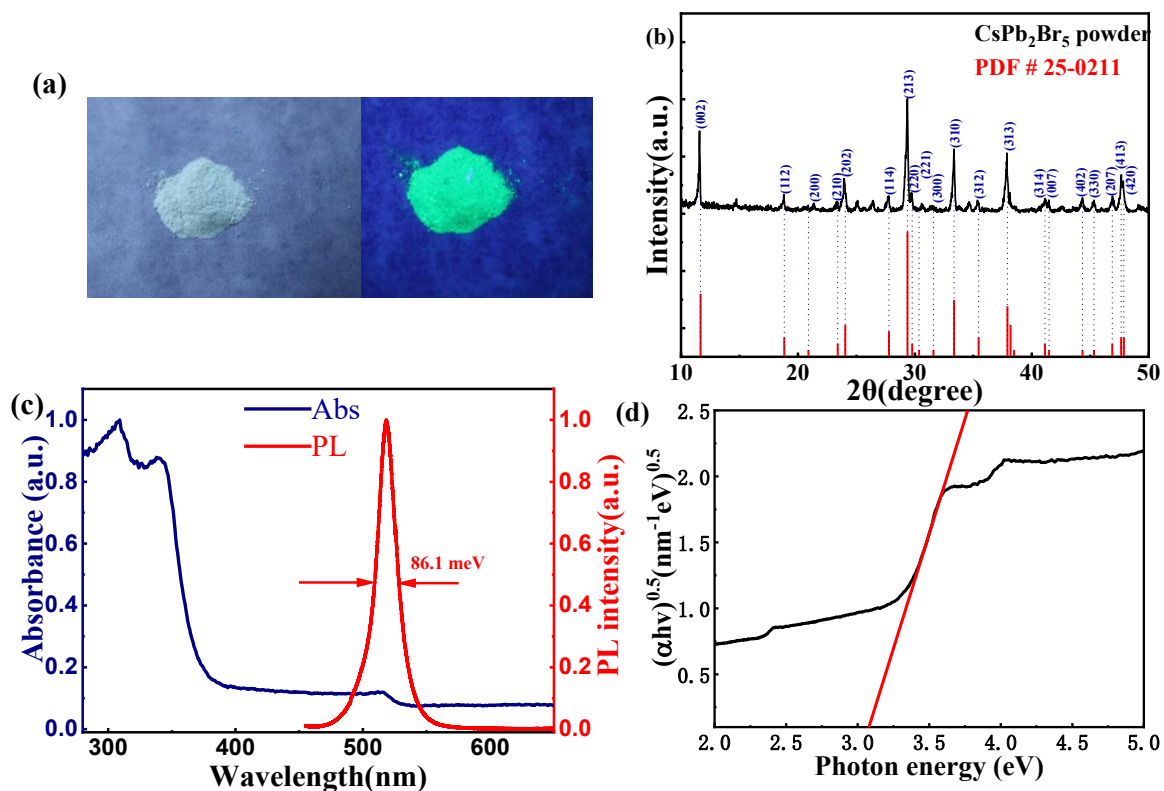


Figure 4. 2 (a) The pictures are $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs under daylight and UV lamp ($\lambda = 365$ nm). (b) PXRD pattern of fresh MCs. (c) Absorption and PL spectra of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs. (d) Tauc plots of $(\alpha h\nu)^{0.5}$ with photon energy ($h\nu$) for the band gap calculation.

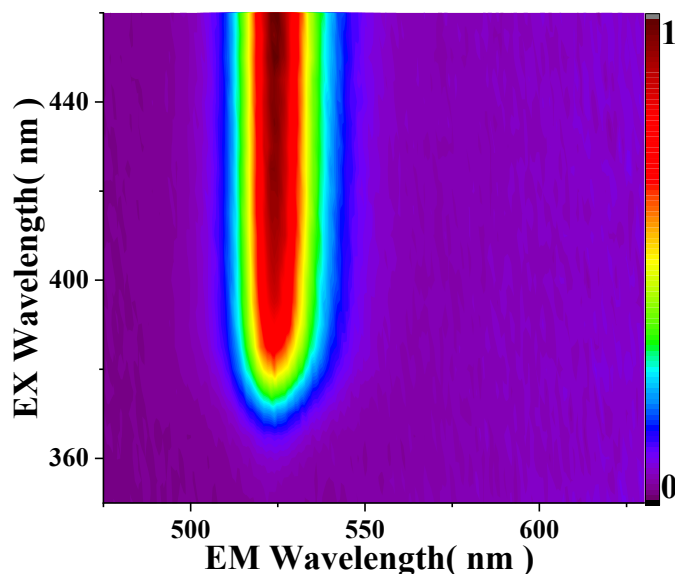


Figure 4. 3 The excitation and emission contour mapping of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs.

In order to investigate the relationship between emission peaks and excitation wavelengths, the fluorescent peaks were excited at different positions. As shown in **Figure 4.3**, the positions of the excitation peaks of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ crystals did not vary with the emission wavelength. Different excitation wavelengths only affected the intensity of the emission peaks but did not change the position of the emission peaks. Thus, the emission originated from relaxation of the same excited state. **Figure 4.4** displays the morphology of the synthesized $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs. The SEM micrograph shows that the size distribution of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs ranges between 2-30 μm , and we can clearly see that their morphology is comparable to platelets in blood.

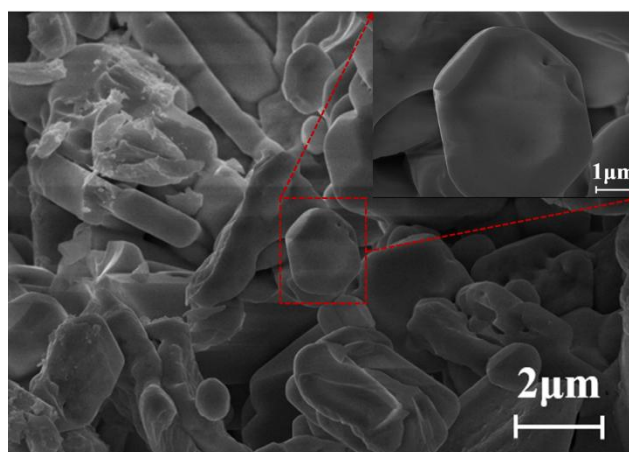


Figure 4. 4 SEM image of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs. The inset is the zoom-in SEM image.

4.4 PL Analysis of CsPbBr₃@CsPb₂Br₅ MCs

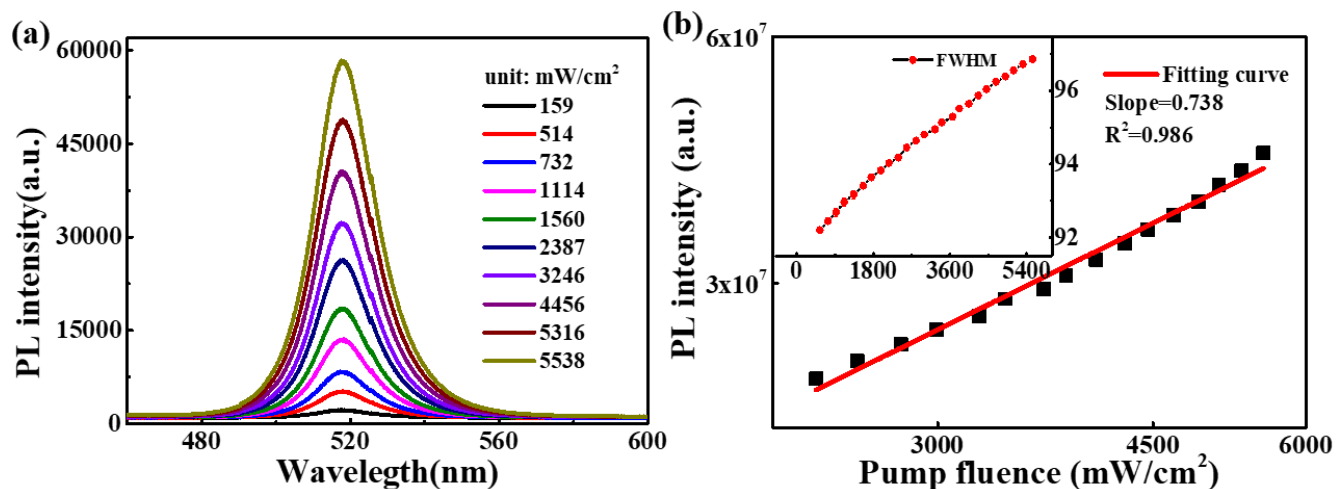


Figure 4.5 (a) PL spectra of CsPbBr₃@CsPb₂Br₅ MCs at 405 nm CW laser excitation. (b) The linear fitting between PL intensities and pump fluences

Band edge transitions in semiconductor materials typically originate from various sources, generally including free-bound carrier recombination, exciton recombination, and free carrier recombination. The PL intensity of semiconductor materials exhibits an exponential relationship with the corresponding excitation light power intensity.¹⁹⁶ When $1 < \alpha < 2$, exciton recombination occurs (encompassing both free and bound excitons); when $\alpha < 1$, free-bound carrier recombination takes place. For more insights into the nonlinear absorption of CsPbBr₃@CsPb₂Br₅ MCs, excitation density-dependent PL spectrum measurement is carried out. At RT, the CsPbBr₃@CsPb₂Br₅ MCs PL spectra-dependent 405 nm CW laser pump-fluence is determined as shown in **Figure 4.5 (a)**, with the pump laser fluence increasing from 159 to 5538 mW/cm². At the same time, the peak wavelength gradually increases and FWHM has a slight increase from 92 to 96 meV in the inset of **Figure 4.5 (b)**. It anticipated that the laser will beam on the material for a considerable amount of time, raising the MCs' surface temperature and creating a thermal impact that will somewhat raise the FWHM. **Figure 4.5 (b)** also displays the pump-fluence relationship of the PL intensities. The presence of single photon excitation is demonstrated by the red line, a linear fitting curve, whose slope is determined to be 0.80. Since the excitation of excitons (electron-hole pairs) via single-photon absorption necessitates the simultaneous absorption of one photon through an imaginary state. Furthermore, a better linear fit is indicated by the correlation coefficient (R^2) of 0.986. The CsPbBr₃@CsPb₂Br₅ MCs' PL intensity rises linearly with increasing pump-fluence, suggesting that persistent flaws are not the source of the PL emission.¹⁹⁷

Exploring the PL of hybrid organic-inorganic perovskites over a wide range of temperature is not only of fundamental interest but also aims to identify the practical applications of the devices based on these perovskites. In order to better understand the recombination properties of semiconductor materials due to heat impacts, temperature-dependent PL can estimate important physical parameters such as band gap, exciton binding energy, and exciton-phonon interaction. **Figure 4.6 (a)** and **(b)** illustrate the intensity-dependent and normalized PL spectral contours as temperature increases. The intensity, emission peak, and FWHM of PL can be discussed as the temperature ranges from 80 to 320 K. As the temperature rises, the crystal lattice of lead-based perovskites expands, broadening the band gap and causing a blue shift in the PL peak.^{198, 199} In contrast, other semiconductors, such as CdTe, show a red shift in exciton absorption and PL peak as temperature rises.²⁰⁰ **Figure 4.6 (c)** displays temperature-dependent PL spectra. As the temperature rises from 80 K to 320 K, the PL peak of CsPbBr₃@CsPb₂Br₅ MCs shifts blue from 528 nm to 518 nm under 405 nm CW laser irradiation, as illustrated in **Figure 4.6 (c)**. The blue shift of PL peaks can be attributed to a struggle between thermal expansion of the crystal lattice and electron-phonon coupling, as theoretically and experimentally explained.²⁰¹⁻²⁰³

The temperature dependence of PL intensities in CsPbBr₃@CsPb₂Br₅ MCs is observed as shown in **Figure 4.6 (d)**. The exciton binding energy can be fitted by **Eq. 3.1**. The E_b of CsPbBr₃@CsPb₂Br₅ MCs is 84.1 meV, which is slightly smaller than that of the previously reported CsPb₂Br₅ film²⁰⁴ and higher than that of CsPbBr₃ films.²⁰³ Increased dielectric screening reduces excitonic binding energy E_b as composition changes.²⁰⁵ The greater E_b value for CsPbBr₃@CsPb₂Br₅ MCs suggests that the excitons are stable even at room temperature, indicating that CsPb₂Br₅ MCs can passivate CsPbBr₃ at the interface. This point is analogous to the effect of Cs₄PbBr₆ on CsPbBr₃. With its lower free energy, tetragonal CsPb₂Br₅ improves the stability of inorganic perovskite devices and offers adequate passivation to lessen charge carrier recombination.⁴²

The FWHM rose while the PL strength decreased as the non-radiation leap got stronger. In addition to the band gap energy and PL intensity, lattice vibrations in a crystal, including the deformation potential, piezoelectric, and Fröhlich interactions, can affect the exciton-phonon coupling of CsPbBr₃@CsPb₂Br₅ MCs. The electronic band structure may be significantly impacted by such an interaction.¹⁹⁸ The exciton-phonon coupling of the MCs is studied by measuring the temperature dependence of the PL linewidth, and the results are shown in

Figure 4.6 (e). The monotonous broadening with rising temperature can be commonly expressed as the sum of two terms, an inhomogeneous broadening term, and a homogeneous broadening term due to the optical phonon-exciton interactions. The temperature-dependent PL linewidth is fitted using **Eq. 3.2**. As the temperature increases, the optical phonon contributions dominate, and the linewidth increases almost linearly with temperature. The significant temperature dependence of the PL linewidth implies strong exciton-phonon interactions, which lead to thermal broadening of exciton PL as the temperature is increased from 80 to 320 K. From the fitting process, the estimated values of Γ_0 , Γ_{op} and $\hbar\omega_{op}$ are determined to be 19.9, 52.2 and 14.9 meV for CsPbBr₃@CsPb₂Br₅ MCs, respectively. It can be seen that the linewidth has a significant temperature dependence, implying strong exciton-phonon interactions in CsPbBr₃@CsPb₂Br₅ MCs.

The bandgap energy (E_g) of semiconductor materials varies with temperature, determined jointly by electron-phonon interactions and lattice thermal expansion. For most semiconductors, as temperature rises, the phonon distribution broadens while thermal expansion effects diminish, leading to enhanced electron-phonon interactions and consequently a decrease in E_g . However, perovskite materials exhibit an anomalous blue shift in their PL peak position with increasing temperature, meaning their E_g increases as temperature rises. This behaviour cannot be explained by the classical Varshni model, which typically describes the gradual red shift of PL peaks in tetrahedral semiconductors as temperature increases. Beyond perovskites, other materials have been successively discovered exhibiting PL peak blue shifts with increasing temperature. Current research indicates this anomalous blue shift originates from temperature-dependent shifts in the valence band maximum (VBM) and conduction band minimum (CBM) of lead-based halide perovskites. Unlike conventional semiconductors, the VBM and CBM of ABX₃ perovskites are both composed of $B_{ns}-X_{mp}$ and $B_{np}-X_{ms}$ antibonding orbitals. Consequently, lattice thermal expansion alters the potential energies of VBM and CBM, thereby widening the perovskite bandgap. Concurrently, it has been observed that as temperature increases, lattice thermal expansion dominates in lead-based perovskite materials, while electron-phonon interactions become negligible. This mechanism accounts for the widening of the bandgap in these materials. To date, the cause of the anomalous blue shift phenomenon in lead-based halide perovskite materials remains subject to further investigation.

To find out more about the temperature dependence of the optical properties of CsPbBr₃@CsPb₂Br₅ MCs, the optical band gap was extracted from the PL spectra to plot the relationship between optical band gap and temperature, as shown in **Figure 4.6 (f)**. The optical band gap is almost linear with temperature from 80 to 245 K, the shift of emission peak with temperature change can be defined as the temperature coefficient, which the calculated value is 0.27 meV/K for CsPbBr₃@CsPb₂Br₅ MCs. It is larger than the pure CsPbBr₃ NCs. The passivation of CsPb₂Br₅ at the interface can reduce the charge carrier recombination and improve the stability of the inorganic perovskite devices. Within the temperature range of 250 to 320 K, the photon energy or wavelength of the luminescence peak remains virtually constant. This indicates that the luminescence peak is unaffected by temperature, rendering it a potential material category for application in cold light LEDs and QDs displays.

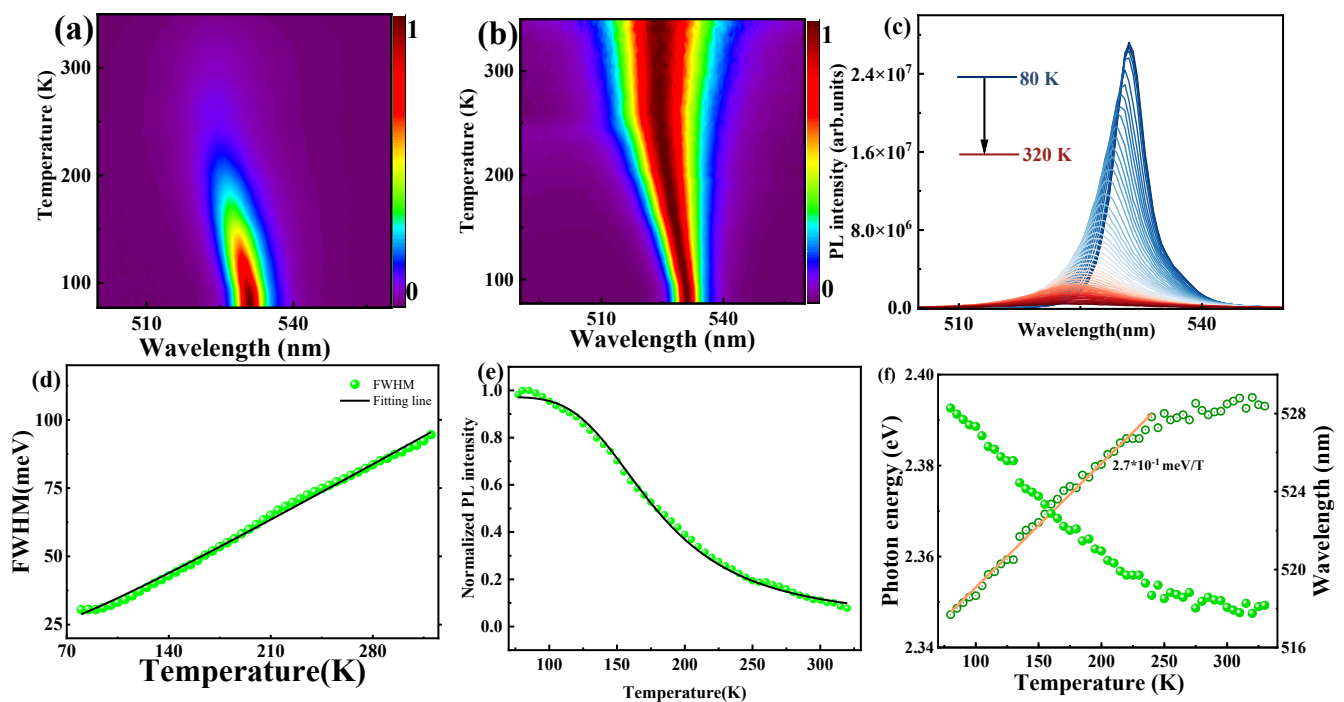


Figure 4. 6 (a) The intensity-dependent PL spectral contour of CsPbBr₃@CsPb₂Br₅ MCs at the temperatures from 80 to 320 K. (b) Corresponding normalized PL spectral contour. (c) The temperature-dependent PL spectra. (d) Temperature dependence of FWHM. (e) Temperature dependence of normalized PL integrated intensity. (f) Temperature dependence of the emission peak position, whereas solid line is the best-fitting curve.

4.5 Wavelength-dependent TRPL of CsPbBr₃@CsPb₂Br₅ MCs

In order to clarify the band-edge PL dynamics, we therefore resort to TRPL measurements based on time-correlated single-photon counting. The morphology and particle size distribution of semiconductor materials significantly influence their optical properties. At 290 K, varying the detection wavelength in time-correlated single photon counting (TCSPC)

measurements and analyzing the corresponding decay lifetimes provides further insight into the internal exciton recombination processes within the material. The PL decays of the samples are not single-exponential as seen in **Figure 4.7**, indicating the existence of several emission centers in the PNCs. The normalized PL curves can be fitted by biexponential decay with convolution expressed²⁰⁶ as

$$I(t) = A + \int_0^t \left(B e^{-(t-t')/\tau_1} + C e^{-(t-t')/\tau_2} \right) e^{-(t'/\tau_{fwhm})} dt' \quad (\text{E.q 4.1})$$

where τ_1 and τ_2 are the lifetimes of short and long-lived PL components, respectively. The biexponential decays strongly demonstrate two different species are involved in the exciton recombination. A represents the baseline of PL while B and C represent the amplitudes of the whole normalized PL. The instrumental response function τ_{fwhm} is considered to convolute to PL decays. The average lifetimes (τ_{aver}) can be calculated as,

$$\tau_{aver} = (B\tau_1^2 + C\tau_2^2) / (B\tau_1 + C\tau_2) \quad (\text{E.q 4.2})$$

The above two processes dominate at high concentrations of NCs or large size distribution of PNCs because the higher photon energy emitted by a smaller NC will be re-absorbed by a larger NC with a smaller optical bandgap, and/or the excited smaller NC nonradiatively transfers its energy to a larger NC.

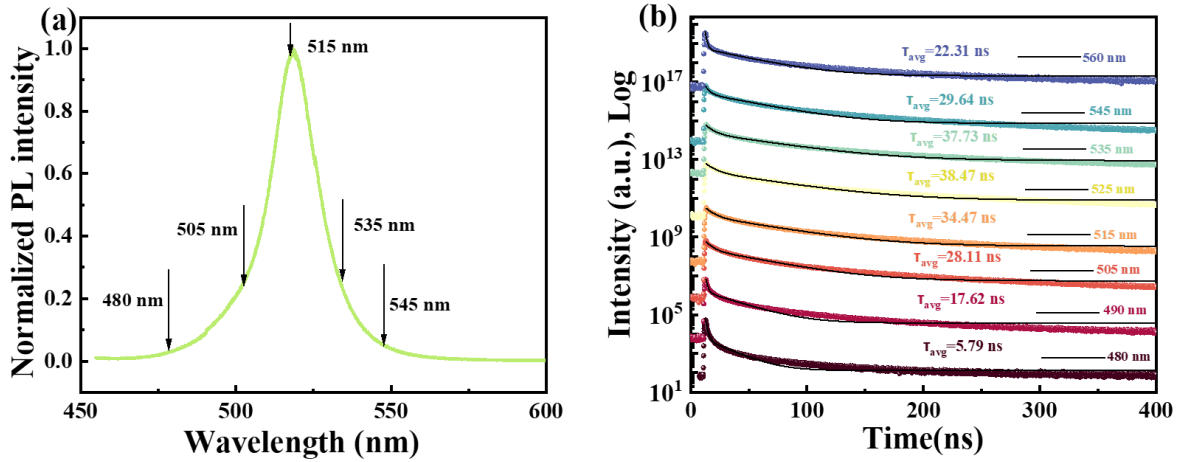


Figure 4. 7 (a) PL spectrum of CsPbBr₃@CsPb₂Br₅ NCs at 80 K. (b) Probe wavelength-dependent TRPL dynamics.

The PL lifetimes are significantly different when the probe wavelengths are changed due to the distribution of the irregular morphology and size. The irregular distribution of CsPbBr₃ in CsPb₂Br₅ results in noticeable differences in PL lifetimes when probed with different wavelengths. The average lifetimes of the *in-situ* CsPbBr₃@CsPb₂Br₅ composites changes from 5.79 to 38.47 ns as the probe wavelength changed from 480 to 525 nm. There is no regular pattern seen in the relationship between probe wavelength and lifetimes, as shown in **Figure 4.7(b)**. The average lifetimes vary from 37.73 to 22.31 ns with the probe wavelength varying from 535 to 560 nm. This is mainly because the thermally activated non-radiative channel

dominates the rapid decay of the lifetime at the 535-560 nm excitation wavelength at room temperature.

4.6 Water stability Measurements

The instability of perovskite materials, which decompose under conditions such as water, oxygen, high temperatures, and ultraviolet light, has long been a significant constraint on their commercial application. Among these challenges, the water stability of perovskite materials is a pressing issue requiring urgent resolution, particularly in the field of lighting where long-operating devices inevitably encounter moisture exposure. As evidenced in **Chapter 1**, when addressing the thermal stability of perovskite materials, most research groups typically modify the ligands or employ more stable materials such as SiO_2 , AlO_x , or directly encapsulating the perovskite with polymeric coatings to enhance stability. This chapter avoids modifying ligands or adding additional materials for passivation. Instead, it regulates the formation of distinct perovskite structures— CsPb_2Br_5 and CsPbBr_3 —solely by adjusting the ratio of raw materials during synthesis. The passivation of CsPbBr_3 by CsPb_2Br_5 enhances the water stability of CsPbBr_3 without requiring additional passivation materials, thereby reducing preparation costs and demonstrating potential for large-scale production. This holds significant implications for the application of perovskite materials in the field of lighting.

The **Figure 4.8 (a)** shows the $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ under the fluorescent lamp and can be clearly seen as white powder and a photograph of the CsPb_2Br_5 under a UV lamp with a visible green emission in the air. In order to prove the water stability of the powder, we completely immersed it in deionized water for 60 days. It can be seen that there is no obvious change in the CsPb_2Br_5 powder in the deionized water. Under the fluorescent lamp, the powder in the deionized water is still white, and under the ultraviolet lamp, the green luminescence of the powder in the deionized water can be observed clearly. **Figure 4.8 (b)** shows the PL spectra of CsPb_2Br_5 powder as time increases in deionized water, and the inset is the 405 nm CW laser irradiating $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ powder immersed in deionized water for 220 mins. As shown in **Figure 4.8 (c)**, it shows the stability of the CsPb_2Br_5 powder in deionized water and it can be observed that the intensity keeps at 83.0% of the initial intensity when the PL remains stable. In order to find out whether the crystal structure of the powder is destroyed by being immersed in water for a long time, the CsPb_2Br_5 powder immersed in water for two days is dried and its PXRD is retested. The PXRD result reveals that the water-treatment CsPb_2Br_5 sample exhibited similar pattern to the sample without water-treatment in **Figure 4.8 (d)**. There is no detectable purity

signal of hydrated products such as CsPbBr_3 , PbBr_2 .²⁰⁷ It exhibits excellent water stability structures.

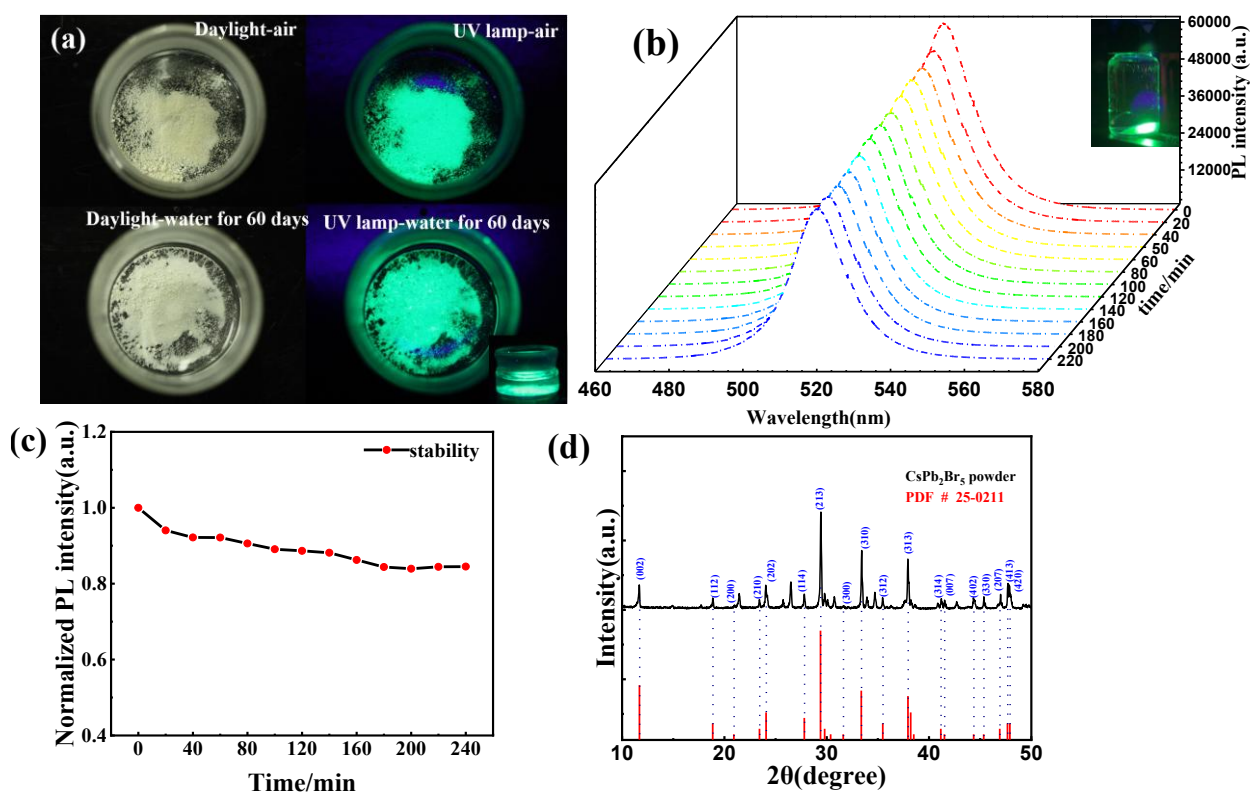


Figure 4. 8 (a) The pictures of powder under air and water. (b) PL spectra of $\text{CsPbBr}_3@ \text{CsPb}_2\text{Br}_5$ powder in the deionized water. (c) Water stability of $\text{CsPbBr}_3@ \text{CsPb}_2\text{Br}_5$ powder. (d) PXRD pattern of tetragonal $\text{CsPbBr}_3@ \text{CsPb}_2\text{Br}_5$ particles which immersed in deionized water for 60 days.

4.7 Conclusion

In summary, we have established a facile and convenient room temperature synthesis strategy for fabricating the $\text{CsPbBr}_3@ \text{CsPb}_2\text{Br}_5$ MCs, which can also obtain different products by changing the $\text{Cs}^+/\text{Pb}^{2+}$ ratio. By fitting the PL intensity with pump-fluence, it demonstrates that it is one-photon absorption. We have studied the temperature-dependent spectral properties of $\text{CsPbBr}_3@ \text{CsPb}_2\text{Br}_5$ MCs using steady-state PL spectroscopy. The optical band gap is determined to be 3.01 eV by finding the x-intercept of the line tangent to the linear region. We immersed it completely in deionized water, and the $\text{CsPbBr}_3@ \text{CsPb}_2\text{Br}_5$ MCs could maintain the initial luminous intensity of 83.0%. This remarkable combination of high luminescence, phase tunability, and water resistance underscores the key role of the CsPb_2Br_5 layer in enhancing both optoelectronic performance and long-term durability. These findings not only provide new insights into the passivation mechanisms of perovskite heterostructures but also open up

promising opportunities for their deployment in high-performance optoelectronic devices and stable perovskite-based LEDs.

5 | Conclusions and Outlook

5.1 Conclusions

All-inorganic metal halide perovskites, typically represented by the chemical formula $A_xPb_yX_z$ have emerged as a highly promising class of semiconductor materials. Their growing appeal is largely attributed to their exceptional optical and electronic properties. In $A_xPb_yX_z$ systems, metal halide perovskites featuring three distinct network architectures, governed by dimensional engineering, are quickly produced, including 3D ABX_3 , 2D AB_2X_5 , and 0D A_4BX_6 . The most researched aspects of the current system are $CsPbBr_3$, Cs_4PbBr_6 , and $CsPb_2Br_5$. All-inorganic metal halide perovskites-based optoelectronic devices have been extensively investigated for potential applications in optoelectronic devices. Among these, All-inorganic metal halide perovskite $CsPbBr_3$ -based solar cells have garnered a lot of interest because of their superior optical characteristics. However, perovskite materials' inherent poor stability restricts their usage in applications involving electric charges. To solve the instability problem of 3D perovskites and make device operation easier, a technique for using 0D perovskite has been presented. In chapter 3, we have synthesized $CsPbBr_3@Cs_4PbBr_6$ crystals with excellent green emission. Interestingly, although the colour of the $CsPbBr_3@Cs_4PbBr_6$ crystals undergoes varying degrees of change under heating conditions, their stability was influenced very little. Through temperature-dependent PXRD and UV-visible absorption spectra, we preliminarily confirmed that the thermochromic mechanism is attributed to changes in the optical band gap of 0D phase Cs_4PbBr_6 , which is determined by the competition between lattice thermal expansion and electron-phonon coupling. The reversible temperature-dependent Raman spectra indicated that the Raman peaks associated with Cs^+ cations gradually disappear as temperature increases and undergo reversible recovery when the temperature returns to room temperature. This proves that encapsulating $CsPbBr_3$ NCs in Cs_4PbBr_6 to form a core-shell structure significantly improves the thermal stability of NCs. Compared to the significant changes in the Cs^+ -related Raman peaks, the changes in the $[PbBr_6]^{4-}$ octahedra-related peaks are relatively mild, indicating that the movement of Cs^+ ions is more vigorous throughout the thermochromic process. This distinct thermochromic phenomenon was successfully applied in optical anti-counterfeiting and temperature-indicating labels.

Inspired by this core-shell structure, we replaced the shell with 2D perovskite CsPb_2Br_5 , thereby forming a new core-shell structure $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$. In chapter 4, we have developed a simple method for synthesizing $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs at room temperature. By fitting the PL intensity with the pump fluence, we confirmed that it exhibits single-photon absorption. Temperature-dependent steady-state PL spectra were measured to investigate the spectral properties of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs. With the temperature changed from 80 to 320 K, the fitted value of the exciton binding energy is 84.1 meV from temperature-dependent steady-state PL. In order to investigate the transitional mechanism of exciton recombination for $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs, time-resolved normal luminescence are performed at room temperature. The PL dynamics of $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs show wavelength-dependent characteristics even at 290 K, the average PL lifetime becomes longer from 5.7 to 38.4 ns when the probe wavelength is changed from 480 to 515 nm. The depopulation can be influenced by the size and surface defects of CsPbBr_3 in CsPb_2Br_5 matrix. After immersing the sample in deionized water for 2 months, the $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs retained 83.0% of their initial luminescence intensity. Due to their high luminescence efficiency and water stability, $\text{CsPbBr}_3@\text{CsPb}_2\text{Br}_5$ MCs hold promising potential for future applications in optoelectronic devices.

5.2 Outlook

This thesis investigated the underlying working mechanisms behind the thermochromic behaviour of $\text{CsPbBr}_3@\text{Cs}_4\text{PbBr}_6$. The optical properties and thermochromic effects of perovskite materials with different dimensional structures from 3D to 0D structures were investigated in detail, which offered valuable insights for the optimization of material design. However, there is still much room for discussion regarding the current mechanism, as most of the current mechanisms focus on octahedrons, and the effects of other components on the thermochromic phenomenon are still unclear. In the future, the perovskite components, such as the A-site elements, can be adjusted to regulate the thermochromic phenomenon, and suitable elements can be obtained through machine learning and other high-throughput theoretical calculations.

Beyond fundamental understanding, practical applications of thermochromic perovskites also face challenges related to stability and device integration. Although thermochromic phenomena are currently mostly applied to smart windows, there is still considerable room for improvement and research in terms of the response speed and stability of smart windows.

Perovskites have poor stability because they are prone to irreversible decomposition when exposed to high levels of oxygen and moisture. Advanced encapsulation technologies are frequently used to shield perovskite materials from moisture infiltration in order to lessen this problem. Other successful tactics include using more stable 2D perovskites, adding polymers or extra structural supports to perovskite films, and enhancing the intrinsic moisture resistance of thermochromic perovskites through halide ion substitution. It has been demonstrated that these methods greatly improve thermochromic perovskites' long-term stability. For core-shell structure, it is still exceedingly challenging to adjust the thickness of the shell layer on APbX_3 NCs, in contrast to the easily controllable thickness of the shell layer produced on the surface of metal and semiconductor NCs. It is important to consider how shell thickness affects the photoelectric characteristics of APbX_3 NCs.

6 | Publications

[2025] **One pot growth of 2D/3D hybrid perovskite vertical heterostructures**

Matta, Selene ; Demontis, Valeria; Simbula, Angelica ; Pau, Riccardo; Argiolas, Simone; Mattoni, Alessandro; Liscia, Silvia; **Wu, Ruirui**; Zhao, Nan; Bhardwaj, Aditya; Mattana, Francesco; Cadeddu, Emanuele; Nehete, Prajкта; Sestu, Nicola; Marongiu, Daniela; Quochi, Francesco; Saba, Michele; Mura, Andrea; Bongiovanni, Giovanni.

ACS materials Letters

[2025] **Nature and Role of the Structural Disorder in Low-Dimensional Hybrid Post-Perovskite Phosphors**

Gong Shunfa, Kama Blaise Antoine, **Wu Ruirui**, Massuyeau Florian, Paris Michael, Gautier Romain.

Inorganic Chemistry

[2025] **Broadband Emission in Low-Dimensional Hybrid Alkali Halide Perovskites**

Gong Shunfa, **Wu Ruirui**, Hassam Christopher, Gabilondo A. Eric, P. Shiv Halasyamani, Houel Julien, Gautier Romain.

In Peer Review

[2025] **Reversible Thermochromism in Cs₄PbBr₆ Microcrystals/CsPbBr₃ Nanocrystals based on the Synergistic Interaction Between Cesium Ions and PbBr₆ Octahedra**

Wu Ruirui, Gong Shunfa, Wang Qi, Demontis Valeria, Lai Stefano, Matta Selene, Wu Wenzhi, Marongiu Daniela, Chen Rui, Saba Michele

ACS Nano, 2025, 25122-25133

[2025] **Switchable Behavior and Applications of Low-Dimensional Halide Perovskites under External Environmental Stimuli**

Wu Ruirui, Gong Shunfa, Wu Yijun, Ren Zhiyuan, Liu Huan, Marongiu Daniela, Saba Michele, Chen Rui.

Crystal Research & Technology, 2024, 2400251

[2025] **Core-Shell Engineering of CsPbBr₃ Nanocrystals: Structures, Properties and Applications**

Wu Ruirui, Gong Shunfa, Wu Yijun, Ren Zhiyuan, Marongiu Daniela, Saba Michele, Chen Rui.

In Peer Review

7 | Acknowledgements

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