

Highly Efficient and Stable Two-dimensional Perovskite Solar Cells via Engineering Crystallization and Orientation

A thesis submitted in fulfillment of the requirements for the degree of
Doctor of Philosophy

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Declaration of Originality

This is to certify that to the best of my knowledge; the content of this thesis is my own work. This thesis has not been submitted for any degree or other purposes. I certify that the intellectual content of this thesis is the product of my own work and that all the assistance received in preparing this thesis and sources have been acknowledged.

Fang Zeng

5 November 2024

Abstract

Recently, while 3D perovskite solar cells (PSCs) have achieved a power conversion efficiency (PCE) above 26%, their inherent instability has hindered commercial progress. In contrast, 2D perovskites offer greater stability but lag in PCE due to the poor conductivity of bulky organic spacers that hinder carrier transport. This thesis aims to narrow the PCE gap between 2D and 3D PSCs by refining crystallization processes, optimizing crystal orientation, and improving film quality, thereby advancing the practical application of 2D PSCs in renewable energy.

In Chapters 1-2, we introduce the origins of solar cells, tracing developments from the initial discoveries of the photovoltaic and photoelectric effects to the evolution of crystalline silicon and thin-film solar cells, culminating in the innovative perovskite solar devices. Initially, we outline and detail the chemical structure of perovskite. We then introduce the unique physical and chemical properties that perovskites contribute to solar devices and analyze the device's operational principles. The basic configurations and components essential to perovskite devices are outlined, along with key parameters critical for evaluating the performance of these photovoltaic devices. Finally, we outline the challenges the primary challenges faced by 3D perovskite solar cells, particularly stability issues, and discuss how 2D perovskites offer promising solutions to these challenges, setting a foundation for further exploration in solar technology. Then we move to 2D PSCs. We first introduced the crystal structure and unique characteristics of 2D perovskites, crystallization and growth theories, and the crystallization mechanisms of 2D perovskite films. We then discussed the multiple quantum well structures that limit the photovoltaic performance and systematically summarized a variety of innovative process engineering techniques to fabricate high-efficiency 2D perovskite films. This includes the hot-casting method, which optimizes molecular alignment and phase purity; vacuum-assisted strategies that enhance film uniformity and minimize defects; and post-annealing strategies that refine crystal orientation and enhance electrical properties. Furthermore, we discuss scalable technologies that demonstrate the potential for transitioning from laboratory to industrial-scale production, ensuring that advancements in 2D perovskite film preparation are aligned with commercial viability. Each technique uniquely contributes to the progression of 2D perovskite technology, paving the path for the next generation of high-efficiency and

durable optoelectronic devices.

In Chapter 3, we introduced some fabrication methods used for each layer of perovskite solar cells, mainly including techniques like magnetron sputtering for transparent conductive oxides, spin-coating for transport layers, and thermal evaporation for back electrodes. We focus on the fabrication of perovskite film, mainly using hot-casting, spin-coating, and anti-solvent methods. Next, we introduce the principles and detailed methods of the primary characterization techniques. These include imaging and mapping techniques such as SEM, AFM, and TEM techniques to analyze film morphology, and XRD and GIWAXS techniques for studying crystallization kinetics. Optical characterization methods such as UV and TA spectroscopy are used to study the optical properties and dynamics of 2D perovskite films. Additionally, we present characterization methods for perovskite devices, including *J-V* Curve, EQE, SCLC, and stability testing.

In Chapter 4, We aim to address the inherent stability in FA-based 2D perovskites, especially lattice strain and poor carrier transport. Through spacer cation engineering, we achieved a stable perovskite lattice structure with relaxed microstrain and reduced carrier-lattice interactions. In order to prevent the photocurrent degradation caused by the parallel orientations, we used a selenourea (SENA) additive that controlled the crystallization process, inhibited the formation of low-*n* phase, and consequently promoted vertical quantum well structures. The resulted FA-based 2D PSCs achieved a high PCE of 20.03% and excellent stability, maintaining over 90% efficiency after rigorous thermal and thermal cycle stress tests [1].

In Chapter 5, we aim to address the issues related to low crystallinity and disordered orientation in low-*n* 2D perovskite solar cell, which restrict carrier transport and efficiency. By systematically exploring the effects of ionic additives of ammonium (NH_4^+) and thiocyanate (SCN^-) additives on crystallization dynamics and orientation, we found that effectively $\text{NH}_4^+\text{SCN}^-$ additives retarded non-uniform crystallization, promoting vertical quantum well growth. The resulting devices achieved a PCE of 18.14% and demonstrated excellent stability, retaining over 90% of their initial efficiency under 1 Sun illumination for 720 hours in a humid environment [2].

In Chapter 6, we introduce a novel de-templated crystallization strategy designed to control the

crystallization kinetics of 2D perovskite film through a stable intermediate phase created during a two-step deposition process. By precisely adjusting the chemical interactions in the precursor solutions and driving the crystallization process, we successfully eliminate the templated in-plane growth near the liquid-air interface and promote the formation of highly out-of-plane orientated crystals, with carrier lifetime increased by four folds. The optimized 2D perovskite solar cell achieves a PCE of 21.16%. Additionally, the devices demonstrate remarkable stability, with a PCE decrease of less than 5% after exposure to $65\pm 10\%$ humidity for 1100 hours, operation under 85°C for 1077 hours, or continuous illumination for 1045 hours.

In Chapter 7, we summarized the development and advantages of PSCs, focusing on innovative crystallization control techniques and engineering to optimize the orientation and film quality of 2D perovskite. This discussion highlights the advanced strategies for narrowing the performance gap between 2D and 3D PSCs and promoting their commercial potential. Additionally, we provided the perspective research directions in 2D halide perovskites for further optoelectronic applications. Firstly, quantum well tuning is explored to enhance bandgap control, crucial for optimizing tandem solar cell performance. Secondly, theoretical simulations and machine learning are employed to accelerate the discoveries of new perovskite materials with superior properties. Lastly, advanced photophysics research using in-situ spectroscopy is essential for understanding carrier dynamics and improving device efficiency.

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Written at sunset at Fisher Library

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Authorship Attribution Statement

This thesis includes research that has been published or is under review for publication. The content from these works is presented in Chapters 2, 4, 5, and 6. Details of my contribution and publication information are listed below,

- **Chapter 2 of this thesis was submitted to a journal as a research review.**

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I proposed this research, surveyed the literature, organized the literature, analyzed data, and drafted and revised the manuscript.

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I proposed this research, designed and fabricated the solar cell devices, carried out the main experimental work, analyzed the data, and drafted and revised the manuscript.

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In addition to the statements above, in cases where I am not the corresponding author of a published item, permission to include the published material has been granted by the corresponding author.

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As a supervisor for the candidature upon which this thesis is based, I can confirm that the authorship attribution statements above are correct.

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List of Abbreviations

μ	octahedral factor
$\langle\lambda\rangle$	quadratic elongation
t	tolerance factor
QWs	quantum wells
E_b	binding energy
ΔG	Gibbs free energy
Cs	saturation concentration
C_{cr}	critical concentration
τ	lifetime
(σ)	bond angle variance
k_B	Boltzmann constant
I_{ph}	light intensity
V_{TFL}	trap filling limited voltage
ϵ_0	vacuum permittivity
GSB	ground state bleaching
RP	Ruddlesden-Popper
DJ	Dion-Jacobson
CdTe	cadmium telluride
CIGS	copper indium gallium selenide

PCE	photoelectric conversion efficiency
<i>J-V</i>	Current density-voltage
EQE	External Quantum Efficiency
<i>J_{sc}</i>	short circuit current
<i>V_{oc}</i>	open circuit voltage
<i>FF</i>	fill factor
<i>R</i>	load resistance
FA	Formamidinium
MA	Methylammonium
FAPbI₃	Formamidinium Lead Iodide
PbI₂	Lead Iodide
2D	Two-Dimensional
3D	Three-Dimensional
PVK	Perovskite
PSC	Perovskite Solar Cell
SQ limit	Shockley-Queisser limit
HTL	Hole Transport Layer
ETL	Electron Transport Layer
LUMO	Lowest Unoccupied Molecular Orbital
HOMO	Highest Occupied Molecular Orbital
<i>E_f</i>	Fermi level

DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
FTO	fluorine-doped tin oxide
ITO	indium tin oxide
ST-PVs	semitransparent photovoltaics
AVT	high average visible transmittance
BA	butylamine
OA	octylamine
DA	dodecylamine
n-BA	n-butylamine
MBAI	alpha-methylbenzyl ammonium iodide
β-FPEA	β -fluorophenethylamine
PEA	phenethylammonium
4FPEA	4-fluorophenethylammonium
MACI	methylamine hydrochloride
TSC	thio-semicarbazide
DFT	Density Functional Theory
ESP	Electrostatic Potential
VASP	Vienna Ab-initio Simulation Package
SED	secondary electron detector
BSE	backscattered electron detector

EDS	Energy Dispersive Spectrometer
AFM	Atomic Force Microscopy
KPFM	Kelvin probe force microscopy
XPS	X-ray Photoelectron Spectroscopy
PL	Photoluminescence
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
HRTEM	High-Resolution Transmission Electron Microscopy
UV-Vis	Ultraviolet-Visible Spectroscopy
TRPL	Time-Resolved Photoluminescence
GIWAXS	Grazing Incidence Wide-Angle X-ray Scattering
GIXRD	Grazing Incidence X-Ray Diffraction
CBM	Conduction Band Minimum
VBM	Valence Band Maximum
TA	Transient absorption spectroscopy
SCLC	Space charge-limited current

Chapter 1 Introduction

The effect of sunlight on certain materials
leads to the generation of electricity.
this phenomenon, though not yet fully understood,
promises great advancements in power generation
----- Edmond Becquerel

The history of human civilization is, in fact, an evolutionary history of the way of continuously obtaining and using energy. From slash-and-burn farming in ancient times to the modern industrial revolution and technological revolution, this journey is like a magnificent epic. Each significant change in energy acts as a crucial driving force for the progress of human society. With the continuous growth of human demand for energy, the consumption of traditional energy is also increasing dramatically. The reserves are limited and non-renewable. How to use and develop new energy has become a common concern of countries around the world. Solar energy stands out as the most efficient and sustainable among the numerous emerging renewable energy sources [3], due to it comes directly from solar energy and can directly harness solar radiation and transform it into electrical power.

In 1839, the French scientist Alexandre Edmond Becquerel first opened the door to the world of photovoltaics and was hailed as the founder of photovoltaic, he observed that under illumination, a photovoltage was generated between the platinum electrodes plated with silver in the electrolyte. This discovery is credited as a foundational figure due to seminal work revealing the "photovoltaic effect", a phenomenon where voltage and current are produced at the junction between a semiconductor or a semiconductor-metal combination when exposed to light or other electromagnetic radiation. Then, why can light be converted directly into electricity? This can be explained by the "photoelectric effect". When photons possess sufficient high energy, typically from ultraviolet light or X-rays, they can cause electrons to be ejected from the metal surface, as illustrated in **Figure 1-1a**. The discovery laid the foundation for the development of quantum mechanics. In 1905, Albert Einstein proposed that the photon

energy is quantized, meaning that each photon's energy is proportional to its frequency. Electrons can only be emitted from a metal surface if the photon's energy exceeds its work function. This theory successfully explained the experimental observations of the photoelectric effect and led to Einstein being awarded the Nobel Prize in Physics in 1921[4]. Typically, when a material absorbs light, the photon's energy could elevate the electrons to higher energy levels, but the excited electrons usually quickly return to their ground state. In the photovoltaic effect observed in solar cells, the internal asymmetric structure of p-n junction enables electrons to be transported to the external circuit before they return to ground state. A potential difference, obtained by the excited electron, drives the load in the external circuit to form a complete loop, as illustrated in **Figure 1-1b**. In 1953, Calvin Fuller, Daryl Chapin, and Gerald Pearson, three scientists at Bell Labs, created a crystalline silicon solar cell, measuring approximately 2 cm² in size with a PCE of around 4%. This breakthrough provided a solid foundation for the progress of modern solar energy technology.

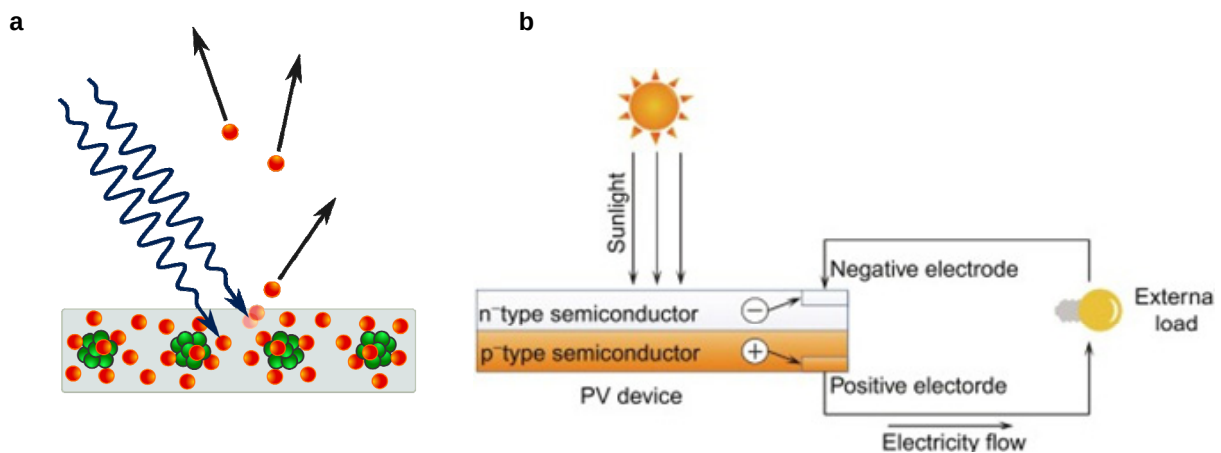


Figure 1-1. (a) The diagram of the photoelectric effect (Source: Wikimedia commons, by W. Oelen, CC BY-SA 3.0). and (b) the photovoltaic effect in solar cells [5].

Chapter 2 2D Perovskite Solar Cells

Solar power is a fantastic energy source.

Our scientific advancements in
nuclear energy have shown its potential,
but solar power is safer and cleaner.

----- Albert Einstein

Recently, the solar photovoltaic market has grown exponentially, and the primary mechanism for converting solar energy directly into electricity mainly relies on the photovoltaic effect exhibited by semiconductor materials [6-8]. Traditional solar cells primarily consist of P-type and N-type materials that form a light-absorbing layer, where energy conversion occurs[9]. When photons with sufficient energy strike the p-n junction, they generate electricity internally. At present, a variety of semiconductor materials have been applied to photoelectric fields utilizing solar energy, and solar energy technology has mainly experienced three important stages of development [10].

The first generation of solar cells was developed using crystalline silicon as the foundation materials, both monocrystalline and polycrystalline silicon [11, 12]. Due to the abundant silicon production, easy access, high efficiency of light energy conversion, and good stability, such cells occupy a dominant position in the photovoltaic field, contributing to about 90% of the annual output of the global photovoltaic industry [13, 14]. The second generation of solar cell mainly includes thin-film solar cell, including cadmium telluride (CdTe) solar cells, multi-compound copper indium gallium selenide (CIGS) photovoltaic cells, and amorphous silicon (a-Si) devices [15-18]. However, the low quality of the thin film poses significant challenges, this type of cell enhanced the non-radiative recombination losses. Additionally, the materials used are toxic, limited reserves, making challenges for the commercialization manufacturing. The third generation is a new type of photovoltaic cells [19, 20], including organic photovoltaics [21], dye-sensitized solar cell [22], and other innovative materials such as graphene and perovskite thin-film solar cells[23-27]. The emerging solar cell is called future

photovoltaic products because of their "high performance and low cost" characteristics. As research progresses, the photovoltaic effect and stability of this class of material have been substantially enhanced, and the industrial application prospects are broad.

Among these, PSCs have gained significant attention for the cost-effective raw materials, simple manufacturing methods, and high photovoltaic conversion efficiencies. Data from the U.S. National Renewable Energy Laboratory illustrates that in just over a decade, the certified PCE of PSCs has exceeded 26% [25]. In contrast, it took half a century for crystalline silicon solar cells to achieve similar efficiency levels. Therefore, PSCs are expected to potentially replace crystalline silicon-based solar cells as the forthcoming generation of photovoltaic material, and they are heralded as the "dark horse of the energy revolution".

In this chapter, we will provide the perovskite properties and explore the applications in solar cell. Firstly, we outline the definition, chemical structure, and basic properties of perovskite materials. Next, we explore the distinct physical and chemical properties in solar devices, including superior light absorption coefficient and exceptional charge transport. Then, we analyze the operational principle of perovskite solar cells, focusing on generation, separation, and transport process of photogenerated electron-hole pairs. And we also introduce the basic configuration and components of perovskite devices, such as electrodes, active absorption layers, and transport layers. Additionally, we introduce the Shockley-Queasier limit in perovskite solar cells. We outline the challenges currently faced by 3D perovskite solar cells, mainly the challenge of stability, which 2D perovskites have the potential to address. In the study of 2D perovskite, understanding the crystal structure and crystallization mechanism is crucial to optimize their solar cells' performance. We first introduce some unique crystal structure characteristics of 2D perovskite. Following this, we explored the crystallization and growth mechanisms of 2D perovskite film using classical nucleation and growth theories. On this basis, we review various optimization strategies aimed at improving the film quality. These strategies include spacer cation engineering, additive engineering, solvent and antisolvent engineering, and process engineering, which regulate the crystallization and growth processes to achieve excellent 2D perovskite solar cell performance.

2.1 Hybrid halide perovskites

2.1.1 What is perovskite?

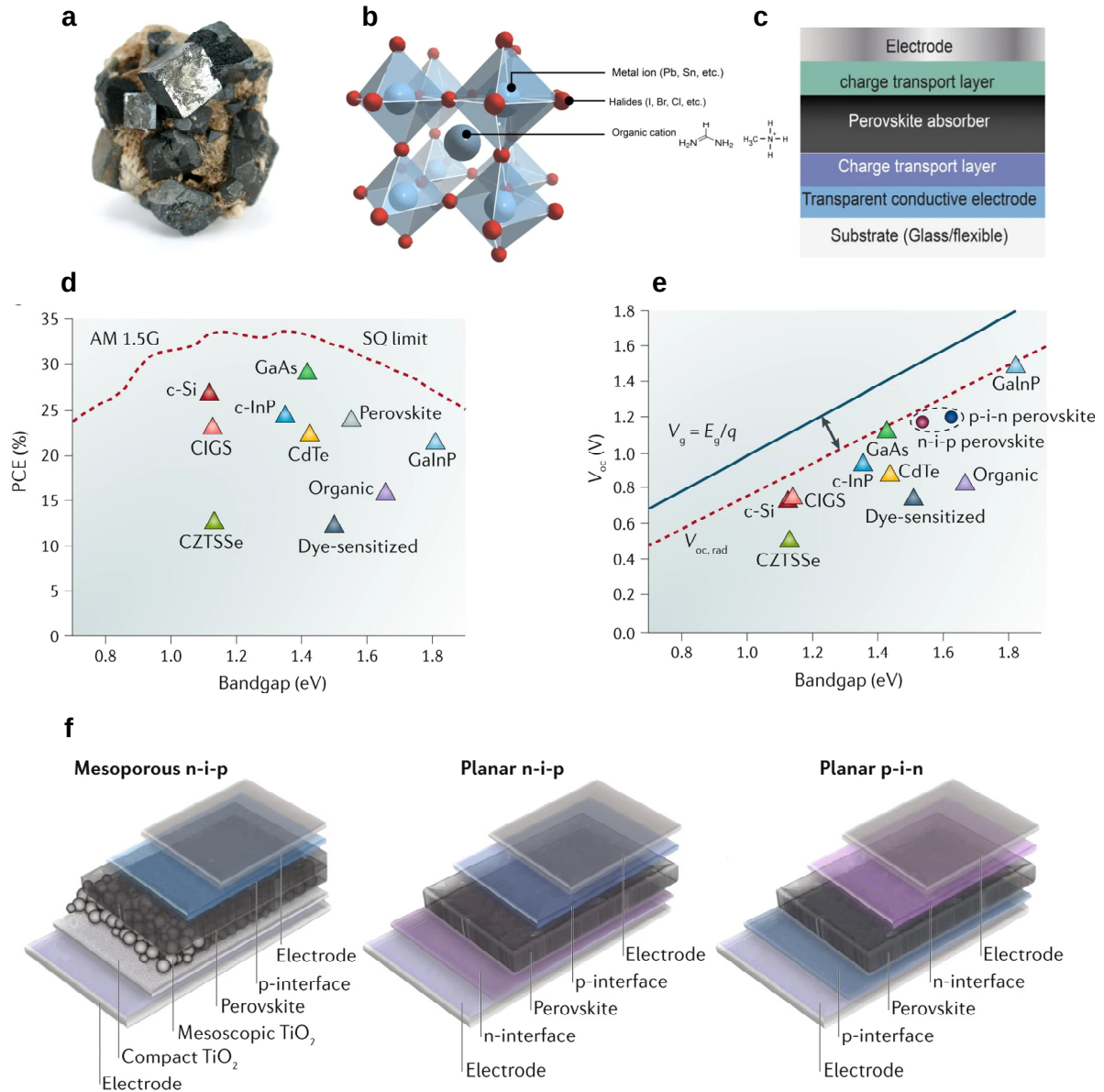


Figure 2-1. (a) Image of perovskite material (Source: Wikimedia commons, by Rob Lavinsky, iRocks.com, CC BY-SA 3.0). (b) Perovskite crystal structure. (c) Multi-layer configuration in a perovskite solar cell showing the main functional layers, (Source: CSIRO, <https://research.csiro.au/printedpv/perovskite/>). (d) Relationship between the PCE limit and bandgap, as determined by the SQ theory (dotted line) [10]. (e) Relationship between the radiative V_{oc} limit and bandgap (dotted line), alongside the V_{oc} of devices with record-breaking

PCEs (represented by triangles). (f) Perovskite solar cells (PSCs) with mesoporous n-i-p architecture, standard n-i-p planar heterojunction PSC, and p-i-n planar heterojunction PSC [10].

The word "perovskite" comes from a mineral called perovskite (**Figure 2-1a**), which was initially discovered by Gustav Rose in 1839 in Russia's Ural Mountains, this mineral was named to honor the contributions of Russian mineralogist Lev Perovski [28]. The chemical formula of perovskite is typically derived from calcium titanate (CaTiO_3), which exhibits a particular crystal structure known as the perovskite structure [29]. Lately, many scientists and scholars have adopted his name to designate all compounds with a perovskite structure, denoted as "perovskite". Therefore, perovskite is a distinctive crystal structure that can be expressed by a formula ABX_3 [10], as illustrated in **Figure 2-1b**. Within this structure, the A-site cation typically occupies the cavities between octahedra. And the B-site metal cations, together with six surrounding X-site anions, form an octahedral structure, where the B-site metal ion is positioned at the octahedron center. These octahedra share corners with six adjacent octahedra, forming a corner-shared $[\text{BX}_6]^{4-}$ octahedral framework that repeats to form a 3D network structure. In PSCs, the A-site typically consists of monovalent cations such as formamidinium (FA^+) [30], methylammonium (MA^+), or cesium (Cs^+); while B-site commonly includes the divalent metal ions (Pb^{2+} , Sn^{2+}) [31]; while X-site is generally filled by halide anions such as chloride (Cl^-), bromide (Br^-), or iodide (I^-) [32, 33]. And in this thesis, only the inorganic FA^+ cations at the A-site and Pb^{2+} cations at the B-site cations have been considered. The ionic radii of these elements are crucial for the stability of the perovskite structure.

In the perovskite structure, the octahedral factor (μ) and tolerance factor (t) are vital indicators of stability [34, 35]. A stable perovskite structure is formed when $0.44 \leq \mu \leq 0.90$ and $0.9 \leq t \leq 1.0$ [36], otherwise, a non-perovskite phase may appear. A modified τ is also used for halide perovskite, where r_i denotes the ionic radius, r_A represents the oxidation state of A, with r_A is greater than r_B , and $\tau < 4.18$ signifies the perovskite structure [37].

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \mu = \frac{r_B}{r_X} \quad (\text{Equation 2-1})$$

$$\tau = \frac{r_X}{r_B} - n_A \left(n_A - \frac{r_A / r_B}{\ln(r_A / r_B)} \right) \quad (\text{Equation 2-2})$$

Additionally, due to mismatches of ionic sizes, the crystal phase of perovskite materials can change with temperature. The halide perovskite structures are usually with lower symmetry than the cubic perovskite (α -phase) structure when it is at room temperature. Consequently, the lattice tends to transform into a tetragonal (β -phase) or orthorhombic (δ -phase) structure. Such as, the crystal phases of MAPbI₃ perovskite transform at different temperatures[38]. When the temperature is below 165K, the perovskite exists in the form of an orthorhombic phase (δ -phase); when between 165K and 327K, it transitions to tetragonal phase (β -phase); and when above 327K, it exists in cubic phase (α -phase). These phase transitions are attributed to changes in the superlattice symmetry at different temperatures [39].

2.1.2 Properties of perovskites

PSCs have garnered widespread attention for high photovoltaic conversion efficiencies, primarily due to the exceptional optoelectronic characteristics of perovskite [40, 41]. First, perovskites possess suitable and easily tunable bandgap widths (Energy Gap, E). For example, the band gap widths (E_g) of MAPbI₃ and FAPbI₃ perovskites are 1.5eV and 1.48 eV [42], which ensures the effective absorption of sunlight by PSCs and belongs to the most suitable range for active materials of photovoltaic devices. The band gap can be adjusted from about 1.48 eV to 2.9 eV, by changing the combination of cations (such as Cs⁺, MA⁺, FA⁺) and halogen ions (such as Cl⁻, Br⁻, I⁻) [43]; In addition, machine learning algorithms can also effectively predict and optimize the band gap of perovskite [42]. Second, perovskites are characterized by exceptionally high absorption coefficients. The absorption coefficient of FAPbI₃ perovskite film is about 10⁵ cm⁻¹ [44], which is ten times greater than GaAs film of the equivalent thickness. The high absorption coefficient indicates that PSCs can fully absorb sunlight, thus ensuring the utilization rate from the source. Moreover, organic-inorganic hybrid perovskites exhibit a low exciton binding energy, which is approximately between 2 meV and 50 meV, much lower than that of materials such as GaAs and CIGS. This low exciton binding energy means that in PSCs, photogenerated excitons easily split into free electrons and holes [45],

reducing the carrier recombination and consequently enhances the photoelectric conversion efficiency. Additionally, the electrons and holes in perovskite materials possess high mobility, which means that carriers can move quickly and reduce the recombination [46]. This long diffusion distance is due to the low defect concentration and bipolar transmission characteristics in perovskite films, which effectively reduces the recombination rate of carriers through the diffusion process. Based on above advantages, investigation on perovskite devices has become one of the latest frontiers and cutting-edge area in modulation technology.

2.2 Perovskite solar cells

2.2.1 Operational principles

The working mechanism of PSCs is introduced using an inverted device as an example, as shown in **Figure 2-1c**. The fundamental principle of perovskite solar cells is primarily divided into five key processes.: i. Photon absorption process: The light absorption layer captures photons, generating electron-hole pairs. ii. Exciton diffusion process: in this process, excitons, with a long diffusion length, travel within the crystal lattice, reducing recombination and allowing most excitons to reach the interface. iii. Exciton dissociation process: due to the internal electric field, excitons dissociate into free carriers [47, 48]. iv. Carriers transport process: the hole transport layer carrier free holes to the anode while the electron transport layer directs free electrons to the cathode. v. Charge collection: Free electrons and holes are collected by the cathode and anode, respectively, forming a potential difference that, in conjunction with an external load, establishes a closed circuit and produces a current [48].

2.2.2 Device structure

The basic structure of perovskite solar cells (PSCs) includes five main functional layers: anode layer, ETL, light-absorption layer (perovskite layer), HTL, and the cathode layer. The materials of each layer and their arrangement order vary according to the specific structure type, mainly including nip-type structure and pin-type structure, as shown in **Figure 2-1f**. In the nip-type structure, the sequence of layers from bottom to top is the cathode, followed by the electron transport layer, the middle is the light-absorbing layer, followed by the HTL, and finally the

anode. Conversely, in the pin-type structure, the sequence of ETL and HTL are opposite. In addition, there is a special mesoporous structure that contains a mesoporous layer, such as Al_2O_3 nanoparticles or TiO_2 , which not only plays the role of transmitting electrons but also supports the perovskite layer. However, due to the complex process and the mesoporous layer morphology affecting the overall performance of device, the device structure of PSCs has gradually developed towards a planar structure [49].

The anode layer material typically is composed of FTO or ITO transparent conductive glass, and its main function is to collect holes and form the cell's anode. Common materials for the HTL include PTAA, spiro-OMeTAD, etc. Its function is to effectively transport free holes generated by the active layer while blocking the movement of free electrons, thereby preventing the recombination of electrons and holes. The light-absorbing layer, constructed from perovskite materials, consists of materials like 3D MAPbI_3 and FAPbI_3 . Its function is to generate electron-hole pairs, serving as the core of the entire solar cell structure. Common materials for the ETL include PCBM, C_{60} , TiO_2 , SnO_2 , etc. Its function is to efficiently transport free electrons produced by the active light-absorption layer, prevent free holes' transfer, and provide an ohmic contact. The cathode layer typically uses highly conductive metals such as aluminum, silver, copper, etc., and its function is to collect electrons and form the cathode of the cell. The different layers and structural designs of perovskite solar cells enable them to efficiently absorb and utilize solar energy, showing great potential and advantages [10].

2.2.3 Shockley-Queasier limit

When a single-junction solar cell absorbs sunlight (AM 1.5G) and operates at a 300 K ambient temperature, the Shockley-Queisser limit [50] can be employed to calculate the maximum PCE and V_{oc} that are achieved at the radiation limit. **Figure 2-2e** shows the relationship between PCE and band gap, as well as the record efficiencies achieved by various solar cells. The band gap of halide perovskites, usually about 1.60 eV, could be tuned by mixing different ions at different components[10]. For instance, the mixed-cation halide perovskites achieved a band gap of about 1.50 eV, with a PCE of over 26%. Nevertheless, this value remains much below the theoretical limit of about PCE of 32% [10] (**Figure 2d**). From **Figure 2-2f**, the V_{oc} of PSCs

is higher than GaAs and GaInP-based solar cells that approach the V_{oc} limit. However, perovskite solar cells have not yet achieved this limit, mainly because of the recombination loss. Meanwhile, the V_{oc} loss in PSCs is markedly lower than that in organic and dye-sensitized solar cells [51-53].

2.2.4 Stability problems faced by 3D perovskite

Despite the high efficiencies of 3D PSCs already meet commercial solar cell requirements, they still face significant stability challenges. Referring to the outdoor application model of current commercial silicon solar cells, PSCs need to demonstrate stable performance under real-world conditions, including exposure to solar radiation, high temperatures, and atmospheric humidity and oxygen, for a duration of up to 25 years. For this reason, the long-term stability of perovskites concerns not only their intrinsic stability, but also their resistance to external environmental changes like light exposure, temperature variation, and high humidity [54]. The structural stability of perovskite and their tolerance to external environmental stress are key factors to ensure their long-term application. Considering thermal stability, perovskite materials are prone to decomposition at high temperatures. For example, the commonly used perovskite material MAPbI_3 easily decomposes into PbI_2 and CH_3NH_3 at temperatures above 85 °C, resulting in a significant decline in cell performance. This decomposition process not only affects the photovoltaic conversion efficiency, but also destroys the lattice structure, and then shortens the lifetime of the device. In addition, 3D perovskites are highly sensitive to moisture and degrade rapidly. For instance, when exposed to water, MAPbI_3 will hydrolyze to PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$, which destroys the physical structure of the material and greatly reduces the photovoltaic conversion efficiency. Additionally, inorganic perovskite degrades easily under long light exposure, especially under high-intensity UV light. Such degradation is mainly due to the interaction of photo-generated electrons and holes produced in the lattice with defects or impurities, which causes structural damage and reduced electrical properties. Further, light exposure may induce the breakdown of organic components in perovskite, and accelerate the degradation process [10].

To address the previously mentioned stability challenges of PSCs, researchers have proposed

a variety of strategies, including component engineering, additive engineering, interface engineering, and package technique. In terms of composition engineering, the thermal and operational stability of perovskite materials is effectively enhanced by the inclusion of elements such as FA⁺, cesium (Cs⁺) [55, 56], Eu³⁺, and bromine (Br⁻) [57, 58]. For example, FAPbI₃ is superior thermal stability to MAPbI₃ and FA⁺ doping facilitates to stabilize the alpha phase (cubic structure) in perovskite lattice. Cesium doping has been shown to significantly stabilize the crystal structure of perovskite and reduce the decomposition at high temperatures. Eu³⁺-Eu²⁺ functions as a “redox shuttle”, which specifically oxidizes Pb⁰ and reduces I₀ defects [59]. Bromine doping improves the phase stability and optimizes the photoelectric performance by selectively adjusting the specific band gap. For high bandgap perovskites, however, phase segregation of iodide and bromide phases can still be observed. In additive engineering, researchers promote the growth of perovskite crystals and enhance their crystal properties by introducing additives such as Lewis acid, Lewis base[60, 61], ammonium salt [61, 62], small molecules [63], or polymers[64]. In interface engineering, researchers use ionic liquids [65], low-dimensional perovskites[66], fullerenes[67] and other materials to optimize the contact between perovskite and the underlying interface, reduce the defect states and impurities at the interface, optimize energy level matching, and further improve the light stability and performance of PSCs [65]. With the advances in packaging technology, such as the "superstrate package" and "flip-chip package"[68], have effectively isolated the erosion of perovskite materials by water and oxygen, thus greatly improving its stability in high humidity environments.

These strategies have improved the external stability of 3D perovskite solar cells, but these methods often cannot fundamentally solve the instability of the intrinsic structure of the material. Its stability has been improved, but it still cannot meet the standards for commercialization. Thus, more attention was turned to 2D perovskite with better natural stability. In this sense, long-chain organic cations in 2D perovskites bring hydrophobicity and inhibit internal ion migration, providing much better intrinsic structural stability. Quasi-2D perovskites have better operational stability compared to their 3D counterparts. The instability of 3D structures is partly due to the low formation energy, which will be further aggravated by

humid conditions. On the contrary, 2D perovskites that have higher formation energy have unique hydrophobic organic ligands, which demonstrate better stability. Most importantly, ion migration has also been a major factor that leads to irreversible device degradation. The quasi-2D perovskites, having a lower rate of ion migration, could give a state of stable ion accumulation and therefore have a huge potential for cell stability.

2.3 2D Perovskite solar cells

2D layered hybrid metal-halide-organic perovskites are constructed by intercalating organic spacer cations into a continuous inorganic framework to reduce dimensionality. Within the 2D perovskite structure, the lead iodide octahedral inorganic framework facilitates essential photophysical properties including high carrier mobility, light absorption, and extended diffusion length, which makes these materials suitable candidates for efficient solar cells [69-72]. Additionally, the introduction of organic spacer cations provides several advantages for tuning the performance of 2D perovskites: (i) Hydrophobic cations act as an intermediate layer, various opt-electronic devices enhancing the material's moisture stability [73]; (ii) Van der Waals forces within organic spacer contribute to maintaining the structural stability [74, 75]; (iii) Introducing additional spacer cations into the lattice could induce distortions in the perovskite lattice, allowing adjustment of the bond angles between metal and halide elements, along with overlapping of metal and halide orbitals, thus modifying the bandgap independently of the number of the layers [76, 77]; and (iv) the incorporation of spacer cations creates inherent quantum well structures featuring high dielectric constants, mitigating the mismatch in work function between inorganic and organic layers, as shown in **Figure 2-2** [78-80]. Thus, the introduction of organic spacer cations enables tunable optical and electronic characteristics. The distribution of quantum wells and the crystallographic orientation significantly impact the performance of PSCs [81, 82].

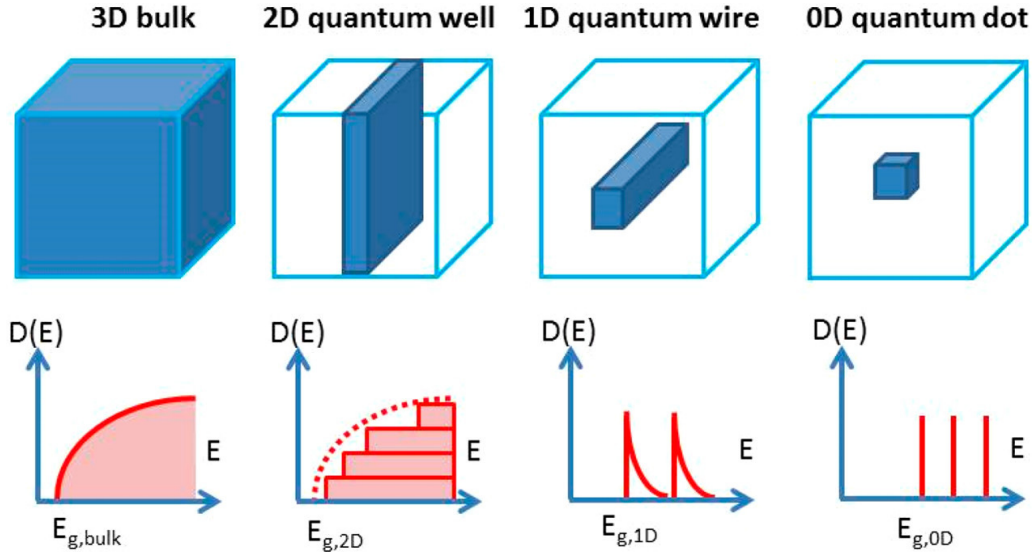


Figure 2-2. Schematic diagram of semiconductor materials with different dimensions (from 3D bulk to 2D quantum wells, 1D quantum wires, and 0D quantum dots) showing changes in structure and electronic density of states (DOS). As the dimensionality decreases, the electronic energy levels transition from a continuous to a discrete state [80].

2.3.1 Crystal structure of 2D perovskite

Layered 2D perovskites, developed by incorporating bulky, hydrophobic organic spacers into the crystal lattice to segment the 3D structure, have been identified as an effective strategy for enhancing the stability of the perovskite lattice. The crystal structure of 2D perovskite generally can be classified into $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ orientations in **Figure 2-3a**. Among them, the $\langle 100 \rangle$ orientation in two-dimensional perovskites is the most common and has been the most extensively studied [78]. Research has shown that $\langle 100 \rangle$ orientated 2D perovskites are the most appropriate structure for cells when compared to those with $\langle 111 \rangle$ and $\langle 110 \rangle$ orientated perovskite [83]. And $\langle 100 \rangle$ oriented 2D perovskites are typically categorized into the Ruddlesden-Popper (RP) phase, Dion-Jacobson (DJ) phase, and Alternating cations in the interlayer (ACI) phases [78, 84-86]. The RP phase's structure is denoted by a formula of $A_2B_{n-1}M_nX_{3n+1}$, the DJ phase by $A'A_{n-1}B_nX_{3n+1}$, and the ACI phase by $A'A_nB_nX_{3n+1}$. **Figure 2-3b** illustrates these related crystal structures. In these formulas, A is monovalent organic or inorganic cations; B denotes the divalent metal site (Pb^{2+} , Sn^{2+}); X is the halide anion site (I^- , Br^- , Cl^-); and n indicates the thickness of the $[PbX_6]^{4-}$ octahedral layer [87].

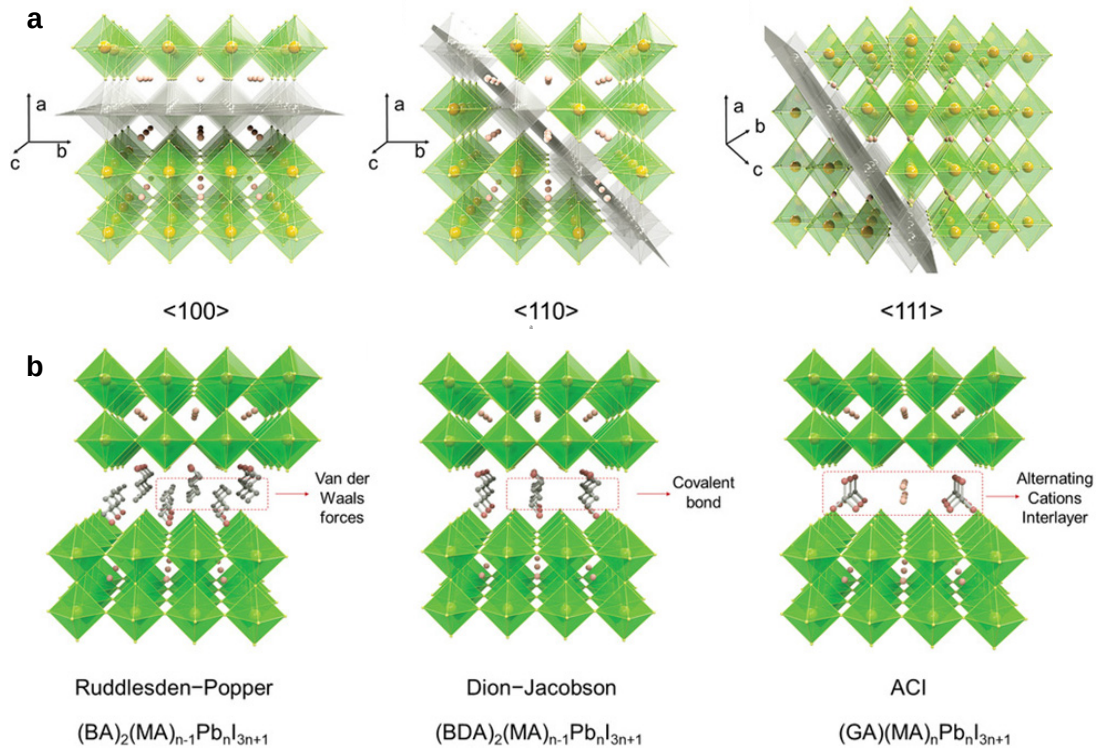


Figure 2-3. (a) Two-dimensional perovskites cut along $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ crystal plane [88]. Corresponding crystal structure of 2D perovskite, including (b) RP phase, DJ phase, and ACI phase, respectively [88].

2.3.2 Unique properties of 2D perovskite

The unique structure of 2D perovskite leads to multiple properties and novel applications in various optoelectronic quantum well effects devices [89-92]. The Goldschmidt tolerance factor (t) is employed to measure the impact of component atomic radii r on the perovskite lattice structure [93-95] (**Figure 2-4a**). For 3D perovskites, t typically ranges between 0.8 and 0.9 [75, 96] (e.g., MAPbI_3 , FAPbI_3). 2D perovskites are composed of larger amine cations, for example, HA and PEA, coordinate within the cages of inorganic BX_6 octahedra [86]. Because of the larger radius of these organic amine cations (where $t > 1$), inorganic sheets positioned at the upper and lower layers are unable to connect via shared corners, thus forming the 2D structure composed of alternating organic and inorganic layers [83]. The apparent relaxation of the t -values allows for the larger and more exotic A' cations, thus providing a new platform for getting the in-depth correlation between lattice distortions and material properties, especially

for the structure stability [97-99].

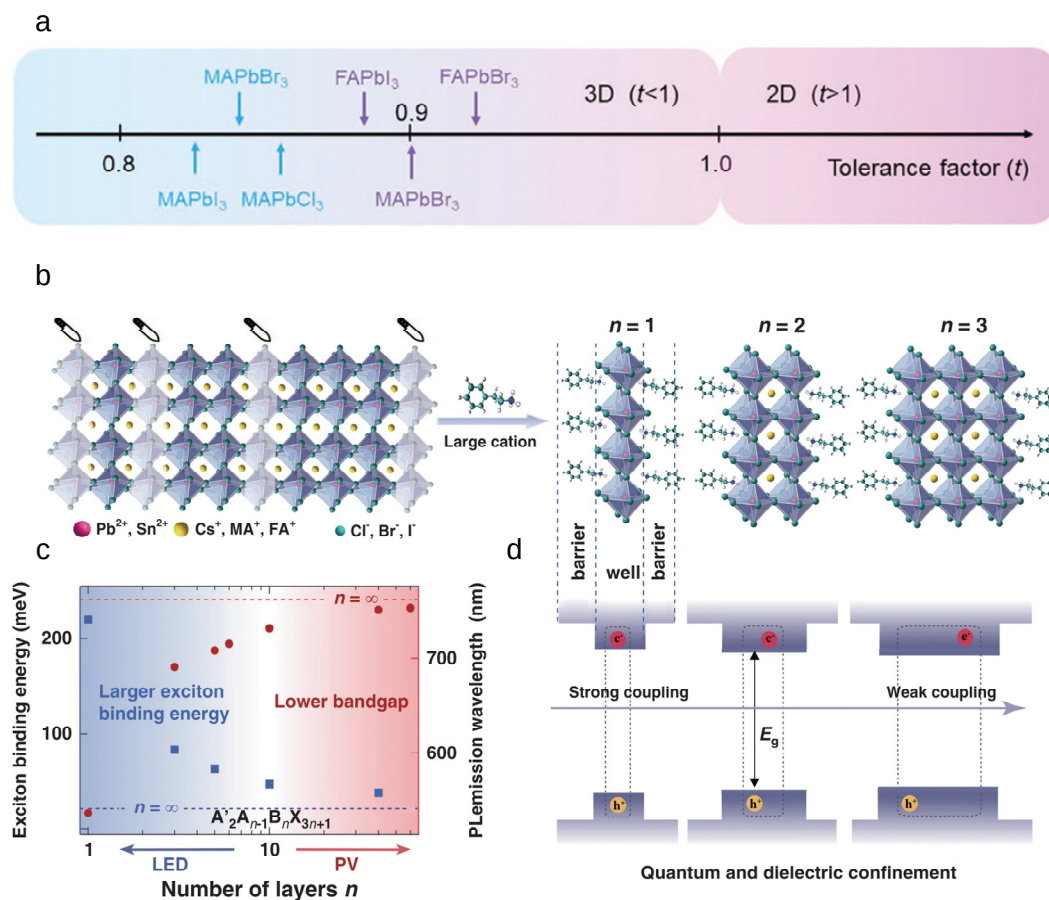


Figure 2-4. (a) The difference of tolerance factor in 2D and 3D perovskites structures [83]. (b) The structural characteristic of quasi-2D perovskite and illustration of crystal structures for 2D perovskites with varying layers. (c) The relationship between the exciton binding energy and bandgap with the layer numbers. (d) The relationship between quantum effects and dielectric confinement effects of two-dimensional perovskites and electronic properties [100].

The selection of organic spacer cations is crucial to regulating the lattice structure, durability, and optoelectronic properties of 2D perovskite [20, 101]. These cations mostly are the monoammonium and diammonium types, in linear, cyclic, aromatic, and heteroatom-containing varieties. Each cation could affect the perovskite interlayer interaction through its different chemical and physical properties. For instance, linear cations typically could facilitate the formation of simpler layered structures, cyclic and aromatic cations are known to enhance structural stability through π - π stacking and other intermolecular interactions. Additionally, when heteroatoms like O, F, or S are introduced into a cation, it can help optimize the

crystallization process in perovskites by hydrogen bonds and halogen interactions, which is significant to enhance the environmental stability and optoelectronic response of perovskite[102].

The terminal cationic groups of larger organic molecules interact with extended inorganic anions through hydrogen bonding. This interaction promotes the formation of natural quantum well structures (QWs) in perovskites (**Figure 2-4b**), where the organic insulation layer functions as a potential "barrier" and the inorganic layer functions as a "well", respectively [88]. The width of QWs influences the band gap of perovskite. An atomic-level sharp interface exists between the "barrier" and "well" (**Figure 2-4c**). Owing to quantum well effects and dielectric confinement effects, the E_b of 2D perovskites is greater than their 3D counterparts. Specifically, electrons and holes are trapped in the inorganic wells; this higher binding energy promotes to formation of stable excitons at room temperature, thus enhancing radiative recombination efficiency [100, 103]. The elevated E_b and notable exciton luminescence performance make quasi-2D perovskites exceptional candidates for LED applications [100]. Moreover, the confinement strength also depends on the thickness of the quantum wells; the E_b value can be influenced by selecting barriers with varying dielectric constants, as dielectric confinement diminishes with an increased n (**Figure 2-4c**) (16). Additionally, Sargent et al. demonstrate the quasi-2D perovskite family combines the superior stability of 2D perovskite with the outstanding optoelectronic properties of 3D perovskite. Density Functional Theory (DFT) results reveal introducing PEA between perovskite layers induces quantifiable van der Waals interactions, thereby increasing formation energy and enhancing material stability. Lower n values correspond to higher stability; higher n values lead to increased optoelectronic efficiency (**Figure 2-5a**) [104]. Thus, quasi-2D perovskites show tremendous potential in achieving efficient and stable solar cells.

2D perovskites, which are created by incorporating large ammonium cations within the three-dimensional perovskite structure, consist of alternating layers of insulating organic spacer layers and inorganic (BX_6) planes [88, 105, 106]. These organic spacer layers provide an effective barrier against ion and water penetration. Additionally, the strong van der Waals forces among the spacer cations result in higher formation energy [107], thus imparting inherent

lattice stability. Furthermore, the inherent dielectric disparity between layers leads to the formation of multiple quantum wells (MQWs) [88]. The disordered tendency of quantum wells to grow parallelly inevitably leads to serious charge recombination. Moreover, the path of carrier transport is obstructed by the insulating spacer layers, resulting in poor carrier mobility and diffusion rates, significantly limiting the photovoltaic performance (**Figure 2-5b**). Thus, achieving vertical growth and fine phase alignment of spacer layers is crucial for realizing efficient 2D PSCs.

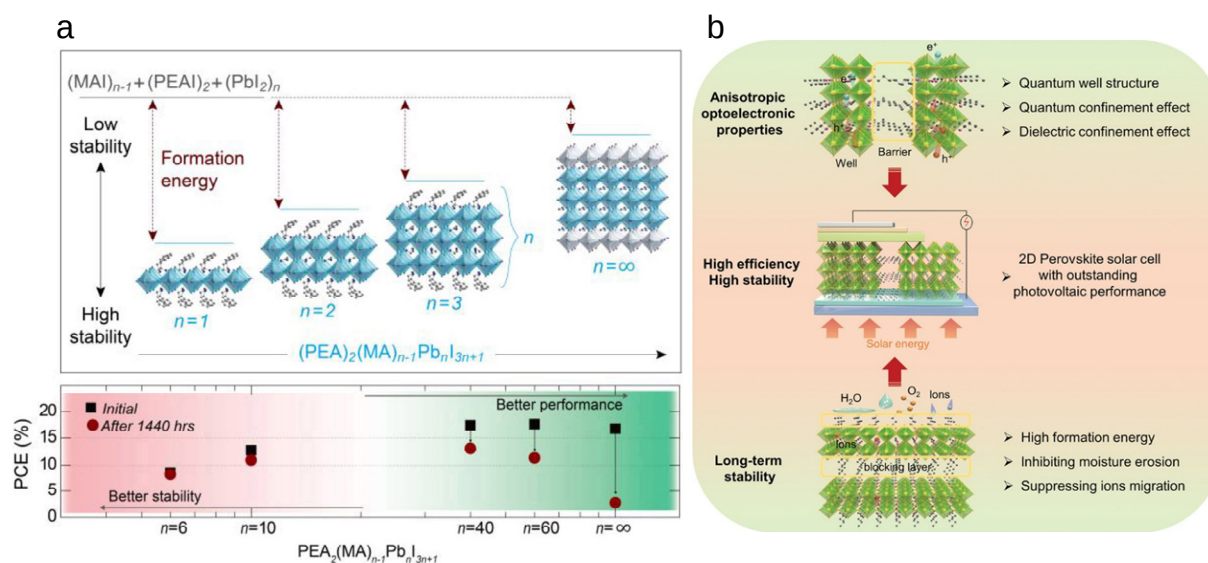


Figure 2-5. (a) Illustrations of halide perovskite with different layer numbers (n). These structures transition of perovskite with the dimensions from low- n to high- n phase of 2D perovskite. The relationship between device performance and the function of n . As n increases, performance improves, but stability declines [104]. (b) The diagram illustrates the advantages of 2D perovskites regarding their optoelectronic performance and stability [88].

2.3.3 Crystallization and growth theory

During the crystallization process of perovskite, nucleation is an essential initial stage involving two basic forms of homogeneous nucleation and heterogeneous nucleation. The solution must be supersaturated to initiate crystallization [108]. This factor ultimately determines the overall quality of perovskite film. In homogeneous nuclei, the crystal nuclei can form naturally in the precursor solution, and this process is mainly analyzed from a thermodynamic perspective and

can be described by Gibbs free energy (ΔG) [86, 109-111],

$$\Delta G = \Delta G_s + \Delta G_v = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 K_B T \frac{\ln(S)}{V} \quad (\text{Equation 2-3})$$

Where γ denotes *the* nucleus surface energy, k_B represents Boltzmann constant, and V is nucleus molar volume. ΔG_s is the surface free energy, which is directly proportional to the square of the nucleus radius (r^2). And ΔG_v is the volume of free energy, which is proportional to the cube of the nucleus radius (r^3). The surface free energy is positive, reflecting the increase in the solid-liquid interface area when new nuclei are formed; the volume free energy is negative, indicating the decrease in free energy when transitioning from liquid phase to solid phase [106, 112]. The homogeneous nucleation rate can be expressed by an Arrhenius-type equation [86, 111, 113]:

$$\frac{dN}{dt} = A \exp\left[\frac{-\Delta G_N}{K_B T}\right] = A \exp\left[\frac{-16\pi\gamma^3 V^2}{3K_B^3 T^3 N_A^2 (\ln S)^2}\right] \quad (\text{Equation 2-4})$$

where ΔG_N is critical free energy, N , A , and N_A represent the number of nuclei, the pre-exponential factor, and Avogadro's constant, respectively. Equation (2-6) reveals the effects of the supersaturation of the solution, the temperature, and the surface free energy of nucleation rate. When the solution's supersaturation temperature is high, the critical nucleation energy decreases, leading to a corresponding increase in the nucleation rate. In practice, heterogeneous nucleation is more common, and nuclei are typically preferentially formed on the surface, substrate, defects, suspended particles, or impurities because these locations provide lower nucleation energy barriers[114, 115]. Therefore, to adjust the free energy in heterogeneous nucleation, the correction factor $f(\theta)$ is introduced, which is dependent on contact angle θ , reflecting the influence of the substrate or impurity on the nucleation process.

$$f(\theta) = \left(\frac{2 - 3\cos\theta + \cos^3\theta}{4} \right) \quad (\text{Equation 2-5})$$

$$\cos\theta = \frac{\gamma_{cs} - \gamma_{sl}}{\gamma_{cl}} \quad (\text{Equation 2-6})$$

The relationship between homogeneous nucleation and heterogeneous nucleation-free energy is as follows:

$$\Delta G_{he}^* = \left(\frac{2 - 3\cos\theta + \cos^3\theta}{4} \right) \Delta G_{ho}^* \quad (\text{Equation 2-7})$$

Where r_{cs} , r_{cl} , r_{sl} represent the surface energy between crystal and substrate surface, crystal and liquid and substrate surface. $f(\theta)$ is a correction factor, $0 \leq f(\theta) \leq 1$. When the saturation of the solution is low, heterogeneous nucleation is more likely to occur, inhibiting homogeneous nucleation on colloidal particles and promoting high-density heterogeneous nucleation.

Crystal growth primarily progresses along two pathways: first, monomers diffuse from bulk solution to particle surface; second, the monomer molecules undergo chemical reactions on the particle surface. The diffusion process can be explained using Fick's first law of diffusion [86, 109, 116],

$$J = 4\pi r^2 D \frac{dC}{dx} \quad (\text{Equation 2-8})$$

Here, J denotes the total monomers flux, D represents the diffusion coefficient, C represents the monomers concentration, and r denotes the radius of particles. When the system reaches a steady state, J at the surface of particles could be represented using the formula as follows [117]:

$$J = 4\pi Dr (C_b - C_s) \quad (\text{Equation 2-9})$$

Where C_b and C_s respectively represent the monomer concentration in the bulk solution and at the interface between the particles and the solution. During the surface reaction phase of the monomers, J denotes the rate of monomer consumption at the surface of particle. This relationship can be described as follows:

$$J = 4\pi r^2 k(C_i - C_r) \quad (\text{Equation 2-10})$$

In this context, k denotes the rate constant for the surface reactions, The solubility of a spherical particle, denoted by C_r , is associated with a particle of radius r . In the growth modes governed by diffusion control and reaction control, the former tends to produce particles of uniform size, while the latter equalizes the concentration of monomers at the surface of particle with that in the solution. Both diffusion and surface reactions can become the rate-limiting steps in the overall growth process.

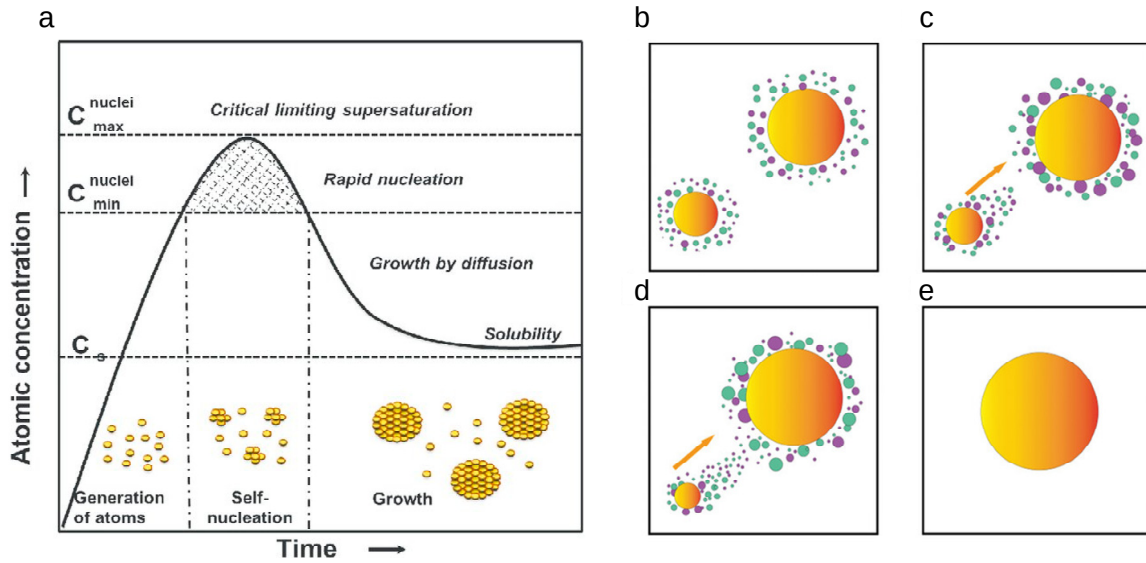


Figure 2-6. (a) LaMer model for explaining the nucleation and growth of perovskite crystals in precursor solutions [118, 119]. Ostwald maturation model of dynamic coarsening of perovskite particles including (b) the beginning phase, (c) the early phase, (d) the middle phase, (e) and the end phase [113].

The classic LaMer mechanism typically is used to explain nucleation and crystal growth process of perovskite[118]. According to the LaMer model (**Figure 2-6a**), the nucleation and growth process can be separated into three stages: the first region is the pre-nucleation stage. Due to the substrate annealing process, which promotes solvent evaporation, the solution concentration continues to increase until it reaches the saturation concentration (C_s), but no obvious nucleation has occurred at this stage[120]. The second stage is the nucleation stage. As the continued evaporation of solvent, the solution concentration reaches the critical limiting

supersaturation. At this time, the nucleation rate increased significantly and formed many crystal nuclei. Meanwhile, the consumption rate of the monomer exceeds the solvent's evaporation rate [121]. The precursor solution concentration gradually decreases, the nucleation rate drops to zero at t_2 , and the nucleation process terminates. The third stage is the crystal growth stage. The crystal nucleus continues to grow, under the continuous supply of monomers. When the solution concentration falls below C_s , crystal growth terminates, and finally the perovskite film is formed [122]. Therefore, controlling the processes of nucleation and growth is essential for perovskite films. Rapid nucleation, followed by slowed crystal growth through shortening the supersaturation period, results in a high-quality film. This mechanism shows that the crystal quality and uniformity of perovskite films can be optimized by precisely regulating the concentration and evaporation rate of the precursor solution [109, 123]. The Ostwald ripening theory is also an important crystal nucleation growth model used to explain the growth process of perovskites. Based on the Gibbs-Thomson mechanism [111], it explains the coarsening of particles via the dissolution of smaller grains and the growth of larger ones, driven by surface chemical potential differences[120]. This theory effectively accounts for the competitive growth of particles in solution, promoting perovskite formation through the dynamic coarsening of smaller particles and the redeposition of material onto larger ones in **Figure 2-6(b-e)**. This classic Ostwald ripening process has been shown to promote perovskite growth [124].

2.3.4 Crystallization mechanism of 2D perovskite films

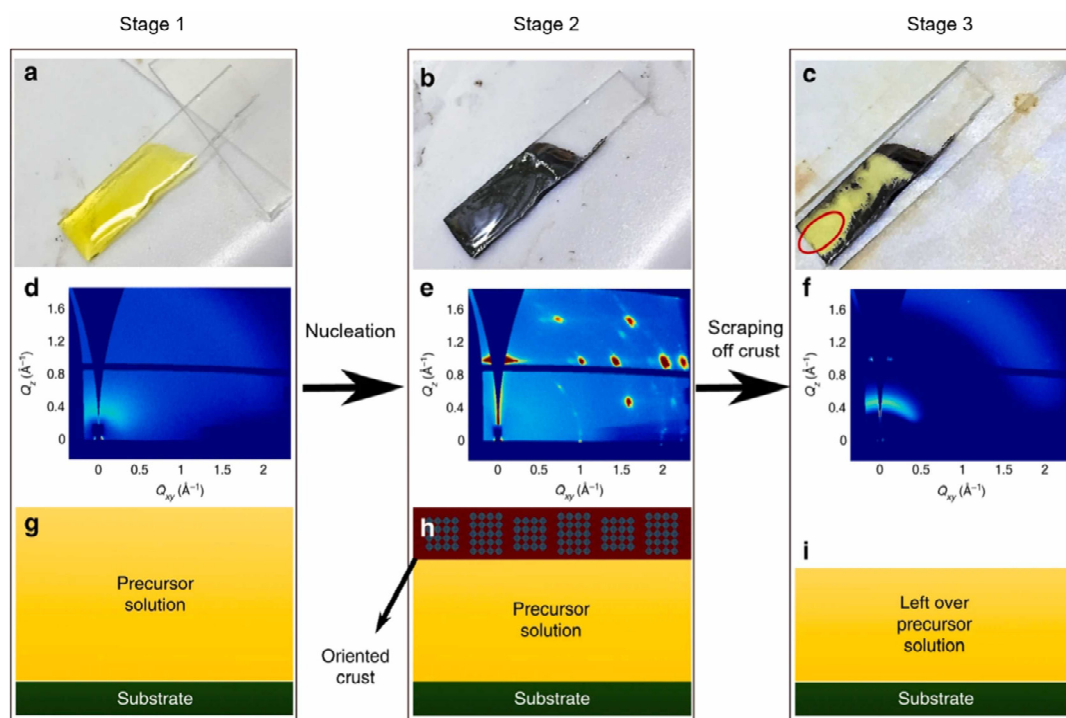


Figure 2-7. (a) Optical images along with GIWAXS data depict the stages of a top-crust scraping experiment. (a) the optical image and (d) corresponding GIWAXS pattern displays a yellow fluid indicative of the absence of crystalline structures (g). As the process into stage 2, the surface darkens upon thermal treatment (b), and the GIWAXS pattern (e) reveals a vertical orientation of 2D perovskite (h). In the subsequent stage 3, this top-crust of 2D perovskite is mechanically removed using a blade-scraping technique to reveal the underlying yellow precursor solution that remains uncrystallized (c). The GIWAXS pattern (f) from this newly exposed area shows only diffuse scattering, suggesting it retains its non-crystalline precursor form (i) [125].

The nature of layered 2D perovskite leads to anisotropy in its conductivity and carrier mobility, and the PSC efficiency depends on the orientation corresponding to the desired charge transport direction [120]. The organic and inorganic layers have the potential to grow parallel or perpendicular to the substrate, and the insulating cations in the parallel organic layers could hinder vertical charge transport. To achieve vertical growth of 2D perovskite film, it is essential to investigate the fundamental mechanisms governing their vertical orientation during

crystallization[126]. Typically, the crystallization of perovskites begins with precursor solutions and primarily includes two stages: nucleation and growth. As the solvent gradually evaporates, the perovskite concentration increases, prompting rapid nucleation of aggregated particles under supersaturated conditions [40]. Within the perovskite precursor solution deposited on substrates, nucleation can occur at three potential sites: the air-liquid interface, the bulk solution, and the solid-liquid interface [125]. Uniform nucleation within isotropic bulk solution typically results in randomly oriented crystal growth. In contrast, the substrate-liquid interface, characterized by anisotropic environmental conditions and interactions like van der Waals forces between the crystal and substrate, tends to favor parallel rather than vertical orientation [127]. Chen et.al., demonstrated the top-crust scraping test to investigate the crystallization process via the in-situ GIWAXS technique, as illustrated in **Figure 2-7**. They meticulously traced the nucleation process based on $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ perovskite across three phases, The first stage involves a yellow precursor solution; in the second stage, following annealing, the air-liquid interface immediately displays a black phase. The third stage, through the top crust test, reveals a yellow uncrystallized perovskite beneath the black phase. These findings reveal that the crystallization starts at the air-liquid interface into spreads throughout the interior of film. Nucleation beginning at the interface between air and liquid can facilitate to form a vertically oriented top layer of solid crystal film, acting as a growth template for subsequent crystals. The heterogeneous environment plays a crucial role in promoting the vertical orientation of 2D perovskite film [128]. Similarly, Yuan et al. reported a mechanism for the templated crystal growth of 2D perovskites based on 3D-like phase perovskite, which also initiative at the surface of solution [129]. The rapid drying of the solvent on the liquid surface leaves behind a 3D-like perovskite with a periodic network of corner-sharing octahedra, driving the formation of 2D perovskites. When A-site small-sized organic cations are continuously consumed, more L-site bulky organic cations engage in the coordination process, which results in the formation of higher- n 2D perovskites [129]. Additionally, the lattice matching between the layered perovskite phase and 3D-like perovskite phase is also responsible for the preferred out-of-plane orientation growth, and this matching offers valuable insights into controlling the layered perovskite's orientation [125].

2.4 Optimization strategies for crystallization

To obtain a highly vertical orientation of 2D perovskite films, researchers have adopted many optimization strategies to control the crystallization kinetics. In this part, we will systematically review efficient optimization techniques, including spacer cation engineering, additive engineering, solvent and antisolvent engineering, and solution processing techniques.

2.4.1 Spacer cations engineering

The strategy of spacer cations engineering plays a crucial role in stabilizing lattice structures and promoting vertical orientation in the field of 2D perovskite film. These spacer cations are crucial for maintaining the stability of the layered structure of 2D perovskites, supporting the stacking of inorganic layers, and significantly influencing the materials' electronic and optical properties [130]. Functionalized spacer cations, which may contain amino, carboxyl, or other polar groups, are critical in research and development for enhancing interlayer bonding through strong hydrogen bonding or electrostatic interactions. These interactions not only stabilize the material structure but also modify the pathways and rates of carrier transport. Martin Kaltenbrunner et. al., have innovated by incorporating a novel large organic cation, alpha-methylbenzyl ammonium iodide (MBAI), into the photoactive layers of perovskites.

The interaction of the ammonium groups ($-\text{NH}^3+$) of MBA with the sulfonic groups ($-\text{SO}^3-$) of the hole transport layer induces surface dipoles at the interface due to electrostatic attraction, enhancing charge extraction and elevating the open-circuit voltage (**Figure 2-8a**). This breakthrough has enabled the development of lightweight, flexible, ultra-thin, and transparent conductive oxide-free 2D perovskite solar cells. A photovoltaic module composed of 24 interconnected 1 cm^2 solar cells has been demonstrated to power a hybrid solar-operated quadcopter autonomously [131]. Additionally, Wei Huang et. al., introduced a bulky alkylammonium species, 2-(methylthio) ethylammonium chloride (MTEACl), which facilitates sulfur-sulfur interactions. These interactions, extending beyond the weaker van der Waals forces, enhance interlayer cohesion and result in pinhole-free perovskite films with preferred orientation, as illustrated in **Figure 2-8b**. This optimized orientation is crucial for efficient charge transfer processes, significantly enhancing the stability of 2D PSCs [132].

Additionally, Huang et. al., innovatively introduce a molten salt spacer, n-butylamine acetate (BAAc), as a replacement for traditional halide spacers, n-butylamine iodide (BAI), to achieve pure phase QWs in 2D RP perovskite devices. The formation of strong chelation and hydrogen bonds formed by BAAc inhibit the colloid aggregation and form a uniform distribution of intermediate phase gel, which promotes the formation of pure phase QWs films[135]. Prof. Liu's team also has made significant advances in developing new spacer cations, synthesizing various new thiophene derivatives that markedly improve the orientation and electronic properties of 2D perovskites [136-139].

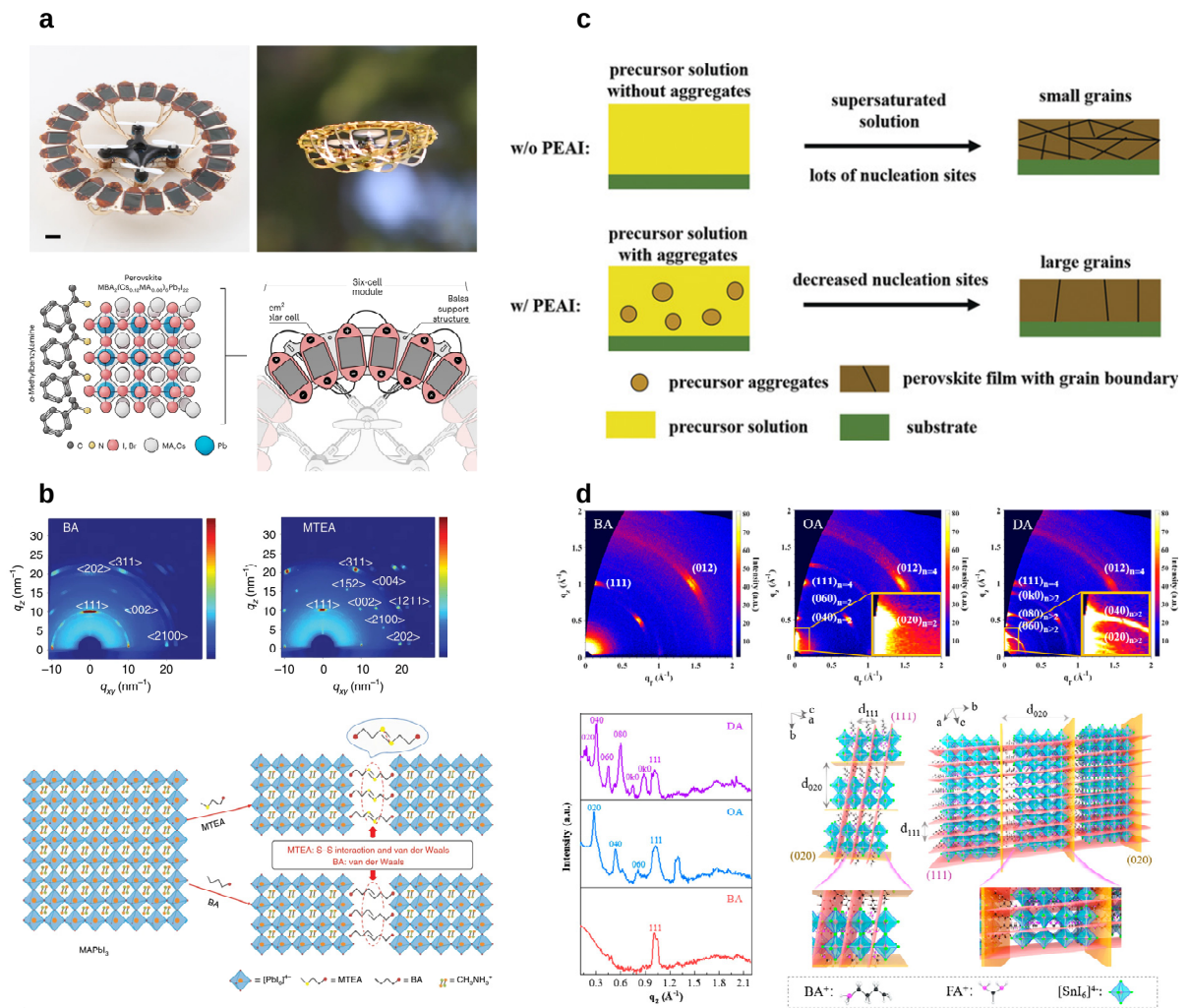


Figure 2-8. (a) Illustration of the 2D perovskite structure of $\text{MBA}_2(\text{CS}_{0.12}\text{MA}_{0.88})_6\text{PbI}_{22}$, a diagram of the assembly of six ultra-light PSCs, and a photograph of the Solar Hopper in flight [131]. (b) GIWAXS data and corresponding explanations of 2D perovskite orientation regulated by large molecular cations BA and MTEA [132]. (c) Formation diagram of 2D

perovskite films with/no additional PEAI spacer cations [133]. (d) 2D GIWAXS pattern showing the intensity distribution along the qz direction for Sn-based 2D perovskite films inserted on different large-volume cations, such as BA, OA, and DA, respectively [134].

Fluorination of large cations in 2D perovskites also represents a potent strategy to enhance the vertical orientation, by increasing the dipole moment of the selected organic ions. This improvement immediately increases carrier lifetime, charge separation efficiency, and crystal overall quality [140]. For example, Professor Yongsheng Liu and his research team have developed a high-performance 2D RP perovskite device using β -fluorophenethylamine (β -FPEA) as its spacer cation within perovskite. The introduction of fluorine atoms on the phenyl rings of PEA cations, synthesized through reactions with glycolic acid, attained an optimal PCE of 19.11%. The improvements in device performance are attributed to the high dipole moment of β -FPEA, which improves the interaction between spacer cation and $[\text{PbI}_6]^{4-}$ octahedra, facilitating charge separation and promoting the growth of high-quality, large crystals preferentially oriented in the vertical direction [140]. Additionally, Ming Shao et al. developed a novel fluorinated phenethylammonium (PEA) cation used as a spacer to fabricate 2D perovskite film. By replacing the hydrogen atom located at the para position of PEA cation's conjugated benzene ring with a fluorine atom, 4-fluorophenethylammonium (4FPEA) was synthesized as the organic spacer. The strong dipole field induced in this structure significantly promotes the dissociation of charges and enables the fluorinated-2D perovskite preferred vertical direction. These improvements significantly improved the efficiency of solar cell from 11% to over 17% [141].

Furthermore, binary spacer cations are also an effective method to improve the orientation. For example, Baomin Xu et al. successfully prepared a series of novel binary spacer 2D perovskite films. The interaction of binary spacers is demonstrated by adding 50% BA to the PBA-based 2D perovskite precursor solution. This decreases the nucleation sites and increases the colloidal size, producing a highly smooth film with bigger grains and greater crystal orientation [142]. Jianbin Xu et al. proposed that by adding guanidine (GA^+), a symmetrical cation with three amino groups, to BA-based 2D perovskites, GA molecules can be inserted into 2D lattice by occupying BA positions [143]. Due to the enhanced interlayer interaction, the crystallinity,

optoelectronic properties, and stability can be improved simultaneously. The resulting new 2D RP perovskite films show a preferential vertical orientation. Additionally, BA/PEA series mixed cations also have been widely demonstrated to improve the vertical orientation of 2D perovskites films [81]. As illustrated in **Figure 2-8c**, Lian et al. demonstrated that the incorporation of 2-phenylethylamine iodide (PEAI) into the $\text{BA}_2\text{MA}_4\text{Pb}_5\text{I}_{16}$ perovskite precursor solution results in aggregation behavior. Due to pre-aggregation reducing the nucleation site, the grain size increases, and the (111) orientation is enhanced [133].

In selecting spacer cations for 2D perovskite materials, it is essential to consider not only their chemical properties and structural forms to ensure charge balance and structural stability, but also their shape of amino head and organic tail. The size of the amino head should be moderate so that it can be accurately embedded in the gap of the inorganic layer. The shape of the organic tail can be branching, linear, or cyclic form [78]. Among them, linear spacer cations can provide the greatest flexibility, which is conducive to optimizing the interlayer spacing and enhancing the dynamic adjustment ability of the structure. However, larger tail structures may lead to increased steric hindrance and reduced freedom of movement, which could detriment the stability of the perovskite structure in some cases. Too large tail structures may lead to increased interlayer spacing, thereby affecting the charge transfer efficiency and the overall stability[78]. For instance, Li et al. investigated the impact of different alkyl chain lengths on the orientation of 2D Sn-based perovskite films by incorporating BA, OA, and DA, alkylamine spacer cations, respectively. These results show that increasing the alkyl chain lengths in perovskite disrupts the phase distribution and reduces the vertical orientation, as depicted in **Figure 2-8d**. Conversely, shorter alkyl chains facilitate the vertical orientation of 2D perovskite films [134].

2.4.2 Additive engineering

Additive engineering is a common method to improve crystallization quality of perovskite. By introducing specific additives into the precursor solution, such as chloride, hydrohalic acid, and sulfur-containing additives, the growth direction and crystallization orientation of perovskite can be precisely controlled. These additives not only affect the crystallization process, but also

participate in the trap passivation of the perovskite surface or bulk, and adjust the interface structure and energy level, thereby improving the overall performance of electronic devices.

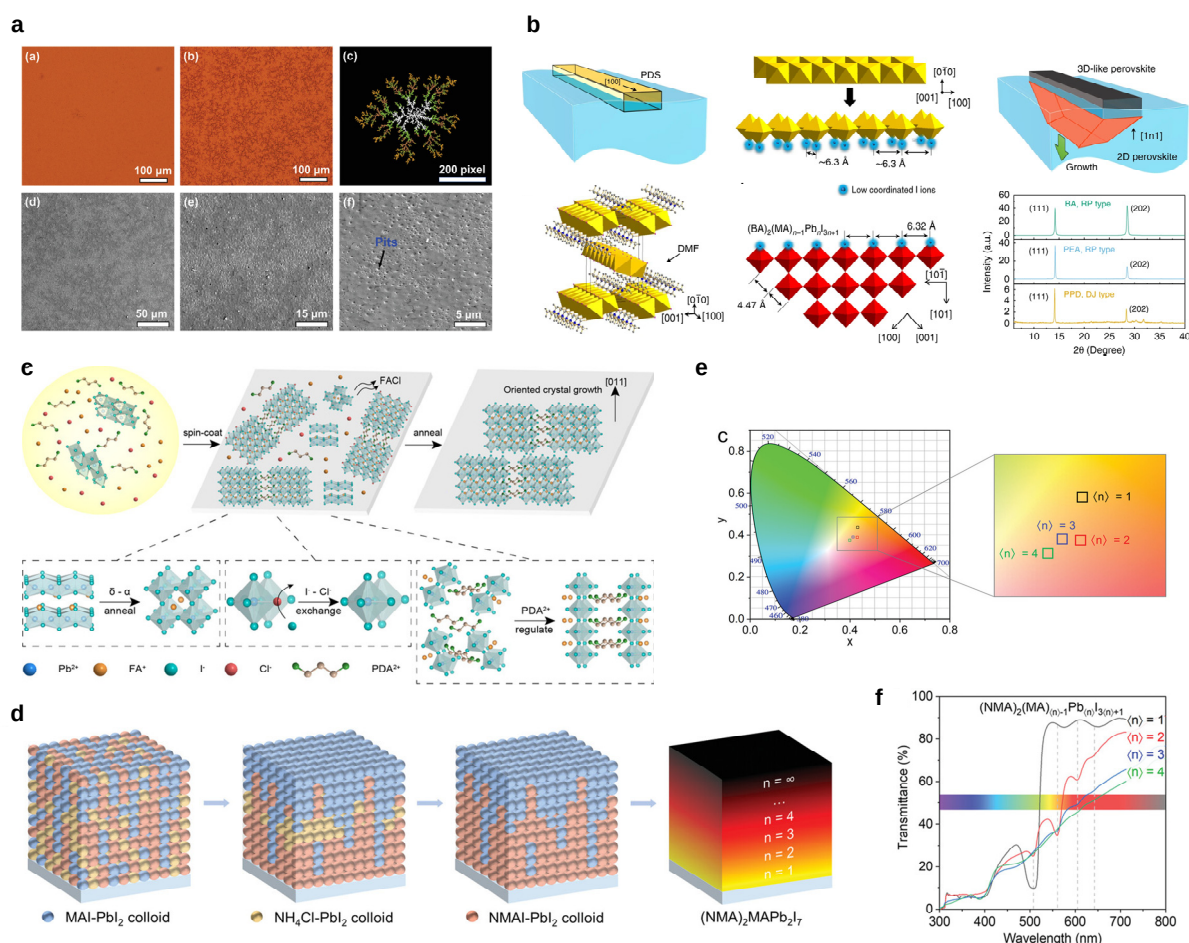


Figure 2-9. (a) Optical transmission images of 2D perovskite films, including a) undoped with MACl, b) doped with MACl. c) Brownian trees generated through DLA-induced simulations. d–f) SEM images of 2D perovskite films captured at different magnifications [144]. (b) Diagram of lattice matching of BA-based RP films determines crystal orientation via NH_4Cl additive [129]. (c) Diagrammatic representation of the microscale growth dynamics of 2D perovskite films facilitated by FACL [105]. (d) Illustrative diagrams showing the formation of well-graded 2D perovskite film with NH_4Cl additives. (e) Color coordinates of the NMA-inserted 2D perovskite films, depicted on the CIE 1931xyY chromaticity diagram. (f) Transmission spectra of NMA-inserted 2D perovskite films with different n [145].

Chloride is a common additive used in halide perovskite (Cl^-). Kenneth P. Ghiggino et al. proposed that adding chlorine-containing additives such as methylamine hydrochloride (MACl)

helps the perovskite film grow preferentially along the (110) direction [146]. Cl^- can effectively reduce the trap density and extend the charge diffusion time and carrier lifetime. Fei Zheng et al., report the formation of Brownian tree-like dendrites in 2D perovskite films by doping methylammonium chloride (MACl) in **Figure 2-9a**. Studies reveal dendrites consist of grains dominated by large- n phase, whereas the non-dendritic areas of the film are made up of small- n RPPs grains, related to surface pits on the film resulting from the evaporation of MACl [144]. It is suggested that dendritic structures in MACl-doped 2D perovskite films result from diffusion-limited aggregation of MA-rich domains, which first crystallize from the precursor, leading to enhanced organization and crystallinity of 2D perovskite. This is beneficial to improve the photovoltaic performance [144, 147]. Yongbo Yuan et al., suggest that the addition of NH_4Cl primarily controls the crystal orientation of 2D perovskites from in-plane to out-of-plane direction, revealing the mechanisms behind the directional growth in 2D perovskite film. Growth initiates with the precipitation in 3D perovskite in the solution during the initial crystal growth phase. Since 2D perovskites dissolve poorly in DMF solutions, the 2D perovskite subsequently grows followed by the 3D-like phase, which serves as a growth template, facilitating the vertical orientation of 2D perovskite layers, with preferential orientation likely due to the lattice matching between the 2D perovskite lattice and 3D-like phase in **Figure 2-9b**. GIWAXS results show that NH_4Cl can increase crystallinity and enhance the quality of films, as evidenced by sharp and discrete diffraction spots [129]. Additionally, Gang Chen et al., have proposed a well-oriented 2D perovskite films using formamidinium chloride (FACl) additives and comprehensively studied the role of chloride in crystallization process. As depicted in **Figure 2-9c**, during thermal annealing with a high temperature, three-phase transitions occur: (I) FAPbI_3 converts from the energetically unstable δ -phase into α -phase; (II) chloride intermediates undergo the transformation into 2D perovskite through ion exchange of I^-/Cl^- , followed by the evaporation of FACl additives; (III) PDA molecules bond with the perovskite slabs through hydrogen interactions. Consequently, the 2D perovskite film treated with FACl demonstrates a strong preference for vertical orientation [105].

To improve the vertical orientation of 2D perovskite films, the application of sulfur-containing additives, such as thiocyanates (SCN^-) using guanidinium thiocyanate (GuaSCN), also plays

an important role [148]. The inorganic lead (Pb^{2+}) within the perovskite interacts with the sulfur and nitrogen donors in the thiocyanate, forming Lewis's acid-base adducts. During the annealing process, the thiocyanate ions facilitate the release of gases such as methylamine (CH_3NH_2) and hydrogen thiocyanate (HSCN). This release of CH_3NH_2 gas enhances the crystallinity and grain size. Moreover, the addition of thio-semicarbazide (TSC) induces significant vertical growth orientation, resulting in superior 2D perovskite performance. Furthermore, Hualin Zheng et al. also demonstrated that by utilizing the synergistic effect of DMSO and TSC in the perovskite precursor solution, which results in 2D perovskite film with increased grain size, uniform morphology, and vertical orientation [121].

The perovskite precursor solution consists of colloids that feature a framework of organic and inorganic lead halide. The colloids can serve as nucleation sites, affecting the coverage and morphology of deposited films. Controlling the dispersion of colloids in precursors is critical to producing uniform films. Changes in colloid concentration can alter the morphology of the perovskite during deposition. He et al. developed a dense(4-AMP) $\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+}$ perovskite film by using a 2-aminophenol-4-sulfonic acid (APSA) additive to inhibit the colloids' formation. The introduction of APSA enhances the precursor solution solubility and substrate coverage. Additionally, the fine control of crystallization kinetics via APSA additives produces 2D perovskite films with a uniform energy landscape. Electrical analysis reveals that this uniformity significantly reduces defect density and energy disorder. Consequently, the quasi-Fermi level splitting is suppressed, and Shockley-Read-Hall recombination is greatly decreased by the uniform energy landscape, thereby minimizing voltage losses [149]. Additionally, Yi Yang et al. optimized the deposition dynamics of organic cation colloids, by the strategic introduction of ammonium chloride. As shown in **Figure 2-9d**, the addition of the yellow $\text{NH}_4\text{Cl-PbI}_2$ colloid effectively separates the MAI-PbI_2 colloid and the NMAI-PbI_2 colloid into two distinct regions, and increases their physical distance, thereby achieving an extended and well-ordered phase distribution that facilitates efficient charge transport within low-n 2D perovskite films [145]. The optical properties of various 2D perovskite films with different layers were also investigated using transmission spectroscopy as shown in **Figure 2-9f**. The chromatic coordinates (x , y) were computed and plotted in **Figure 2-9e**, to assess the color-

rendering properties of semitransparent photovoltaics (ST-PVs). Two-dimensional perovskite films with the lowest feasible n -value and a gradient multiphase distribution could be considered potential light absorbers for ST-PVs applications. The resulting 2D perovskite films achieved a high average visible transmittance (AVT) of approximately 47%, and realized a gradient phase structure ($n=2$), thus meeting the stringent requirements of ST-PVs [145].

2.4.3 Solvent and antisolvent engineering

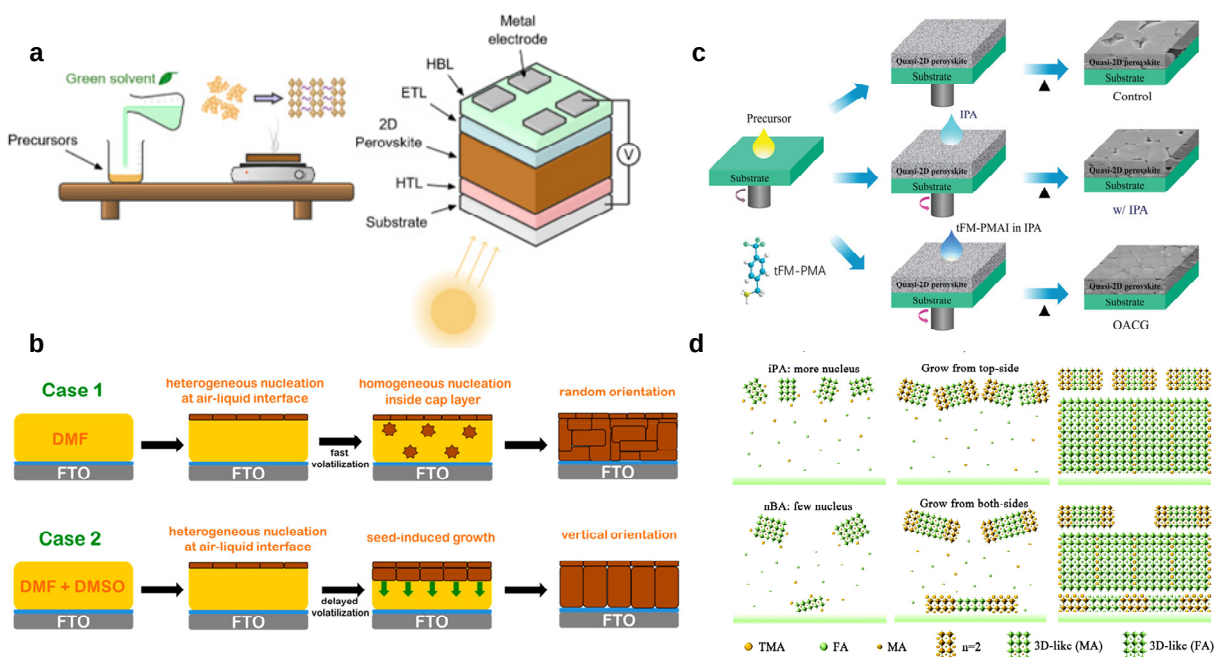


Figure 2-10. (a) Solvent Engineering Strategies for 2D-Perovskite Crystallization, adapted from [L. Andrés Guerrero-León, 2024]. (b) Crystallization process of 2Dperovskite with/no DMSO addition to DMF solvent [150]. (c) Fabrication of 2D RP perovskite films by adding tFM-PMA into IPA antisolvent [151]. (d) Schematic representations illustrating the crystallization process of forming films using nBA and iPA as antisolvents [152].

The role of solvents in preparation of perovskite films by solution deposition is important. The nucleation and crystal growth are controlled to a large extent by the solvent through its physicochemical properties, such as polarity, evaporation rate, boiling point, and coordination ability with precursors, which influence the crystallization kinetics. Particularly, solvents with a high boiling point and low volatility enhance the stability of the solution, thereby promoting more uniform and orderly crystal growth. In contrast, rapidly evaporating solvents may

accelerate nucleation process and often lead to uneven crystal size and increase the grain boundaries number. The coordination ability of the solvent modifies the surface energy, adjusts the threshold of the nucleation-free energy, and effectively controls the orientation of the perovskite films.

Polar aprotic solvents, such as DMF, DMSO, and NMP, due to their moderate boiling points, have found great utility in perovskite film preparation [115, 153, 154]. DMSO and DMF, in particular, have been extensively studied for their strong interactions with inorganic octahedral frameworks [155]. Due to the lower DMF polarity resulting in weak coordination with precursor components, perovskite films often exhibit random crystal orientation and poor film morphology when DMF is used as a single solvent. The higher relative polarity of DMSO compared to DMF (0.444 for DMSO compared to 0.386 for DMF) allows it to form stronger interactions with its precursors, resulting in better film formation. For example, Zhiwen Jin et al. demonstrated that controlling the crystallization rate and crystal growth can be achieved by adjusting the DMSO content. Adding 10% DMSO to pure DMF optimizes the solvent mixture, stabilizing the intermediate phase. This stabilization yields perfect coverage, fewer grain boundaries, larger grains, and improved orientation perpendicular to the substrate [156]. Ke Fan et al., innovatively applied binary solvent engineering with DMF/DMSO to 2D perovskites in **Figure 2-10b** [150]. While the rapid evaporation of DMF as a single solvent favors uniform nucleation resulting in randomly oriented 2D perovskite crystals, the binary solvent system slows down the crystallization process. The presence of an intermediate phase further slows the crystallization, allowing the perovskite cap to function as a seed, promoting the vertical alignment of subsequent perovskite crystals within the film's inner layer. Chan Myae Soe et al. also reported the deposition of highly oriented films from DMF/DMSO mixtures based on 2D RP perovskite using hot casting method, through adjusting the solvent ratio in the film to achieve the crystal growth direction and grain size [157].

In the production of perovskite film, transitioning to eco-friendly solvents represents a significant step towards more sustainable and renewable energy solutions. Against this background, L. Andrés Guerrero-León and colleagues explored innovative solvent formulations in their study for 2D-perovskite crystallization, tailored specifically to the

manufacturing needs of 2D perovskites (**Figure 2-10a**). By optimizing the solubility parameters of the solvent, as well as predicting and experimentally verifying new green solvents, they successfully promoted the efficient formation of 2D perovskite by focusing on new solvent formulations. According to the solubility parameters of the solvent and the prediction of new green solvents, the development of 2D perovskite can be considerably promoted by focusing on developing new solvent formulations. These new solvents, together with cutting-edge production procedures, are intended to improve control over crystal formation and reduce defects. It also emphasizes sustainable and environmentally beneficial green techniques, adapted from [L. Andrés Guerrero-León, 2024]. Additionally, Jinpeng Li et al., proposed triethyl phosphate (TEP), an environmentally friendly solvent, together with petroleum ether (PE), a lower polarity antisolvent, to synthesize FA-based quasi-2D perovskite precursor [157]. The study revealed that TEP together with PE, greatly enhances the film's quality, leading to larger grain sizes and reduced defect density. Notably, this approach yielded a PCE of 17.42%. Additionally, Yiqiang Zhan et al. developed a simple yet effective surface polishing method using 2,2,2-trifluoroethanol (TFEA), a naturally friendly green solvent. TFEA is regarded as an ideal solvent because of its robust hydrogen bond donor ability, high ionization capacity, and environmentally friendly characteristics [158]. After solvent polishing, the surface's randomly oriented phase containing trap sites is successfully removed, revealing the dense, vertically oriented phase beneath. This phase has fewer defects and a smoother surface, significantly enhancing carrier transport and charge extraction at the interface. Therefore, selecting appropriate solvents is crucial for fabricating high-quality 2D perovskite films, with green solvents emerging as a forward-looking trend in materials processing.

In general, polar aprotic solvents are frequently employed in the preparation of perovskites including DMF, NMP, DMSO, Acetonitrile (MeCN), gamma-butyrolactone (GBL), Methyl acetate (MeOAc), and so on. These solvents exhibit low evaporation rates and high room-temperature boiling points, generally resulting in slow evaporation under mild annealing conditions. This may inhibit the nucleation process of perovskite films, trigger random growth, and ultimately affect both crystallinity and morphological integrity. To mitigate these effects, researchers explored the antisolvent drip technology, by depositing the antisolvent into the

center of the film to support the effective nucleation and crystallization of the perovskite film. Common antisolvents include some of the less polar or non-polar solvents, commonly used antisolvents such as chlorobenzene (CB), toluene (Tol), and diethyl ether (Et²O) [78]. The antisolvent polarity is different from the solvent in the perovskite precursor, so it can be mixed with the precursor solvent, but not with the solute itself. This property enables anti-solvent could rapidly eliminate residual solvent and supply essential driving force required for crystal growth [159]. Through the introduction of anti-solvent in the spin coating process, the substrate surface quickly produces a local supersaturation state, which greatly promotes heterogeneous nucleation, thus improving crystal quality and morphology of films. Yongsheng Liu et al. developed an organic salt-assisted crystal growth technique using toluene as an antisolvent. High-quality 2-D perovskite films were prepared by adding 4-(trifluoromethyl) benzyl ammonium iodide to the antisolvent in **Figure 2-10c** [151]. The method effectively induces the crystal orientation and growth, minimizes the charge recombination loss, optimizes the surface energy level, and the PCE reaches 19.1%. In addition, Yuan et al. reported a green solvent ethyl acetate (EA) as an antisolvent for the production of two-dimensional perovskite films with uniform energy landscapes [151]. And Chun-Chao Chen et. al. used a green alcohol antisolvent of medium polarity (isopropyl alcohol) to regulate the crystallization kinetics of 2D perovskite [152], a quantum well reversely graded 2D perovskite film is obtained (**Figure 2-10d**), the vertically oriented layer structure with larger grains appeared on film surface, and the PCE reached a record 20.12%.

Antisolvents play a critical part during the crystallization of 2D perovskite films by rapidly extracting the solvent. The timing of antisolvent addition significantly influences the crystallization process. Premature addition of antisolvents generally causes the antisolvent to be washed away by the precursor solution, while delayed addition leads to the appearance of large pinholes, which could be attributed to the long growth time of the solvent intermediates. Antisolvent-assisted treatment can quickly increase the precursor solution concentration and accelerate nucleation. This effect can produce dense and homogenous perovskite films but may result in 2D random orientation. Therefore, the rational selection of antisolvents is an effective way to regulate the crystallization process and improve film quality [160].

2.4.4 Process engineering

Spin-coating has remained the favored technique for fabricating quasi-2D perovskite films in laboratory settings. This method allows for controlled deposition of the material, which is vital in achieving the precise crystal orientation required for optimal photovoltaic performance. The films' vertical alignment is particularly significant, as it directly influences the efficiency and stability of the resulting PSCs. To meet the rigorous demands for high-performance photovoltaic devices with highly ideal crystal orientation, a variety of auxiliary methods refining spin-coating processes and exploring alternative methods have been applied, such as hot casting, post-annealing, vapor-assisted, vacuum poling methods, etc. [40, 161]. In order to meet the needs of scalable preparation for further industrialization, the scraper coating method, and slit die coating are applied to prepare 2D perovskite films on a large scale. Hence, it is crucial to select an appropriate technique for manipulating the structure and alignment of 2D perovskite to achieve superior performance in PSCs.

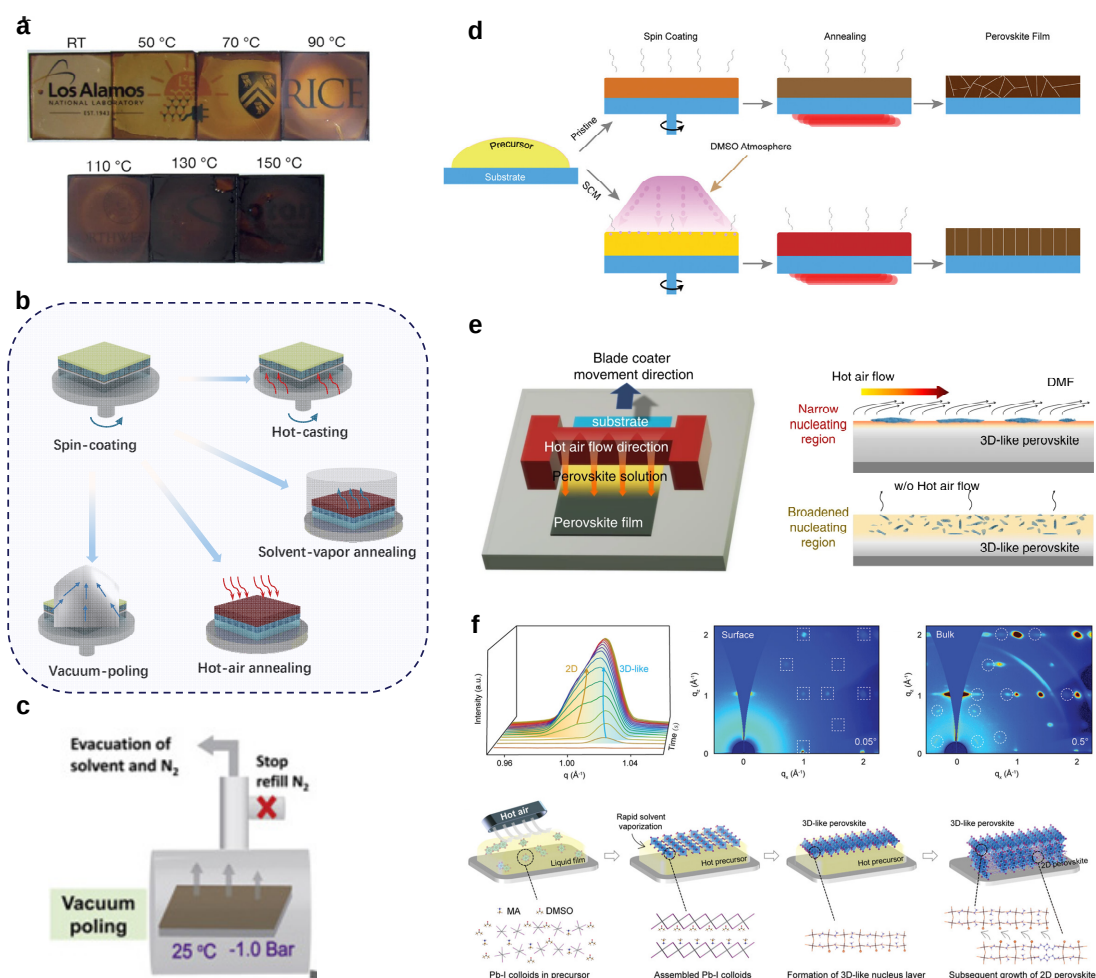


Figure 2-11. (a) Hot casting method for 2D perovskite film based on different substrate heating temperatures [72]. (b) Diagram depicting various assisted strategies for spin-coating in quasi-2D perovskite deposition [125]. (c) Vacuum poling techniques [162]. (d) Diagram of the crystallization process of 2D perovskite film with/no DMOSO atmosphere [163]. (e) The doctor blade technique utilizes room temperature (RT) substrates, precursor solutions, and hot air flow, narrow 3D perovskite nucleation region induced by hot air flow on the liquid surface, and dispersed 3D perovskite nucleation region induced by slow evaporation (without hot air flow) inside the precursor solution [129]. (f) Hot air-assisted annealing, including the evolution of the primary diffraction peaks of 2D perovskite film [164].

Hot casting

Among various deposition strategies, hot casting is regarded as one of the most common methods for 2D perovskite films [165-167]. In 2016, Tsai et al. for the first time used hot casting spin coating technology for synthesizing high-quality 2D perovskite by preheating the substrate [72]. (BA₂MA₃Pb₄I₁₃ (n =4) 2D perovskite films achieved a near-single crystal characteristic, as shown in **Figure 2-11a**. GIWAXS analysis proved that in the traditional method, the film displays a continuous ring shape, signifying random crystal orientation. Conversely, the hot-casting film presents a dot pattern, which suggests an orientation perpendicular to the substrate. Hot casting technology significantly promotes the phase transformation of perovskite through the preferential orientation mechanism, which is mainly based on the high-temperature preheating substrate. The high-temperature environment accelerates the transform of perovskite phase from an intermediate phase. In the hot-casting process, the substrate is initially heated, which rapidly evaporates the solvent from the intermediate product. Subsequently, the residue of PbI₂ can interact with organic cations, accelerating the transition from the sol-gel state in the precursor into crystalline 2D perovskite. The gradient QWs distribution in 2D PSCs enhances the spontaneous transit of charge carriers and energy, resulting in improved photoelectric conversion efficiency and performance. Preheating the substrate increases the solubility of the perovskite precursor, which in turn decreases supersaturation and reduces the formation of crystal nuclei. Therefore, the hot-casting temperature is key in determining the orientation and phase distribution of 2D

perovskite films, crucial for the transition from intermediate states and facilitating heterogeneous nucleation. However, a limitation of this technique is that the film is the non-uniformity of the film, often resulting in a thinner central region of the film. Because the process requires rapid execution using a heated substrate, it is challenging to replicate, and prone to more human error compared to room-temperature spin-coating [40].

Vacuum-assisted strategy

During the crystallization process, the atmospheric pressure has a significant effect on the solvents' evaporation rate and then affects the overall crystallization kinetics [168]. Vacuum quenching, a technique that rapidly removes solvents, has been extensively employed to enhance the nucleation rate of 3D perovskites. This approach is equally important in 2D perovskites, the rate of solvent evaporation is directly associated with the supersaturation degree in the solution and the crystal nucleation. At the gas-liquid interface, the solution first reaches critical supersaturation. This initiates the emergence of 3D-like crystals on the upper surface, which then guide direct the formation of organized 2D perovskite phases in a downward orientation. Thus, vacuum processing's major goal is to improve crystal development by adjusting the rates of solvent evaporation and crystallization [169, 170]. Bin Hu et.al., adopted a technique called vacuum poling and applied it to the preparation of 2D perovskites to evenly arrange nanoplates with different n -values [162], as illustrated in **Figure 2-11c**. Firstly, the precursor solution was spin-coated on a preheated substrate by spinning coating to rapidly form high-density crystal nuclei. This is followed by an 8-minute vacuum poling in a chamber where the gauge pressure rapidly drops to -1 bar within 14 seconds, initiating the effects of vacuum poling. This vacuum polarization treatment not only promotes the nucleation process but also effectively limits the grain size by rapidly removing the residual solvent, thus achieving a uniform distribution of nano-plates with different n -values. This uniform distribution is essentially achieved by a mechanically forced nucleation mechanism under vacuum polarization conditions, ensuring isotropic charge transfer from the low- n phase to the high- n phase [162].

Post-annealing strategy

Common techniques like spin coating with rapid annealing present challenges to effectively

control the crystallization in 2D perovskites. To address this, seeking fine management of the environmental conditions during deposition, like temperature and humidity, can improve the uniformity and quality of the films. The post-annealing technique has proven to be an effective method for promoting grain growth and recrystallization, strain release, defect repair, and passivation. For instance, Yuan Zhang et al. developed a slow post-annealing technique to optimize perovskite film structures, enhancing crystal orientation and layer-specific phase arrangement from 2D to quasi-3D. This technique boosts carrier mobility and reduces the Shockley-Read-Hall charge recombination [171]. The solvent vapor post-annealing technique is also used to remold the film structure, progressively enhance the crystal quality, and thermodynamically adjust the crystal orientation. Yueh-Lin Loo et al. reported the use of isopropyl alcohol (IPA) solvent vapor annealing (SVA) as a universal post-deposition method that promotes preferred vertical orientation and improves grain growth [172]. During the annealing process, Chen et al. proposed a DMSO solvent vapor atmosphere, which promoted the formation of 2D perovskite from the gas-liquid contact (**Figure 2-11d**). The corresponding solar devices based on the optimal films ($n \leq 3$) show a record -breaking PCE of 15.04% [163].

Scalable technology

Traditional 2D perovskite films often require tightly controlled environments, such as in glove boxes, by non-scalable techniques like spin coating. This limits its actual industrialization application. To address this problem, Wang et al. proposed a technique using a hot-air-assisted doctor blade coating at the liquid-air interface surface (**Figure 2-11e**), significantly increasing the nucleation rate in the crystallization process. Under the condition that the solution and the substrate are not heated, the DMF volatilization is accelerated by the hot gas flow, and the narrow-saturated region is quickly formed on the liquid surface, which realizes the main out-of-plane orientation in the RP 2D perovskite [129]. Mei Gao et al. described a straightforward, scalable drop-casting technique that eliminates the need for spin coating. This method involves directly depositing the precursor solution in air, leading to the self-assembly of highly oriented 2D perovskite films. In addition, they investigated the method of depositing 2D perovskite layers using a slit die coating process, and achieved PCE of 12.5% and 8.0%, respectively, using batch slit die coating techniques on glass substrates or implementing roll-to-roll (R2R)

slit die coating on flexible substrates [173]. Chen et al. developed a method utilizing hot air to fabricate 2D perovskite films. (**Figure 2-11f**), achieving a Ba-based 2D perovskite film with optimal orientation, superior crystallinity, and ideal morphology by controlling the hot air temperature [164]. Hot air induced solute solidification and formed intermediates at the gas-liquid interface, and then transformed into 3D perovskite phase to facilitate the downward growth of 2D phase. The resulting HAA film preparation technology includes high material utilization, insensitive to environmental humidity, suitable for large area production, suitable for different 2D perovskites, etc., which is suitable for the actual commercial deployment of perovskite-based optoelectronic device.

Chapter 3 Methodology

The energy from the sun is immense,
and we must strive to learn
how to convert it into useful work.
-----William Thomson, Lord Kelvin

3.1 Fabrication methods

Perovskite solar cells typically consist of a multi-layered structure, and the synthetic methods of each layer are critical to the overall performance of the device [86, 161, 174]. The transparent conductive oxide layer, such as ITO, or FTO, is usually prepared using physical vapor deposition (PVD, e.g. magnetron sputtering) techniques or chemical vapor deposition (CVD) techniques [175, 176], acting as a light entry point and electron extraction layer. The electron transport layer (TiO_2 , ZnO , SnO_2 , and PCBM) is generally deposited via spin-coating of colloidal solutions, followed by annealing to form a dense and uniform film. Typically, C60 is deposited on PCBM layer using vacuum thermal evaporation [177-179]. Because it can be easily sublimed at a high temperature, the evaporation rate and deposition thickness can be precisely controlled. The hole transport layer (Spiro-OMeTAD, PEDOT, PTAA) is usually applied using spin-coating, with the subsequent solvent evaporation and device annealing. For large-area fabrication, spray coating is frequently employed, whereas NiO_x is commonly deposited via PVD method. The back electrode, made of materials such as Au, Ag, carbon, or Al, is usually formed by thermal evaporation under vacuum to produce a dense metallic film. Additionally, sputtering technique is widely employed for the deposition of metal or carbon electrodes[180], particularly in industrial-scale production. Carbon electrodes can also be produced cost-effectively using blade coating techniques [181]. More details on the parameters of certain devices chosen in this thesis will be provided in the experimental sections of each chapter.

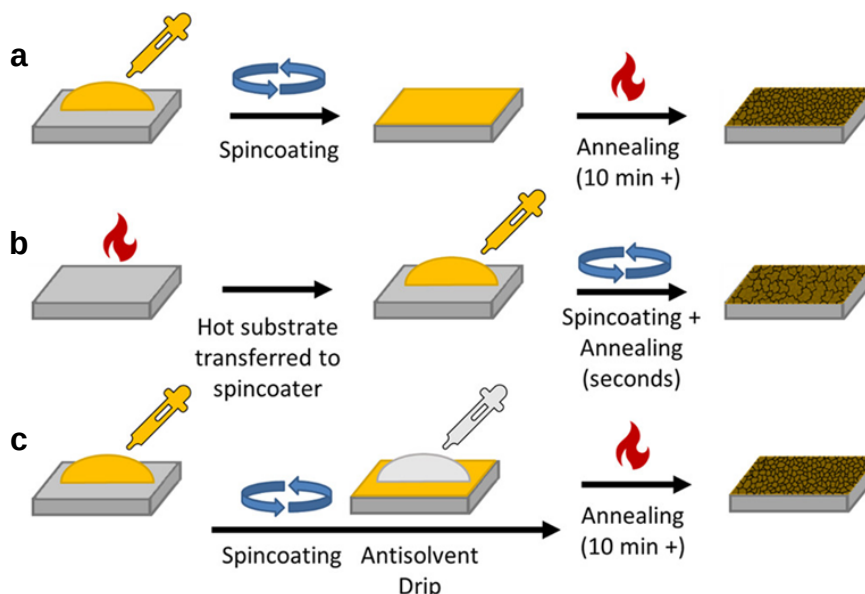


Figure 3-1. Illustrations of three widely used thin-film fabrication techniques: (a) one-step, (b) hot casting, and (c) anti-solvent [78].

The perovskite layer is the core of solar cells, responsible for capturing light and generating electron-hole pairs, which are fundamental to electricity generation. Common laboratory fabrication techniques mainly include spin coating [182-186], hot casting [108, 187], and antisolvent deposition [108, 188], as illustrated in **Figure 3-1**. The one-step spin coating technique, known for its simplicity, involves dissolving perovskite components in an organic solvent, spin-coating onto a substrate, and annealing to crystallize the film (100°C to 150°C). The two-step method offers more control, with metal halides deposited first, followed by organic halides to form the perovskite structure. Hot casting improves grain size by spin-coating onto a heated substrate (70°C to 150°C). While the antisolvent method modulates the crystallization by removing the solvent rapidly, by using the properties of insolubility to the perovskite phase and the immiscibility with the precursor solvent. Advanced fabrication techniques like blade coating [189], inkjet printing [190], and roll-to-roll processing [191] enhance efficiency and scalability, paving the way for the large-scale commercialization of perovskite photovoltaic devices.

After perovskite film is prepared, it is necessary to systematically analyze the various characteristics of the perovskite film, which requires the use of various testing and

characterization methods. In this section, we will detail the principles and methods of several main characterization methods involved in film morphology, crystallization dynamics, absorption spectrum, and photoluminescence ability of perovskite. Each of these provides critical insights into the material properties and device performance, it's a powerful tool for further optimization and application development.

3.2 Perovskite film characterization

3.2.1 Imaging and mapping characterization

Scanning Electron Microscope (SEM) is an effective method for detecting surface micromorphology of perovskite film. The working principle of SEM is shown in **Figure 3-2a**. First, the electron beam is produced by the electron gun and then focused and modulated by the electromagnetic lens. The scanning coil can make it scan the surface of the sample along the trajectory. The signal emitted after interacting with the sample, such as secondary electrons or backscattered electrons, is captured by the detector and converted into an electrical signal. After processing, a high-resolution image can be generated (**Figure 3-2b**). Generally, the secondary electron detector (SED) can provide high-resolution images of the sample surface morphology, and then the backscattered electron detector (BSE) mainly can provide relevant details about the composition and relative density of a sample. SEM characterization is widely employed to detect the surface morphology and microstructure, size and shape, the distribution of grains, and the cross-section and top view of PSC, which can reflect the crystallization quality and uniformity of films, grain boundaries, defects, etc. It can also be combined with an energy dispersive spectrometer (EDS), through the detection of characteristic X-rays, and elemental analysis of perovskite films, to determine the distribution of elements and composition ratio.

Atomic Force Microscopy (AFM) is a highly effective method for analyzing surface texture, roughness, and uniformity of perovskite films [192] (**Figure 3-2c**). AFM is conducted by using a nanoprobe to contact with the perovskite film surface. The move and scanning are controlled by the piezoelectric actuator. The existence of interaction between the probe and the films will cause the probe to deflect, and the deflection and displacement signal can be measured by an

optical detection system installed on the back of the probe. It is then converted into electrical signals, and after processing, the corresponding high-resolution surface morphology images can be generated. Additionally, AFM also facilitates the measurement of contact potential difference, providing insights into the electrical properties and carrier distribution of perovskite. Furthermore, AFM can also gather photocurrent and voltage data at the nanoscale, enabling detailed analysis of the photovoltaic conversion efficiency and charge transport characteristics in perovskite devices.

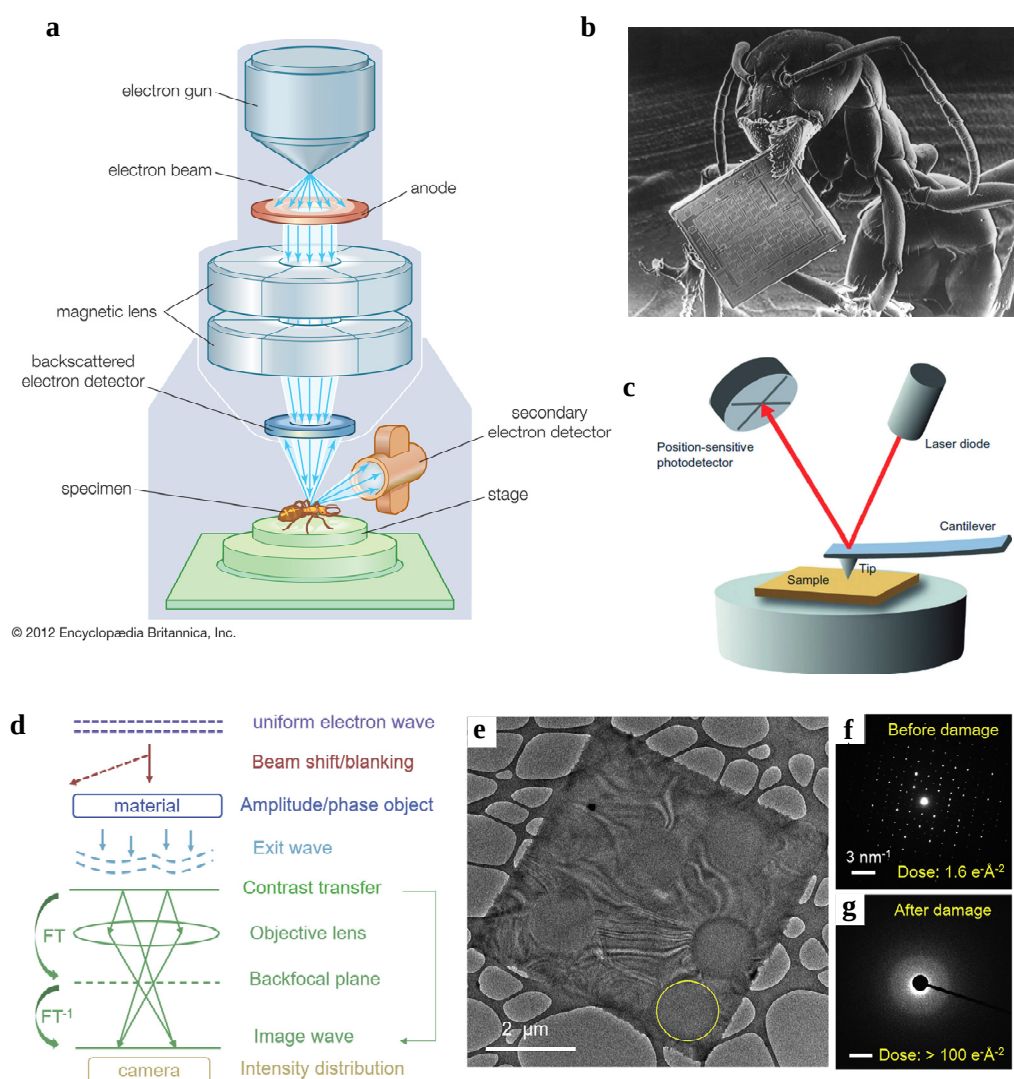


Figure 3-2. (a-b) Schematic and corresponding images of SEM imaging. (c) schematic of AFM working principle [193]. (d) the principle of HRTEM imaging [194]. (e) the 2D perovskite nanosheets low-magnification TEM picture and two SAED pictures that correspond to the yellow area in (e). The picture in (f) was captured before significant electron beam damage

occurred in that area. The pattern in (g) was recorded after the area was completely damaged [195].

Transmission Electron Microscope (TEM) is a powerful microscopic technique used to obtain detailed information about the internal structure of an ultra-thin sample, by penetrating a high-energy electron beam through it [196]. TEM offers higher resolution than SEM and AFM methods, allowing for the observation of crystal structures at the atomic level. **Figure 3-2d** shows the schematic diagram of the final imaging of a parallel beam, following the same Abbe imaging theory [197]. When this parallel beam penetrates the ultra-thin sample (usually tens to hundreds of nanometers thick). The atomic structure inside the sample produces elastic or inelastic scattering of the electron beam. Consequently, the electron wavefront becomes modulated, carrying comprehensive information about the sample. The modulation includes amplitude changes and phase changes, after which the outgoing wave continues to propagate forward and is further modulated by the objective lens. Finally, the detector (such as a fluorescent screen, CCD, or CMOS camera) captures the transmitted electron signal and converts it into an electrical signal. After processing, a high-resolution 2D image of the sample is generated.

TEM technology enables a detailed study of defects (such as dislocations, vacancies, and impurity atoms) and phase interfaces in perovskite films. By in-situ TEM technology, we can observe the dynamic change process of perovskite materials in real time under external conditions such as heating and illumination and study its stability and degradation mechanism. When studying halide perovskites, their beam sensitivity under the electron beam makes research challenging. The all-inorganic compound CsPbBr_3 is relatively stable when exposed to electron beams and can endure moderate doses of electron radiation [198], that is, thousands of electrons per square angstrom ($\text{e}^-/\text{\AA}^2$) [10]. However, these structures possess higher sensibility to the incident electron beam when perovskite contains organic ammonium cations (e.g., formamidinium (FA^+) or methylammonium (MA^+)) [199]. At radiation doses below $100 \text{ e}^-/\text{\AA}^2$, their structures may collapse [200]. **Figure 3-2e** shows a comparison of the perovskite structure before and after TEM imaging, revealing irreversible changes and damage to its

structure. Therefore, this electron beam sensitivity has somewhat limited the use of TEM technique for perovskite characterization [195].

3.2.2 Crystallization kinetics characterization

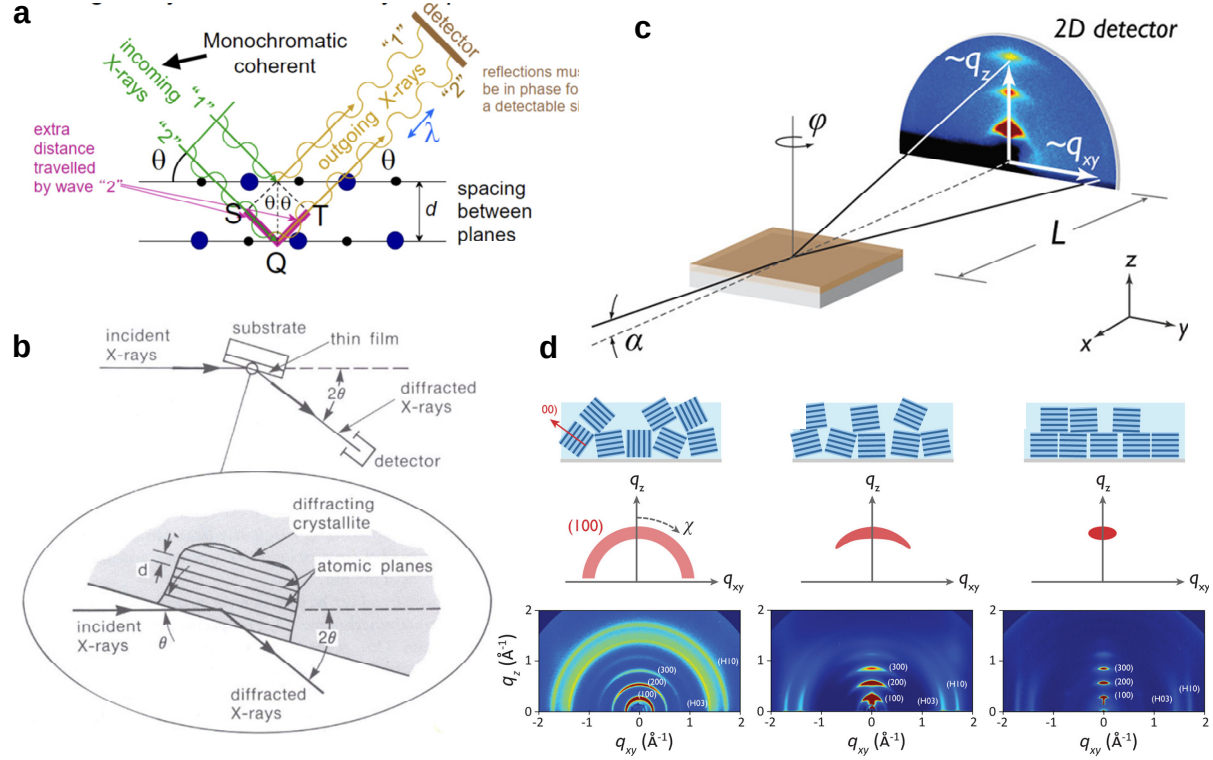


Figure 3-3. (a) Bragg Diffraction Calculation (b) working Principle of XRD [adapted from MECH5311 lecture slides, provided by Xiaozhou Liao] (c) working Principle of GIWAXS: Crystals with random orientations produce rings in the diffraction pattern [192]. (d) Films with a texture or oriented distribution of crystals generate the arcs of diffraction intensity, and highly orientated films result in spots or ellipses [192].

X-ray Diffraction (XRD) is a crucial method to study atomic structure of perovskite. It is based on Bragg's Law, as illustrated in **Figure 3-3a**, and was formulated by William Henry Bragg in 1913. Bragg's Law can be formulated as [4]:

$$SQ + QT = d * \sin \theta + d * \sin \theta = 2d * \sin \theta = n\lambda \quad (\text{Equation 3-1})$$

In Bragg's Law, n denotes an integer that signifies the order of diffraction, d represents the crystal plane spacing, θ is the X-ray incident angle, and λ is X-ray wavelength. When the

incident X-rays penetrate the sample and interact with the atomic planes as shown in **Figure 3-3b**, a reflected wave is generated. When the difference in path length of the reflected rays matches an integer multiple of the X-ray wavelength, that is, when satisfying the Bragg law, the reflected waves will be coherently superimposed, and a diffraction peak will be generated. Grazing Incidence X-Ray Diffraction (GIXRD) operates under principles similar to XRD but differs primarily in the incidence angle. In GIXRD, X-rays strike the sample surface at very shallow angles, making it particularly suited for surface-sensitive analyses. XRD technique has been widely employed to analyze the crystal structure of perovskite materials, for example, we can use it to identify crystalline phases and lattice parameters, evaluate phase purity, and measure grain size. By analyzing the positions and shapes of XRD peaks, we also can investigate the lattice stress and strain within perovskite films.

Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) is a specialized method designed to analyze the structure properties of thin film surfaces (**Figure 3-3c**). This method makes full use of the high penetrative and scattering capabilities of X-rays, and by setting specific incidence angles to detect structural information from the sample's surface. When the incident X-ray waves penetrate the thin film, a portion of them is diffracted by the periodically arranged atomic or molecular planes. The reflections from adjacent planes interfere constructively, resulting in high-intensity spots. The diffraction angle is associated with the spacing distance. The scattering vector magnitude and the Bragg condition are specified as follows, [192, 200, 201]:

$$q = \left(\frac{4\pi}{\lambda} \right) \sin \theta \quad (\text{Equation 3-2})$$

$$q = q_B = \frac{2\pi}{d_{hkl}} \quad (\text{Equation 3-3})$$

where θ is the scattering angle, λ denotes X-ray wavelength. And h, k, l are the Miller indices specifying the crystal plane, q_B is oriented perpendicular to the lattice planes, and d_{hkl} is the distance between these planes. GIWAXS method offers a comprehensive analysis of the crystal structure of thin films, facilitating qualitative evaluations of their ordered or disordered states. By examining the positions of scattering spots, researchers can precisely ascertain lattice

spacings. In reciprocal space (q_{xy} - q_z), the distribution and intensity of diffraction peaks provide insights into crystal orientation. If the crystal orientations of films are uniformly distributed within a disordered matrix, the diffraction pattern in reciprocal space manifests as evenly intense rings. When perovskite films have both an "ordered" out-of-plane orientation and a "disordered" in-plane orientation, the resulting diffraction pattern consists of discrete diffraction spots and circulars [201] (**Figure 3-3d**). Films only exhibiting out-of-plane orientations will feature sharply defined and intense diffraction spots [192, 200]. To gain a more detailed understanding of the crystal structure, the sample can be rotated during the experiments, to enhance comprehensiveness of the structural data obtained.

3.2.3 Optical characterization techniques

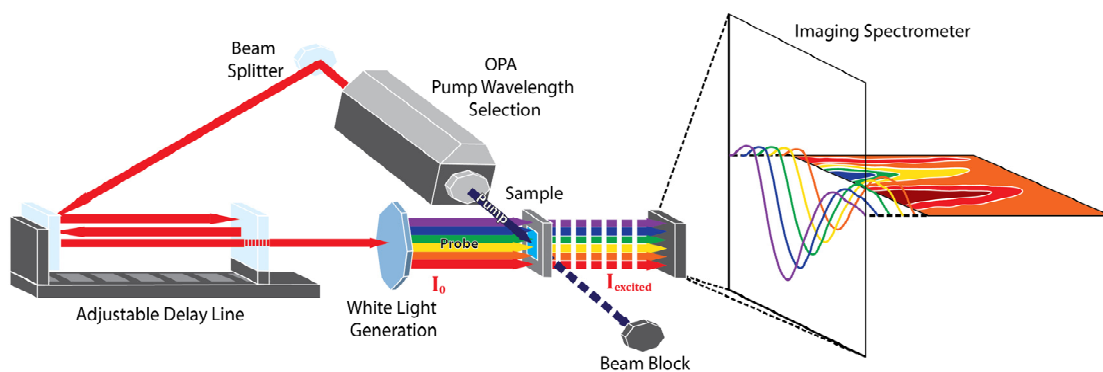


Figure 3-4. (a) Schematic diagram of a femtosecond broadband transient absorption spectrometer [202].

Ultraviolet-visible absorption spectroscopy (UV-Vis) is a commonly used method for analyzing the optical properties of perovskite [203-205] by measuring its absorption of different wavelengths of light. UV-Vis spectrometers are generally equipped with deuterium lamps (200-400 nm) and tungsten lamps (400-800 nm) for the ultraviolet and visible regions, respectively. The light is emitted from the source and then is subsequently dispersed into different wavelengths by a monochromator (such as a prism or grating). And we selected a specific wavelength of monochromatic light to illuminate the sample. The molecules in the sample can absorb the photon energy, resulting in the transition of their electrons from a ground state to an excited state. Thus, by analyzing the position of the edge of the absorption spectrum, we can obtain the optical band gap of perovskite thin film. Usually, we use a Tauc curve to linearly fit

the absorbed data to accurately determine the direct or indirect band gap. Notably, in 2D perovskite films, different n phases have their own absorption characteristics. By analyzing the characteristic peaks in the absorption spectrum, we can determine the phase distribution and its proportion in the film. In addition, the stability and degradation mechanism of perovskite films can also be studied, by comparing UV-Vis spectra before and after light or heat treatment. Photoluminescence (PL) is a technique for studying electron transitions and energy level structures in thin perovskites [206-209]. By the incident light excited perovskite film, electrons will absorb photons and transition from their ground state to a high energy state, and then return to ground state through a relaxation process and emit photons [54]. The wavelength distribution of these emitted photons forms the photoluminescence spectrum. By analyzing PL spectra, we can study the exciton fluorescence peaks in perovskite films, and then obtain the information of energy level structure, defect state, and photoelectric properties of the materials. In addition, time-resolved Photoluminescence (TRPL) is an extended PL-based technique that can be used to measure the decay of photoluminescence as a function of time [210, 211]. By monitoring the attenuation of luminescence intensity with time after light excitation, we can understand the carrier dynamics and recombination mechanism in perovskite. The results were fitted with a biexponential function then [212, 213]:

$$Y = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + \gamma_0 \quad (\text{Equation 3-4})$$

where τ_1 and τ_2 are the fast and slow decay time constants and are associated with trap-assisted recombination at interfaces and inside grains, respectively.

Transient absorption spectroscopy (TA) is generally used to study the phase distribution and energy transfer within perovskite films, especially for 2D perovskite [214-216]. TA spectrum is based on the pump-probe principle, as illustrated in **Figure 3-4a**. During the test, the sample was exposed to two short-pulse lasers, a pump laser to excite the sample, and a probe laser to monitor the excited state absorption. Initially, the sample is stimulated using a femtosecond pump laser pulse. After a certain time delay (typically ranging from picosecond to nanosecond range), the sample's absorption in the excited state is measured using a broad spectrum of absorbed femtosecond probe light. The absorption change of the detected light (ΔA) reflects

the dynamic process of the material returning from the excited state to ground state, including carrier recombination and energy transfer. In the study of quasi-2D perovskite, it is commonly used to trace the energy transfer of different n phases in pure perovskite films [202]. The kinetics extracted from TA spectrum are described by multiple exponential functions, as shown in equations (2-9&10) [217]:

$$I(t) = 1/2 \sum_{i=1}^{\infty} H_i(t) A_i e^{-\frac{t}{\tau_i}} \quad (\text{Equation 3-5})$$

$$H_i(t) = \left[1 + \text{erf} \left(-t/r - r/2\tau_i \right) \right] \quad (\text{Equation 3-6})$$

Where t is the detection delay; $H_i(t)$ is the ascending function; r indicates the pulse width of the Gaussian laser; A_i is the amplitude; τ_i is the attenuation time constant.

3.3 Perovskite device characterization

3.3.1 Current density-voltage curve

To evaluate the PSCs under standard conditions, a solar simulator with an energy spectrum of AM 1.5G operating room temperature was used. At an ambient temperature of $T=300\text{K}$, the relationship between current and voltage is described by the I - V curve in **Figure 3-5a**, which is typically used to define performance. Since current I is proportional to the solar cell area (A cm^2), so the current density (J , A/cm^2) is defined as $J_{\text{sc}}=I/A$ to describe the volt-ampere characteristic [218]. Solar cells are intended to convert solar energy to electrical energy, which is quantified by power density P (in W/cm^2). When integrated with the load resistance R , the functional form of Ohm's law J (V) is a straight line with a slope of $1/AR$ [219]. The voltage and current obtained at the intersection of the volt-ampere characteristic curve are the operating voltage and current [220]. The primary performance indicators mainly include V_{OC} , J_{sc} , FF , PCE, and maximum power point (P_{max}). These indicators are important for evaluating and comparing device performance.

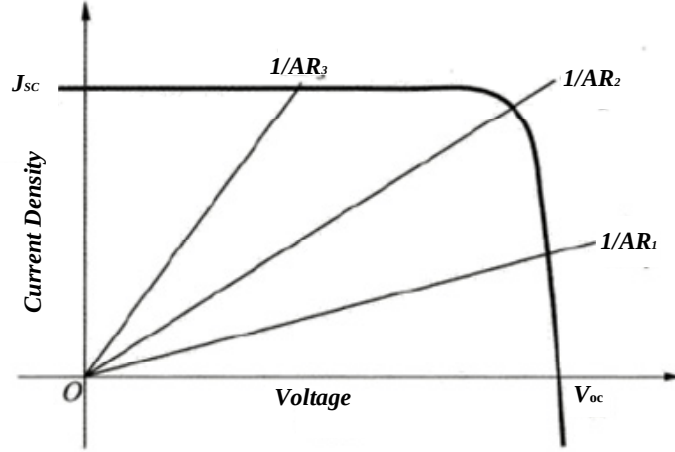


Figure 3-5. (a) Schematic diagram of J-V curve, and $R_1 > R_2 > R_3$ [219]

When there is no external load connection, that is, the load resistance (R) approaches infinity, and the load current approaches zero [220]. The voltage in this state is defined as open circuit voltage. On the I - V characteristic curve, the intercept of the voltage shaft is marked with V_{OC} , indicating the maximum voltage that the equipment can produce under no-load conditions. Theoretically, V_{OC} is influenced by the band gap of perovskite, but the actual value is often lower due to factors such as charge recombination. The loss sources mainly come from the internal defects of perovskite films, grain boundary defects, interlayer interface defects, and energy level mismatch [221, 222].

When the solar cell is short-circuited, it means zero load resistance and zero voltage across the cell, the current at this state is termed short-circuit current [223]. J_{SC} represents the maximum current density, indicated by the intercept on the current axis of the I - V curve. It represents the maximum photocurrent per unit active area under short-circuit conditions. The FF is a key parameter quantifying the efficiency of a solar cell's electrical output relative to its theoretical potential. It is calculated as the ratio of P_{max} to the product of J_{SC} and V_{OC} . This ratio indicates the cell's ability to provide effective power to an external circuit [224].

$$FF = \frac{P_{Max}}{I_{SC} \cdot V_{OC}} = \frac{I_{Max} \cdot V_{Max}}{I_{SC} \cdot V_{OC}} = \frac{J_{Max} \cdot V_{Max}}{J_{SC} \cdot V_{OC}} \quad (\text{Equation 3-7})$$

PCE is calculated as the device's maximum output power density divided by the power density of incident light. It represents the efficiency of PSCs in converting light energy into electrical energy, the formula can be described as:

$$PCE = \frac{P_{\text{Max}}}{P_{\text{in}}} = \frac{J_{\text{sc}} \cdot V_{\text{oc}} \cdot FF}{P_{\text{in}}} \quad (\text{Equation 3-8})$$

The PCE value can more defectively reflect the overall solar cell performance. Since it is also closely associated with the other three parameters, so several important parameters should be considered comprehensively when describing the performance.

3.3.2 External quantum efficiency

EQE refers to the relationship between the quantity of electrons output by the solar cell and the quantity of photons input under the condition of illumination. EQE measures how efficiently a device converts photon energy into electricity at a particular wavelength. Ideally, a higher EQE value means that more incident photons are efficiently converted into charge carriers, thus improving the photoelectric conversion efficiency of the cell. The EQE spectra obtained by direct testing can show the changes in EQE at different wavelengths. The EQE values at different wavelengths can reflect the response of solar cells under illumination. By integrating the EQE spectrum, the J_{sc} can be calculated using the following formula [225],

$$J_{\text{sc}} = \int_{\lambda_1}^{\lambda_2} q \cdot \phi_{\lambda} \cdot EQE(\lambda) d\lambda \quad (\text{Equation 3-9})$$

Here, q is the electron charge, ϕ_{λ} is the incident photon flux density, and λ_1 and λ_2 are the initial and final wavelengths of the integral respectively. To increase the J_s of PSCs, the performance of EQE can be improved by expanding the wavelength range of absorbed light and increasing the EQE value at specific wavelengths.

3.3.3 Space charge limited current

SCLC testing is usually performed in the dark state, by measuring the J - V curve of the devices, it is divided into different current transmission regions, which can be divided into three main regions: Ohmic region, trap fill region (TFL), and Child region. Each region possesses a

different current-voltage characteristic, indicating the charge transport and defect state.

In the Ohmic region, the current and voltage are linear and follow Ohm's law. The current at this stage is mainly affected by the external injection charge, and the trap state is not filled, so the conductivity is low. With the further increase of voltage, the trap state is gradually filled by the injected charge, the conductivity is greatly improved, and the current shows a nonlinear increase with the voltage. This phase is called the trap-filled Limit (TFL) region, indicating that the trap state no longer restricts charge transport. When the voltage has increased to a high enough level, enter the Child zone. At this stage, all trap states have been completely filled, and charge transfer is no longer limited by the trap state. At this time, the current increases with the square relationship of voltage, following the SCLC model, the relationship between current and voltage is as follows:

$$J \propto V^2 \quad (\text{Equation 3-10})$$

The current in this stage is mainly dominated by the space charge effect, and the carrier transport depends on the size of the electric field and the charge mobility of the material. The density of defect state n_t can be calculated by the intersection of the TFL region and Ohmic region. The formula is as follows [226],

$$n_t = \frac{2\epsilon\epsilon_0 V_{TFL}}{eL^2} \quad (\text{Equation 3-11})$$

Where ϵ and ϵ_0 represent the relative dielectric constant and dielectric constant of vacuum, L denotes the thickness of the device, and V_{TFL} is the voltage in the trap filling area.

3.3.4 Stability measurement

The stability of PSCs is a key issue for their commercial application, so it is crucial to conduct a comprehensive characterization of their stability. The stability characterization methods of perovskite solar cells mainly include light stability tests, thermal stability tests, humidity stability tests, and oxygen stability tests. The International Summit on Organic Photovoltaic Stability (ISOS) standards, such as ISOS-L for light soaking, ISOS-D for dark storage, and ISOS-T for thermal cycling, are widely used to evaluate stability under real-world conditions. Additionally, the International Electrotechnical Commission (IEC) standards 61215 and 61646

are commonly applied in perovskite stability testing, including tests for thermal cycling, damp heat, humidity-freeze, and UV exposure.

The illumination stability test is to test the stability of PSCs under long-term exposure to light conditions. The purpose of this test is to assess the photodegradation of perovskite. A common illumination stability test method is to place the device under simulated sunlight (e.g., AM 1.5G, 100 mW/cm²) and monitor the change in PCE. The MPPT test of the device is carried out under light conditions to observe the change of its power output at the maximum power point with time and evaluate the light stability.

Thermal stability tests are used to assess the ability of solar cells to maintain performance at high temperatures. Since perovskite materials are sensitive to temperature, it is necessary to understand their physical and chemical changes at high temperatures, and devices are commonly conducted under high temperatures (e.g., 85°C or higher) to assess whether their performance will significantly degrade. Organic components in perovskite materials, such as methylamine ions (MA⁺), may evaporate at high temperatures, leading to a breakdown of the crystal structure. Temperature cycle test: Simulate rapid changes in ambient temperature and evaluate the stability of the device under rapid changes in temperature by alternately exposing the device to high and low temperatures for cycle testing.

Perovskites are extremely sensitive to humidity, and the device is placed in a high-humidity environment (e.g., 65% RH or higher) for a long time, and the change in its performance is regularly monitored to evaluate its moisture resistance. Oxygen is another significant factor that results in the degradation of perovskite. The reaction of oxygen with perovskite materials can lead to a deterioration in battery performance, especially under light or high-temperature conditions, and the oxidation reaction is intensified. The photoelectric performance of the device is tested in an environment with sufficient oxygen to evaluate its decay rate under oxygen. Alternatively, the device is exposed to both light and oxygen to analyze the synergistic effect of oxygen and photoinduced degradation.

Chapter 4 Highly Stable and Efficient Formamidinium-Based 2D Ruddlesden– Popper Perovskite Solar Cell via Lattice Manipulation

The action of light on matter, though mysterious,
opens up vast possibilities
in harnessing energy from the sun
-----William Grylls Adams

Formamidinium-based (FA) 2D perovskites have emerged as highly promising candidates in solar cells. However, the insertion of 2D spacer cations into the perovskite lattice concomitantly introduces micro-strain and unfavorable orientations that hinder efficiency and stability. In this study, by finely tuning the FA-based 2D perovskite lattice through spacer cation engineering, we achieved a stable lattice structure with balanced distortion, micro-strain relaxation, and reduced carrier-lattice interactions. These advancements effectively stabilize the inherently soft lattice against light and thermal aging stress, particularly extreme temperature changes. To reduce the photocurrent loss induced by undesired crystal texture, we further employed a polarity-matched molecular-type selenourea (SENA) additive to modulate the crystallization kinetics. The introduction of the SU significantly inhibits the disordered crystallization induced by spacer cations and drives the templated growth of the quantum well structure with a vertical orientation. This controlled crystallization process effectively reduces crystal defects and enhances charge separation. Ultimately, the optimized FA-based perovskite photovoltaic devices achieved a remarkable power conversion efficiency (PCE) of 20.03% (certified steady-state efficiency of 19.30%), setting a new record for low-n 2D perovskite solar cells. Furthermore, the devices exhibited less than 1% efficiency degradation after operating at maximum power point for 1000 hours and maintained 92.3% and 91.1% of the initial efficiency

after aging at 85°C for 720 hours and 50 cycles of cold-warm shock, respectively.

4.1 Introduction

In recent years, the power conversion efficiency (PCE) of formamidinium (FA)--based perovskite solar cells has experienced significant advancements and rapidly approaching 26% [227-230]. These remarkable achievements place them on par with the currently prevailing silicon solar cells. However, FA-based perovskites are highly susceptible to lattice instabilities and structural deterioration and are prone to transforming into a photo-inactive phase at room temperature when exposed to external dynamic stimuli [228, 231, 232]. Consequently, long-term stability remains a critical challenge toward commercializing FA-based perovskite technologies [233].

In general, the unstable perovskite phases can be thermodynamically stabilized by introducing lattice distortion. Such approaches allow for the modulation of lattice entropy, adjustment of ion interactions, and alteration of energy barriers for ion migration and phase transition [162, 234-236]. Previous studies have demonstrated that typical three-dimensional (3D) phase-sensitive FA-based perovskites can be stabilized by introducing macroscopic contractive lattice distortion through methods like interface strain engineering [237, 238], octahedral tilting [239-242], or small cation alloying (like Rb^+ , Cs^+ , MA^+) [242-245]. However, strain engineering and octahedral tilting typically rely on applying external strain to the surface of the thin film to achieve stability, limiting the effect near the surface/interface only [239, 246, 247]. Meanwhile, the strategy of alloying with small cations is constrained by the Goldschmidt tolerance factor (TF), which restricts fine-tuning of the lattice structure. Moreover, these methods often lack microscopic control at the lattice scale [230]. Distortion fluctuations and micro-strains further exacerbate the carrier-lattice interaction in the soft FA-based perovskite lattice [230, 248, 249], leading to increased degradation of perovskite materials and devices. These internal sources pose significant challenges to the long-term stability of FA-based halide perovskites [250].

Encouragingly, the two-dimensional (2D) perovskites assembled by quantum-well structures can significantly relax the constraints on the perovskite framework imposed by the Goldschmidt rule and expand the selection of A-site cations in thermally favorable

ways [2, 74, 251-253]. The unique quantum-well structure, typically characterized by a thickness spanning several Pb-Pb distances and consistently integrated with the incorporated organic spacer cations, allows for both macroscopic and microscopic fine-tuning of the soft Pb-I framework [78, 254]. The choice of spacer cations plays a critical role in regulating the Pb-I framework. The inherent self-assembling properties of the layered structure and tunable quantum-confinement effects, both derived from organic spacer cations, influence the Pb-I lattice distortion by modifying the geometric deformation or octahedral tilting in quantum-well structures [97-99, 255].

It is worth noting that the introduction of organic spacer cations in FA-based perovskites provides a promising strategy to stabilize the perovskite lattice. However, this approach also presents additional challenges in achieving high-efficiency perovskite solar cells, particularly for more stable perovskites with lower layer numbers (low- n , corresponding to more spacer cations). On one hand, the enhanced quantum-confinement effect in low- n perovskites leads to increased exciton binding energy, limiting the transport and collection of photogenerated charge carriers [105, 256]. On the other hand, the specific polarity of spacer cations regarding solution chemistry can easily lead to crystallography problems that are not beneficial for carrier management, which is becoming the most intractable problem in the development of efficient 2D (or quasi-2D) devices. The increased number of organic spacer cations always results in the disordered growth of quantum wells and a parallel-to-substrate orientation [257, 258], posing challenges in achieving high photocurrent. Therefore, achieving textured and vertically integrated quantum wells between the electrodes of the devices is crucial for achieving high-efficiency 2D perovskite solar cells.

Here, we present a novel design and fabrication of low- n FA-based 2D perovskite, aiming to simultaneously achieve both high efficiency and stability. We fine-tuned the FA-based 2D perovskite lattice through spacer cation engineering, resulting in a stable lattice structure with balanced distortion. The resultant lattice demonstrates less symmetry breaking, micro-strain relaxation, and reduced carrier-lattice interactions, consequently improving structure stability against aging stresses induced by light and heat, particularly extreme temperature variations. Building upon this foundation, we further modulate the crystallization kinetics through the

incorporation of a molecular type selenourea (SENA) additive. SENA demonstrates a lower polarity and exhibits strong interaction with organic spacer cations, which guarantees effective modulation of crystal texture while keeping the stabilized lattice structure. The optimal HA (Hexylamine)-inserted perovskite devices achieved a remarkable small-area PCE of 20.03% (certified PCE of 19.30%, 0.08 cm²) and large-area PCE of 18.68% (1.02 cm²), respectively. The unencapsulated devices maintain initial efficiencies of 99%, 91.1%, and 90.3%, after maximum power point (MPP) operation at room temperature for 1000 hours (AM1.5G, 100 mW cm⁻²), aging at 85°C for 720 hours, and cold-thermal cycling for 50 cycles, respectively.

4.2 Experimental section

4.2.1 Materials and methods

Formamidinium iodide (FAI, 99.99%), lead iodide (PbI₂, 99.99%), and organic spacers including (Butylamine Hydroiodide) BAI, (Pentanamine Hydroiodide) PAI, (Hexylamine Hydroiodide) HAI, (Heptylamine) LAI, and (Octylamine) OAI, 99.5%, Selenourea (SENA) were purchased from Xi'an Polymer Light Technology Corp. FAPbI₃ powders were purchased from Advanced Election Technology Co, Ltd. Methylammonium chloride (MACl, 98%) was purchased from Xi'an Polymer Light Technology Corp. 2,2',7,7'-Tetrakis [N, N-di(4-methoxyphenyl) amino]-9,9'-spirobifluorene (Spiro-OMeTAD) was purchased from Borun New Material Corp. Bis-(trifluoromethane) sulfonimide lithium salt (Li-TFSI) and 4-tert-butylpyridine (tBP) were purchased from Sigma-Aldrich. SnO₂ colloidal dispersion (15%) was purchased from Alfa Aesar. All solvents including N, N'-dimethylformamide (DMF, 99.8%, anhydrous), dimethyl sulfoxide (DMSO, 99.8%, anhydrous), and chlorobenzene CB (>99.8%) were purchased from Sigma-Aldrich. The Indium-Tin Oxide (ITO) glass and Fluorine-doped Tin Oxide (FTO) glass were purchased from Advanced Election Technology Co, Ltd.

4.2.2 Preparation of perovskite precursor solutions

The precursor solutions of (BA)₂FA₃Pb₄I₁₃, (PA)₂FA₃Pb₄I₁₃, (HA)₂FA₃Pb₄I₁₃, (LA)₂FA₃Pb₄I₁₃, and (OA)₂FA₃Pb₄I₁₃ were prepared by dissolving FAI, BAI, PAI, HAI, LAI, OAI, PbI₂ and MACl in mixed solvents of DMF and DMSO (volume ratio 9:1) with a stoichiometric ratio of

2:3:4:1.5 (1.0 M). The additives of SENA were then added to the precursors at concentrations of 5%, 7%, and 10% molar ratio of PbI_2 , respectively. For FAPbI_3 perovskite, 1.4M FAPbI_3 powder was dissolved in $\text{DMF/DMSO}=9:1$ solution, with 0.45M MACl involved as an additive.

4.2.3 Device fabrications

Perovskite solar cells were fabricated on pre-patterned FTO glass substrates. The substrates were washed with detergent, deionized water, ethanol, and acetone under ultrasonic, and then were treated with UV Ozone cleaner (each step for 15 minutes, respectively). SnO_2 colloidal dispersion (15%, diluted by deionized water with a volume ratio of 1:5) was spin-coated onto the substrates at 3000 rpm for the 30s, which were then annealed at 150 °C for 30 min. After that, the perovskite films were fabricated by spin-coating the precursor solution at 6000 rpm for 30 s, during which 300 uL chlorobenzene (CB) as anti-solvent was dropped at 15 s before the end. Thereafter, the as-fabricated films were thermally annealed on a hotplate at 150 °C for 30 min. For surface passivation, the corresponding spacer cations were dissolved in an IPA solution of 10mM and spin-coated on top of perovskite film at 5000 rpm for the 30s. Subsequently, the hole-transport layer was deposited on top of the active layer by spin-coating Spiro-OMeTAD solution at 3000 rpm for 30 s. The Spiro-OMeTAD solution was prepared by dissolving a 73-mg Spiro-OMeTAD in a 1-ml CB with a 17.5-uL Li-TFSI (520mg/ml, acetonitrile) and a 28.8-uL 4-tBP as dopants. Finally, the devices were completed by thermal evaporation of the 60-nm Au electrodes.

4.2.4 Characterization of perovskite films

The X-ray diffraction (XRD) patterns were obtained from the Rigaku Dmax 2600 diffractometer using $\text{Cu K}\alpha$ radiation with a Nickel filter. GIWAXS data were collected at beamline BL14B1 and BL03HB of the Shanghai Synchrotron Radiation Facility (SSRF) using X-ray with a wavelength of 1.2398 Å. Both the top-view and cross-sectional SEM and EDS measurements for perovskite samples were conducted on Tescan Maia3 Gmu (model 2016). AFM measurement data were obtained with Dimension Fast Scan Bio Atomic Force Microscope. FTIR was conducted on a Thermo Scientific Nicolet 6700 Spectrometer. PL Measurements were performed using an FLS1000 spectrometer (Edinburgh Instruments) with

470 nm excitation wavelength, and PL mapping was collected on a Leica TCS SP8 STED 3X super-resolution system. Time-resolved photoluminescence spectra (TRPL) were obtained by using the same spectrometer as that for the steady PL experiments. The temperature-dependent PL spectra were recorded under light excitation with a 470 nm laser ($1.4 \mu\text{J cm}^{-2}$). The samples were quenched to 77 K at a 30 K/min cooling rate and then heated up to 298 K at a heating rate of 10 K/10 min. X-ray photoelectron spectroscopy (XPS) was performed on the AXIS Ultra DLD (Kratos) spectrometer. Transient absorption (TA) spectroscopy was carried out by using an optical instrument combined with a frequency-doubled mode-locked Ti: sapphire femtosecond laser (coherent) and an optical parametric amplifier (OPA) system. The amplified Ti: sapphire femtosecond laser generates seed pulses with a 35 fs pulse width and a repetition rate of 1 kHz. The seed pulses are divided into two distinct beams. The strong beam is sent to the OPA system and provides the 400nm pump laser pulse, and the other one is focused onto a sapphire crystal to generate a white light continuum, providing a broad band of 430-800 nm UV-vis probe light. The excitation beam has a low energy of 0.01 μJ per pulse to avoid the exciton-exciton and exciton-charge annihilation effects. The samples were sandwiched between two quartz glasses, which were filled with nitrogen. The analysis was carried out by using Surface Xplorer software. The nuclear magnetic resonance (NMR) spectra were measured on an Avance III 400MHz NMR spectrometer.

4.2.5 Device characterization

Current density-voltage (*J-V*) curves were collected using a Keithley 2400 source-meter under AM 1.5G 1-sun illumination from a 3A simulator (Newport, Oriel[®] Sol3A[™], 94023A), calibrated by standard silicon reference cell (Newport, Newport Oriel 91150-KG5), the mask area is 0.08cm². Incident photo-to-electron conversion efficiency (IPCE) spectra measurements were characterized using monochromatic incident light of 1×10^{16} photons cm⁻² with the alternating current mode. The space-charge-limited-current (SCLC) was recorded on an electrochemical analysis instrument (Zahner, Germany).

4.2.6 Stability measurement

The long-term operational stability was tested on the solar cell light resistance testing system

of Model BIR-50. Heat stability was assessed by applying the PSCs without encapsulation on the hotplate which was stored at the aging box (85 °C, RH~50%), and the PCE evolutions of the devices were obtained through the periodical *J-V* measurement. For the temperature cycling tests, the PSCs without encapsulation were placed in the temperature-dependent hotplate in an N₂-filled glovebox, with the 50-temperature cycle between -25±2 °C to 85±2 °C. The temperature was stable for at least 10 min at the temperature point of -25 °C and 85 °C, respectively. The heating rate is 2 degrees per minute, 1 point per 10 cycles. The power conversion efficiency (PCE) evolutions of the devices were obtained through the periodical *J-V* measurement every 10 cycles at room temperature (Newport, Oriel® Sol3A™, 94023A). For the stability tests, the hole transport layer for all the devices was alternated by ion-exchanged PTAA, and the specific method can refer to previous work [259]. The 3D FAPbI₃ device was encapsulated by a cover glass, stuck by an ultraviolet-curable epoxy resin.

4.2.7 Computational method

The calculations were based on DFT as implemented in the Vienna ab initio simulation package (VASP). Projector-augmented wave (PAW) pseudopotentials were used to model the valence states and the interactions between core and valence electrons. The Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) was employed for describing the exchange and correlation function, and the spin-orbit coupling (SOC) was included. The Tkatchenko-Scheffler (TS) scheme was adopted for describing van der Waals (vdW) interactions. The cut-off energy for basic functions was set at 500 eV with a Monkhorst-Pack sampling of an 8*8*2 k-point grid. All the geometries were fully relaxed until the forces on each atom were less than 0.01 eV/Å. Before the above geometry optimization, the unconstrained *ab initio* molecular dynamics (AIMD) calculations with the Nose-Hoover thermostat at 300 K were performed to determine the orientation of the FA cations, since they can undergo rotational and translational motion at elevated temperatures.

4.3 Results and Discussion

4.3.1 Fine-tuning the perovskite lattice distortion via spacer cations

By introducing different Ruddlesden-Popper (RP) type flexible linear organic spacer cations, specifically, butylamine (BA), hexylamine (HA), and octylamine (OA) organic spacers, we successfully manipulated the lattice distortion within the 2D FA-based RP perovskites (stoichiometric ratio $n=4$) as illustrated in **Figure 4-1a**. These amino head groups are inserted into the lead iodide framework and interact with the surrounding lattice, while the organic tail groups exhibit end-to-end attraction, resulting in an interlaced arrangement. To verify the lattice distortion induced by various spacer cations, we first employed grazing-incidence wide-angle X-ray scattering (GIWAXS) along the out-of-plane and in-plane directions. As shown in the integral intensity curves in **Figure 4-S1**, we observed that the dominant diffraction peaks of (101) planes around $q_z = 1.0 \text{ \AA}^{-1}$, with a slight shift toward higher values in the out-of-plane direction but a slight shift toward lower values in the in-plane direction, as the carbon chain lengths of the spacer cations increase from BA to OA. The shift signifies a reduction in the lattice spacing along the out-of-plane direction and an increase along the in-plane direction, as summarized in **Figure 4-1b**. Additionally, the diffraction peaks of the HA-inserted perovskite gradually shift toward the low q_z with the detection depth increasing, which further indicates a progressive decreasing trend of compressive lattice distortion from the surface to the interior of the perovskite film (**Figure 4-S1(f)**). This intriguing phenomenon can be attributed to the interlaced arrangement of organic spacer cations within the 2D RP perovskite structures, which exert a shear force on the octahedral Pb-I framework and lead to various degrees of lattice distortion (**Figure 4-S3**).

When the BA and OA organic spacer cations are introduced, the lattices are altered, and the lattice symmetry is broken (**Figure 4-1a**). As shown in **Figure 4-S1(d-e)**, two distinct split diffraction peaks near the $q = 1.0 \text{ \AA}^{-1}$ peak were observed, naturally resulting from the disproportionate lattice distortion along different axes (**Figure 4-S2**). This symmetry-breaking effect negatively impacts grain boundaries and creates more internal strain and defects in perovskite films. In contrast, the 2D perovskite with the HA spacer cation exhibits negligible

peak splitting, indicating a proportionate lattice distortion along the out-of-plane and in-plane directions. A similar phenomenon was observed in BA-, HA-inserted 2D FA-based perovskite film (n=2) as depicted in **Figure 4-S4**. Density Functional Theory (DFT) simulations based on pristine n=4 perovskites (**Table 4-S6**) provide further evidence that the HA-inserted lattice possesses a relatively lower degree of variations from the center. This is demonstrated by the smallest Pb-Pb average bond length quadratic elongation ($\langle\lambda\rangle$) and Pb-I-Pb average bond angle variance (σ^2) in **Figure 4-1C&Note 4-S3**. Consequently, the HA-inserted perovskite lattice with minor symmetry breaking may be favorable for lattice stabilization. Furthermore, improved orientations were observed for the films with longer alkyl chains, this could relate to the enhanced steric hindrance that hinders redistribution of spacers around the nucleating surface, thus inhibiting parallel growth.

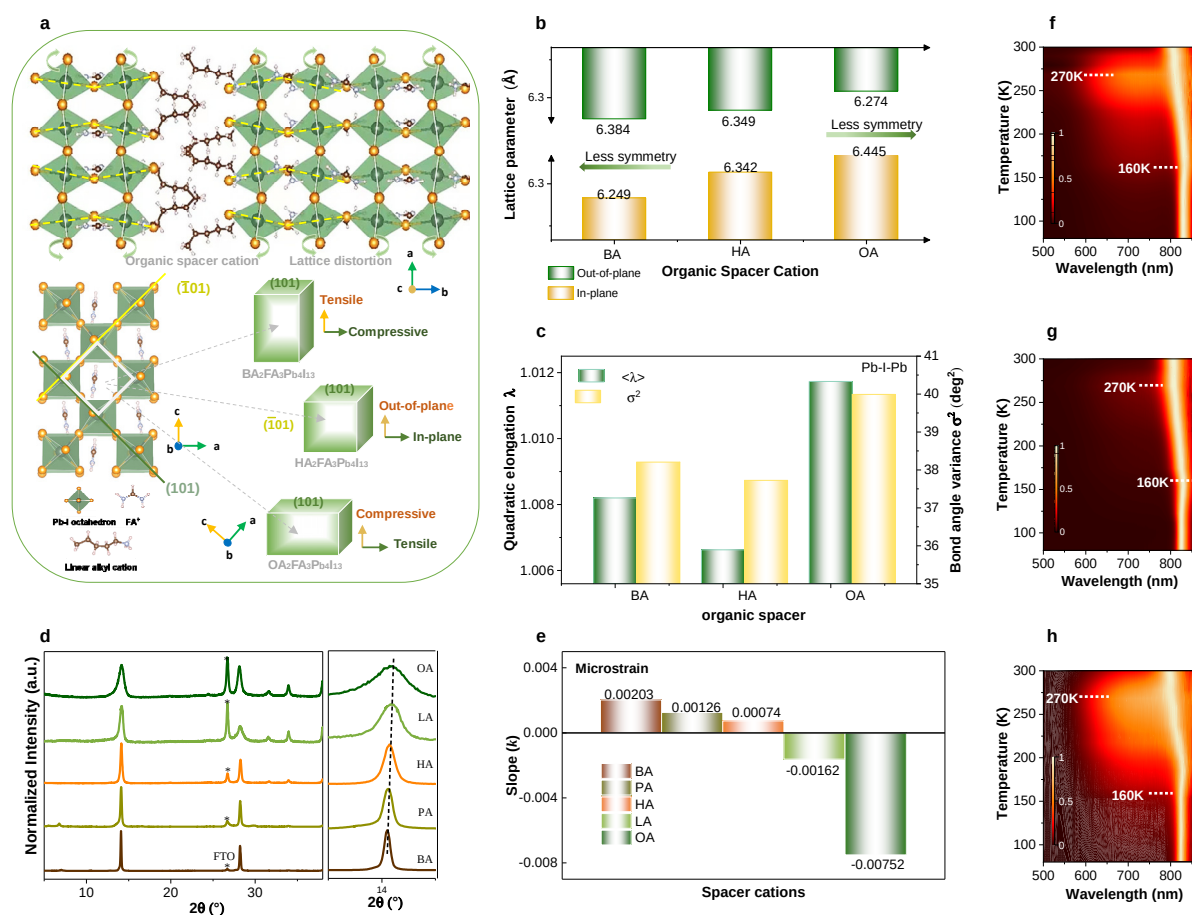


Figure 4-1. Fine-tuning the lattice distortion via spacer cations engineering. (a) Schematic illustration of the interleaved organic spacer cations that distort the lead iodine octahedral framework and evolution from BA- HA- to OA-inserted 2D RP perovskites. (b) Corresponding

lattice spacing (d_{101}) from GIWAXS patterns along out-of-plane and in-plane directions. (c) The Pb-Pb bond length quadratic elongation ($\langle\lambda\rangle$) and bond angle variance (σ) of Pb-I-Pb between adjacent octahedrons. (d) XRD patterns of FA-based 2D perovskite films based on BA, PA, HA, LA, and OA organic spacer cations, respectively. (e) The micro-strain of various distorted FA-based 2D perovskites based on the W-H analysis. (f-h) 2D pseudo-colour contour of the normalized PL as temperature changes corresponding to BA-, HA-, and OA-inserted 2D perovskites, from 77K-298K, respectively. And 77 K to 160 K for the first stage, 170 K to 270 K for the second stage, and 270 K to 298 K for the third stage, respectively.

The perovskite lattice distortion caused by the incorporated organic spacer cations was further investigated by different techniques. X-ray diffraction (XRD) results shown in **Figure 4-1d** exhibit the same trend of compression in the out-plane direction from BA- to OA-inserted perovskites, consistent with the GIWAXS results. The distinction between peak splitting for XRD and GIWAXS could relate to the difference in diffraction mechanism, with Bragg-Brentano geometric for XRD and Debye-Scherrer for GIWAXS, thus making the distinction in detection depths and resolutions. Additionally, PL spectra shown in **Figure 4-S6** show obvious blue shifts from 802 nm to 788 nm as the carbon chain lengths increase from BA to OA-inserted perovskites, which agrees with previous reports and indicates that the lattice compression is induced by the twist of the Pb-I bond (that decreases orbital coupling) rather than the direct Pb-I bond length contraction [260-262]. The electronic structures of the perovskites were also verified by the X-ray Photoelectron Spectroscopy (XPS) measurements (**Figure 4-S7**). The binding energy of the Pb-4f and I-3d core levels progressively shifted towards lower binding energy with the increase of carbon chain lengths. The decrease in the binding energy of Pb ions could be attributed to the enhanced distortion of the Pb-I framework, the distortion would reduce the overlap of the Pb-I orbitals which decreases the sharing of bonding electrons between Pb and I atoms accordingly and increases the valance electron density of Pb [263]. The contracted Pb-I framework can also reduce the atomic distance between FA and I ions, which promotes the strength of H-bonding between N-H and I, consequently enhancing the electron density of the I valance state [99, 262]. All these results demonstrate the introduction of organic spacer cations offers an effective means to precisely modulate the lattice distortion,

which also merits future investigations based on the single crystal or other forms of pure phases.

4.3.2 Micro-strain relaxation and reduced carrier-lattice interaction

In general, strain usually occurs in distorted lattices due to the high degree of atomic displacements. To evaluate the strain states in these perovskite films, we further analyzed the XRD results. The overall tensile or compressive strains (macro-strains) change lattice spacings, resulting in shifts of the corresponding diffraction peaks. As a comparison, the microscopic non-uniform strains (micro-strains) are manifested by the broadening of Bragg peaks in diffraction patterns (schematics for macro- and micro-strains are shown in **Figure 4-S8**). It is noteworthy that micro-strains often arise from deviations from the ideal crystalline lattice and are typically attributed to various factors, including residual stresses, dislocations, vacancies, grain boundaries, and any other defects that cause nonuniform lattice distortions in the crystal [230] [264]. Subsequently, we further calculated the micro-strains in the perovskite films by extracting the broadening of the diffraction peaks using the Williamson-Hall analysis [249, 265]. This analysis enables us to statistically assess the information and derive the overall strain states from the entire sample. As shown in **Figures 4-1e&4-S9**, the slope values for the BA, HA, and OA-inserted 2D perovskites are determined as +0.00203, +0.0007, and -0.00752, respectively. These values indicate that the micro-strains transition from tension to compression as the lengths of organic spacer cations increase. Notably, among these FA-based 2D perovskites, the HA-inserted 2D perovskite demonstrates the most effective relaxation of micro-strains, confirmed by the lowest slope (+0.0007). Furthermore, DFT simulations reveal that the HA-inserted perovskite exhibits the lowest formation energy, indicating the incorporation of HA spacer cation can effectively stabilize the fragile Pb-I framework of the 2D FA-based perovskite (**Figure 4-S5**).

To further investigate the impact of spacer cations on structural stability and carrier-lattice interaction, temperature-dependent photoluminescence (PL) was conducted over the temperature range from 77 K to 298 K. As illustrated in **Figures 4-(1f-h)** and **Figures 4-S10&S11**, the PL emission peaks of both the BA-inserted and OA-inserted 2D perovskites show significantly higher variations than that of the HA-inserted perovskites with temperature

changes, particularly at the temperatures above 160K, thereby underscoring the superiority of the HA spacer cations in stabilizing the perovskite lattice and carrier-lattice interaction. This enhanced stability can be attributed to the appropriate interlayer spacing provided by the flexible HA cations, which mitigates the overall structural variation and dielectric disorder in the lattice, resulting in narrower PL emissions.

Furthermore, we analyzed the peak intensities and full width at half maximum (FWHM) of the PL spectra, to quantify the evolution of the exciton properties and the carrier-lattice interaction with different spacer cations. It is worth noting that, unlike extensively studied methylammonium (MA)-b-based perovskite counterparts, the exciton binding energy (E_b) has not been reported for the FA-based 2D perovskites. Here, we present the first measured E_b values for BA-, HA-, and OA-inserted 2D FA perovskite, which are 123.93, 75.95, and 64.3 meV, respectively (**Figure 4-S12**). These results demonstrate that the 2D FA-based perovskites with longer alkyl carbon chains possess lower exciton binding energy. Notably, all the determined values are significantly larger than those of the FA-based 3D perovskites (about 18 meV) [266, 267], indicating the existence of the quantum-confinement effect within all the 2D perovskites.

The FWHMs of the PL spectra of the BA- and OA-inserted perovskites gradually increase from 40meV at 77K and reach the maximum values of 360meV and 580meV at around 270 K, respectively, as illustrated in **Figures 4-S13&Note S5**. The asymmetric emission peak tail in the 2D RP perovskites is typically associated with the exciton-phonon coupling [268]. Hence, the loss of symmetry in the PL emission peaks of the BA-and OA-inserted 2D perovskites is likely due to strong exciton-phonon interactions, consistent with the reduced structural stability and dielectric disorders [268]. These findings highlight the distinct carrier-lattice interaction in FA-based 2D perovskites, compared with the continuous broadening observed in the MA-based 2D perovskites over the temperature variations [267]. In contrast, the PL peaks of the HA-inserted perovskite are more symmetrical and their FWHMs exhibit a uniform broadening, with only a slight increase of approximately 40 meV across the entire temperature range. Therefore, the HA-inserted perovskite exhibits notable structural stability under temperature variations,

which is crucial for long-term stability when encountering cold-warm or other types of strain fatigues in perovskite films and devices.

4.3.3 SENA additive regulated vertical growth

While spacer cation engineering has improved the stability of the FA-based 2D perovskite lattices, achieving high efficiency in low-*n* FA-based 2D perovskite solar cells remains a significant challenge. The parallel growth tendency of quantum wells along the substrate not only leads to uncontrollable heterogeneous nucleation and crystallization processes but also hinders efficient current collection. The introduction of more spacer cations (low-*n*) into the precursors aggravates this issue, as the amphiphilic alkyl ammonium cations tend to reside at the air-liquid interface and induce parallel growth of quantum wells (**Figure 4-S17**). To address this challenge, we carefully selected a molecular-type SU additive to control the crystallization process (**Figure 4-2a**).

Fourier-transform infrared (FTIR) spectroscopy (**Figure 4-2b**) was used to investigate the interaction between SENA additive and 2D perovskite precursor. Upon introduction of SENA additives, the C=N symmetric stretching vibration of FAI increases from 1690 to 1699 cm^{-1} , which is typically considered a sign of strengthened hydrogen bonding [269]. Meanwhile, the C-N stretching vibration decreases from 1599 to 1589 cm^{-1} , which could be attributed to the weakening of the C-N stretching vibration by hydrogen bonding interactions. On the other hand, the SENA additive also displays interactions with PbI_2 . Upon the interaction with PbI_2 , SENA exhibits enhanced C-N stretching vibrations (from 1599 to 1612 cm^{-1}) and weakened C-N bending vibrations (from 1389 to 1378 cm^{-1}), because the coordination interaction between the electron-acceptor Pb ions and the electron-donor Se ions enhances the C-N stretching vibrations and weakens bending vibrations. **Figure 4-S15** further presents a comparison of the electrostatic potential distributions between SENA and a stronger Lewis base, namely thiourea (SENA). Notably, a significant decrease in electron density surrounding the selenium (Se) atom in SENA is observed, in contrast to the corresponding sulfur (S) atom in TU. The lower electronegativity of Se renders it a softer Lewis base, thereby imparting enhanced coordination capabilities towards soft acid lead iodine. The chemical shifts in NMR (^{207}Pb) spectra of PbI_2 upon the introduction of SENA additives (**Figure 4-2g**), and the shift of Pb 4f and Se 3d core-

level XPS spectra (**Figure 4-S16**) further prove the coordination between SENA and PbI_2 . The lone pair electrons from Se and N atoms can coordinate with Pb^{2+} ions and FA^+ cations in the precursor solution through soft-soft interactions, which exhibit strong covalent interactions. This leads to the formation of a more stable intermediate structure and a retardation of the crystallization process.

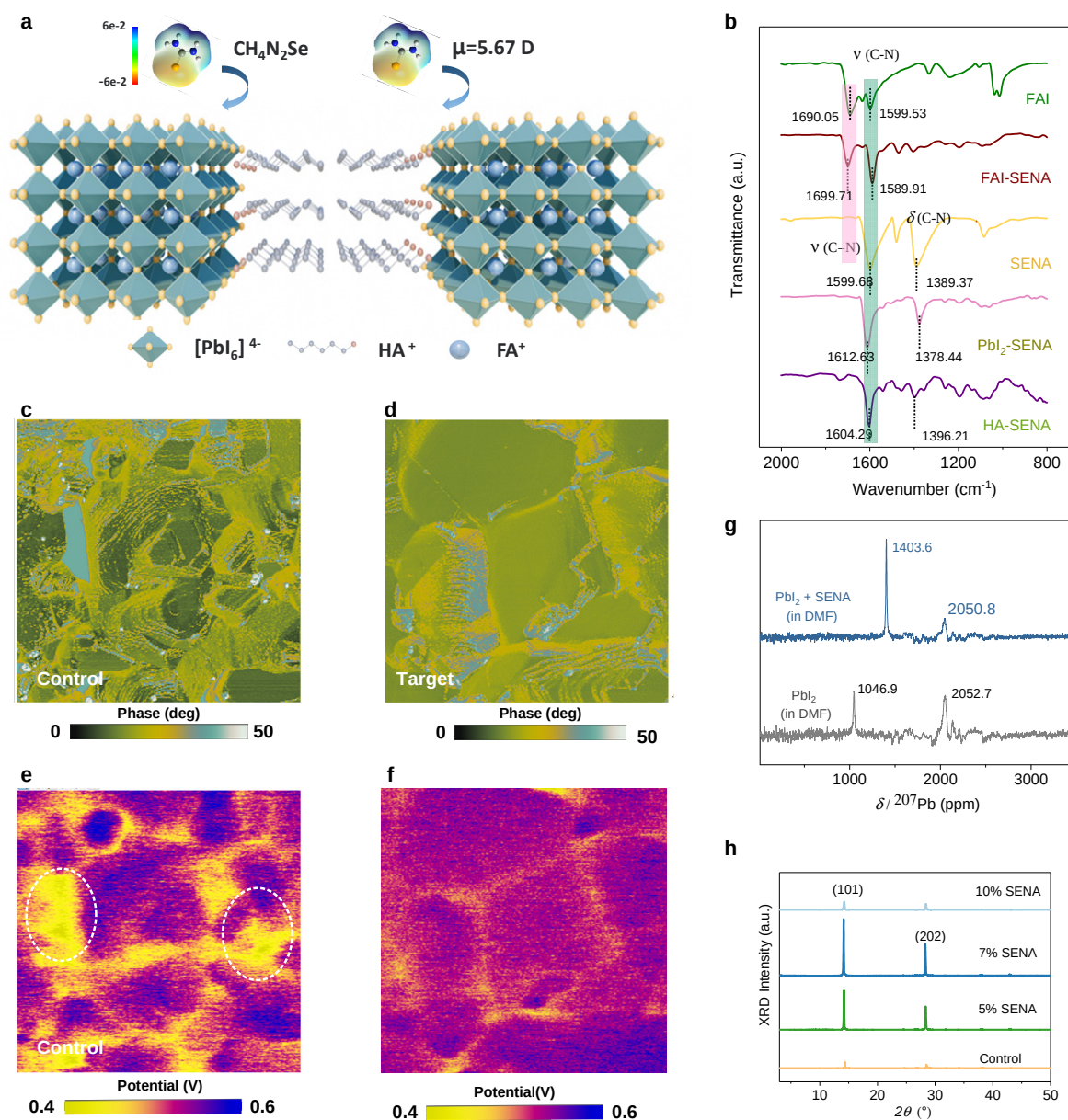


Figure 4-2. SENA additive strategy drives the vertical orientation. (a) Schematic of SENA additive ($\text{CH}_4\text{N}_2\text{Se}$) strategy which drives the orientation of FA-based 2D perovskite. (b) FTIR spectra of the different perovskite components with SENA (c-d) Phase images ($2 \mu\text{m} \times 2 \mu\text{m}$)

of control and target perovskite films measured by AFM, and the target (HA-SENA) perovskite films are treated with 7% SENa additives. (e-f) KPFM images of control and target perovskite films at the same area as the phase image. (g) ^{207}Pb NMR spectra of PbI_2 individually and interacted with SENa additives dissolved in DMF. (h) XRD of perovskite films with different ratios of SENa additives, respectively.

The most important advance of the SENa additive is its strong interaction with alkyl ammonium cations. The signals of the C-N stretching and bending vibrations in the HAI-SENA complex show significant position shifts, further indicating the occurrence of chemical interactions. The interaction between HAI-SENA reduces the heterogeneous nucleation sites at the liquid-air interface induced by HA^+ cations, indicating the preference for template-driven parallel growth is impeded at the liquid-air interface [128]. It can be predicted that the SENa additive acts as a bridge between octahedral and alkyl cations and this also avoids segregation of spacers in the precursor film. To verify the influence of SENa on the crystallization kinetics, the PL was performed from the front side (air/perovskite) and backside (perovskite/glass substrate interface) for comparison. As depicted in **Figure 4-S18**, the PL spectra of the annealed control films (particularly probed from the backside) exhibit more low- n phases, indicating layer-by-layer growth with a stratified structure at the interfaces. In contrast, the introduction of the SENa additive significantly inhibits the formation of the low- n phases, especially at the bottom. These results demonstrate that the chemical interaction between SENa and perovskite constituents facilitates a controllable crystallization process based on 3D-like templates at the air/liquid interface after anti-solvent extraction, thus enhancing the vertical orientation of the layered structure[129].

We further utilized XRD and GIWAXS measurements to investigate the film orientation. Following the Bragg-Brentano diffraction geometry, the XRD diffraction intensity corresponds to the out-of-plane orientation of specific lattice planes. **Figure 4-2h** shows a significant enhancement in the diffraction intensities of the (101) and (202) crystal planes of the 2D perovskites, indicating the effective modulation of the film crystallization by the SU additive. Notably, the films fabricated with 7% SENa exhibit the strongest (101) diffraction. GIWAXS patterns in **Figure 4-S19** show that film treated with 7% SENa displays sharper and more

discrete diffraction spots, along with a reduced distribution of parallel orientations and significantly enhanced intensity in the out-of-plane orientation. This enhanced film orientation is expected to promote the directional transport of photogenerated charge carriers between the electrodes and consequently increase the photocurrent of the device.

We further employed energy-dispersive X-ray spectroscopy (EDS) and XPS characterization to investigate if there is residual SENA after the annealing process. Notably, a negligible signal corresponding to the Se element was detected after annealing (**Figures 4-S20&S21**), indicating that the SENA additives separated from the perovskite during annealing. Additionally, compared with the films without the SENA additive, the XPS binding energy of Pb and I core levels did not change significantly with the SENA treatment after annealing, as illustrated in **Figure 4-S22**, further proving the SENA additives have negligible influence on the resulting lattice.

The atomic force microscopy (AFM) results (**Figure 4-S23**) manifest that the incorporation of 7% SENA additives results in larger grain size and denser, smoother surface morphology. The surface roughness is significantly reduced from 36.3 nm to 15.5 nm. Furthermore, the phase mapping also shows a more ordered texture and more uniform phase distribution on the SENA-treated film (**Figures 4-2c&d**), indicating a high crystal quality and preferred orientation. The surface potential results revealed that the control films exhibited a discontinuous potential distribution and wide potential barriers across grain boundaries (**Figures 4-2e&f**). In contrast, the SENA-treated film displays a more uniform potential distribution and smaller potential barrier at the grain boundaries, suggesting the formation of uniform contacts and a reduction in trap states (**Figure 4-S24**). Time-resolved photoluminescence (TRPL) decay measurements further demonstrated reduced carrier traps and enhanced lifetime after the SENA treatment (**Figure 4-S25**). The carrier lifetime increased from 174.5 ns to 268.5 ns, indicating reduced non-radiative carrier recombination, thereby reducing potential losses, and improving the photovoltaic performance of devices (**Figures 4-S29& Table 4-S1**).

We further conducted femtosecond transient absorption (TA) spectroscopy comprehensively to

characterize and analyze the phase distribution and carrier dynamics of the resulting perovskite films. **Figure 4-3c&f** depicts 2D contour plots of the TA corresponding to the HA-based 2D perovskite films before and after SENA treatment. The TA spectrum reveals that the film exhibits a mixture of multiple n -valued 2D phases and 3D-like (high- n) phases. Notably, the evident ground state bleaching (GSB) peaks appear at approximately 490, 570, 630, 670, 690, and 775 nm corresponding to the n values of 1, 2, 3, 4, 5, and high- n phases, respectively (**Figure 4-S26**). The distribution of 2D phases with varying n values may be influenced by differences in cleavage energy and growth rate [128, 270, 271]. **Figures 4-3a&d** illustrate the evolution of absorption at different time delays. As time progresses, the decay of the GSB peaks of the low- n phase is accompanied by a rise in the GSB peak of the high- n phase, indicating the charge transfer. The introduction of the SENA additives significantly reduces the formation of low- n phases that induce parallel growth, as revealed by the significant reduction of the GSB signals corresponding to $n=1$, and $n=2$ phases. Simultaneously, the fitting results of the carrier dynamics demonstrate faster decay (lifetime τ_1) of lower- n phases and faster establishment (lifetime τ_{et}) of the high- n phase in the HA-SENA films (**Figures 4-3b-c&Table 4-S5**). This observation indicates that the SENA-treated films exhibit enhanced charge transfer from the low- n phase to the high- n phase, enabling efficient charge separation and further extraction.

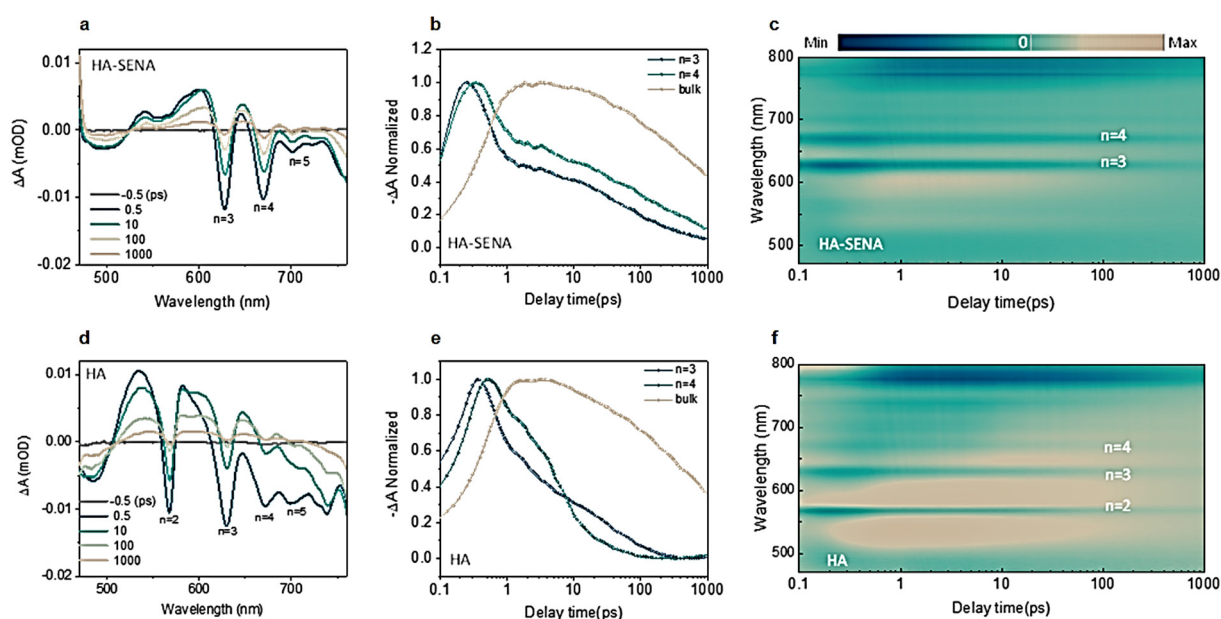


Figure 4-3. Transient absorption (TA) of 2D perovskite films. (a, d) Representative TA spectra at indicated delay time; (b, e) TA kinetics probed at different-n perovskite bands ($n=3$, 4 and large n); (c, f) TA contour map spectra with or without SENA treatment.

4.3.4 Enhanced air stability

We conducted a comprehensive evaluation of the stability of the FA-based 2D perovskite films using spacer cation engineering combined with the SENA treatment. To assess the effects on films of the direct exposure under an AM 1.5G illumination (30-50% relative humidity, room temperature), we employed confocal PL mapping with a scanning laser power density of 0.5 mW/cm². The initial PL maps of the HA- SENA perovskite films exhibit the highest intensities and display a more uniform and dense distribution across the entire scanning region (10.57 μ m $\times$ 10.57 μ m), compared with the BA SENA and OA-SENA perovskites, as depicted in **Figures 4-(4a-f)**. As the illumination time increases, the HA-SENA 2D perovskite films exhibit better photostability with only a slightly reduced luminescence intensity (**Figures 4-4b&4-4e**), outperforming the BA-SENA perovskite films with progressively decreased intensities (**Figures 4-4a&4-4d**) and the OA-SENA perovskite films with localized non-uniform spots and decomposition (**Figures 4-4c&4-4f**). The histograms of the PL peak intensity distributions extracted from the PL mapping data further confirm these observations. (**Figure 4-4g**). Even after aging, the HA-SENA perovskite films mostly demonstrate high intensities with a well Gaussian distribution, but the OA-inserted perovskites show a significant decrease in strength with an uneven distribution. These findings are consistent with the optical morphology results presented in **Figure 4-S27**. In summary, the HA- SENA 2D perovskites exhibit superior phase stability under light illumination.

To evaluate the thermal stability of the films, we monitored X-ray diffraction (XRD) patterns of various FA-based 2D perovskite films at 85 °C in ambient air with 85% relative humidity (RH). **Figure 4-4h-j** reveals that the BA- SENA perovskite films show a slightly reduced diffraction intensity and slightly broadened FWHM, indicating a potential deterioration of crystallinity after thermal aging. The OA-SENA 2D perovskite films exhibit an increased intensity of the diffraction peak at 12.8°, particularly after 100 to 200 hours, suggesting a gradual structural change. In contrast, the XRD diffraction peaks of the HA-SENA perovskite

films show no significant change, demonstrating excellent thermal stability. Furthermore, none of these three 2D perovskite films has shown the δ -phase FAPbI_3 (the featured diffraction peak is at about 11.9°), indicating the transition pathways to the one-dimensional (1D) photo-inactive structures were greatly suppressed in 2D structures. Additionally, water contact angles were measured to study the hydrophobic properties of the obtained 2D perovskite films (**Figure 4-S28**). The HA- SENA perovskite films demonstrate favorable hydrophobicity, indicating their ability to prevent the infiltration of external moisture. To conclude, the combination of organic spacer cation engineering and SENA additives strategy led to the outstanding properties and stability of the HA- SENA perovskite film.

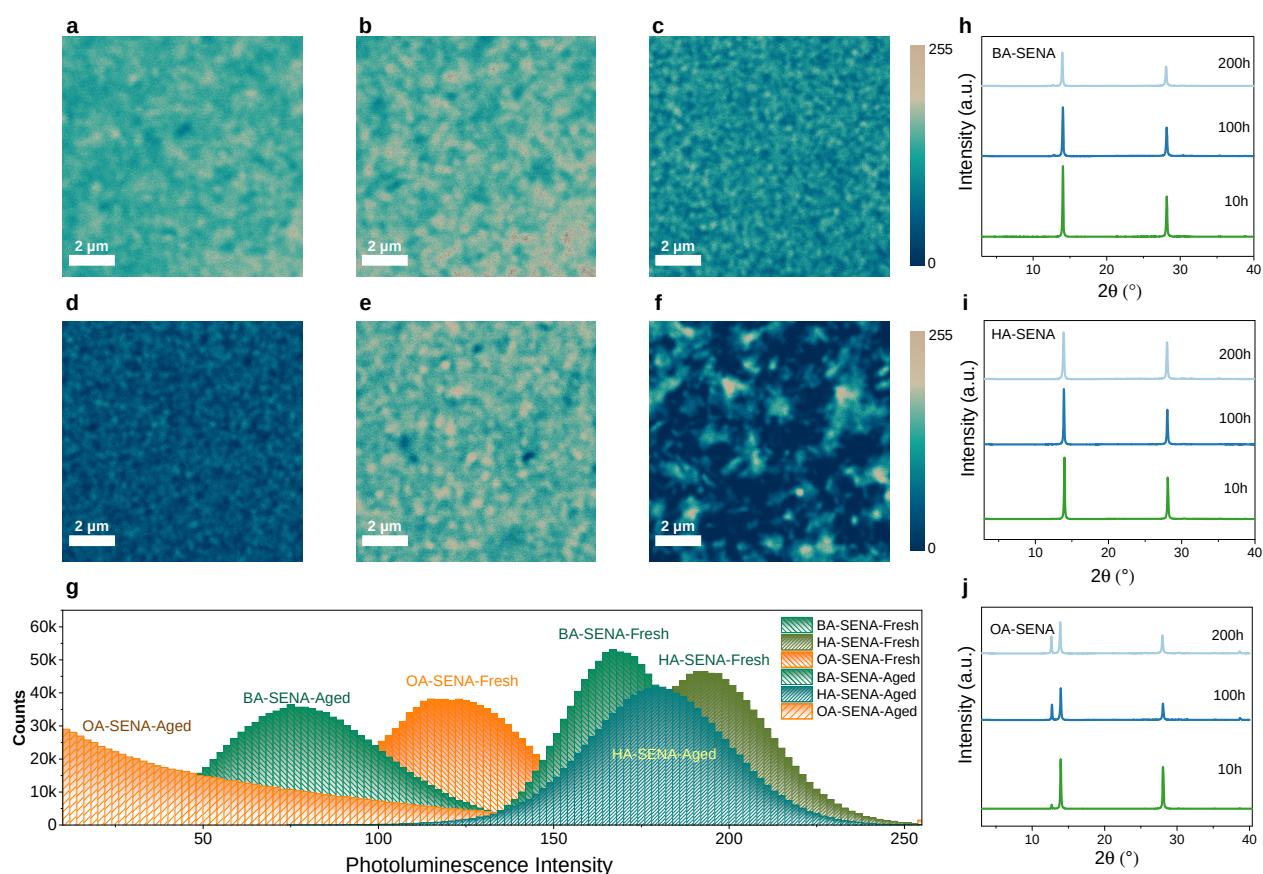


Figure 4-4. Stability of optimized low-n 2D perovskite films. (a-c) Confocal PL mapping comparison (from left to right) of fresh BA- SENA, HA- SENA, and OA- SENA 2D perovskite films, respectively (the area is $10.57 \times 10.57 \mu\text{m}$). (d-f) Confocal PL mapping of the corresponding aged FA-based 2D perovskite films, the aging condition is 1sun illumination, 30-50% RH, room temperature for 200 hours. (g) Statistics of photoluminescence intensity of

above perovskites. **(h-j)** XRD patterns of aged 2D perovskite films, under 85°C in ambient air with ~85% relative humidity.

4.3.5 Photovoltaic performance

We fabricated low-*n* FA-based 2D perovskite solar cells with a device structure of FTO/SnO₂/PVSK/Spiro-OMeTAD/Au, as depicted in **Figure 4-5a**. As expected, the device incorporating the HA spacer cation with 7% SENA treatment achieves an exceptional PCE of 20.03%, combined with a V_{oc} of 1.09 V, a J_{sc} of 23.60 mA/cm², and an FF of 77.86 % (**Figure 4-5b**), surpassing those achieved with other spacer cations (**Figure 4-S30**) and setting a new record for low-*n* 2D perovskites devices, as summarized in **Figure 4-5d** and **Table 4-S4**. The integrated current densities of 23.21 mA/cm² from the external quantum efficiency (EQE, **Figures 4-5c&4-S31**) match well with the J_{sc} values obtained from the *J-V* characterization. The enhanced photocurrent is consistent with orientation variation from BA to HA as characterized by GIWAXS. The obtained J_{sc} and V_{oc} values of the HA-SENA perovskite devices are higher than BA- and OA-inserted devices (**Table 4-S2**), thus further confirming its superiority. The relationship between V_{oc} and natural logarithmic current density, along with the results from the space-charge-limited current (SCLC) measurements in **Figures 4-S32&S33**, further proves that the HA-SENA perovskite devices effectively eliminate trap-induced non-radiative recombination losses.

The performance of photovoltaic devices summarized in **Tables 4-S1&S2** highlights significant enhancement in photocurrent and series resistance achieved through the SENA additive strategy in the FA-based 2D perovskite devices (**Figures 4-5e&S30**), thereby demonstrating the promise for the fabrication of large-area 2D perovskite solar cells (**Figures 4-5f&S34**). Particularly, the large-area device (1.02 cm²) also achieved a remarkable PCE of 18.70% (V_{oc} = 1.09V, J_{sc} = 22.08 mA cm⁻², FF = 77.68%), placing it among the top-performing PVSCs of similar sizes reported to date. Importantly, the V_{oc} and J_{sc} values of the large-area device are comparable to those achieved in smaller-area devices, thanks to the modulated orientation and significantly improved series resistance enabled by the SENA additive strategy (**Table 4-S3**). These findings underscore the promising prospects for scaling up the most stable 2D perovskite devices.

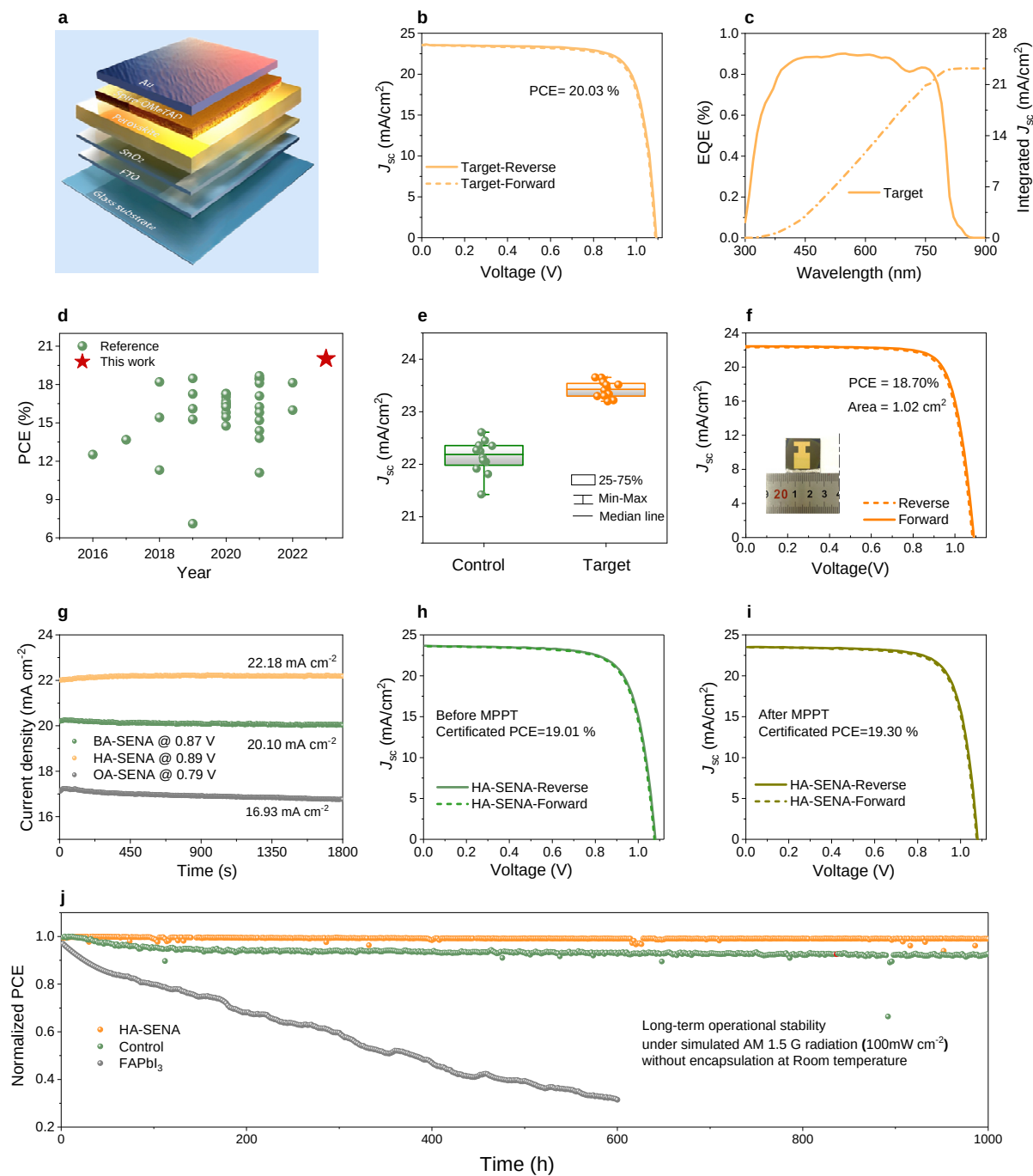


Figure 4-5. Photovoltaic performance and stability of PVSCs. (a) Schematic of the device structure of low-*n* 2D perovskite solar cell. (b) *J*-*V* curves (under forward and reverse scanning direction) and (c) EQE spectrum of the target (HA-SENA) PSCs. (d) Summary of PCE evolution of low-*n* 2D PSCs reported in the related literature (listed in Supplementary Table S4). (e) *J*_{sc} distribution for control and target PSCs (w/o SENA and with SENA additives). (f) *J*-*V* curves and optical photograph of 1.02 cm² large area low-*n* 2D devices. (g) The maximum

power output of BA-, HA- and OA- SENA -based devices. **(h-i)** The certificated PCE of the target devices before and after the MPPT. **(j)** Long-term operational stability of HA- SENA, control, and FAPbI₃ perovskite solar cells under simulated AM 1.5 G radiation 100mW cm⁻² without encapsulation at room temperature within the testing chamber.

We further monitored the power output stability of the fabricated low-*n* 2D devices, as illustrated in **Figure 4-5g and Table 4-S4**. Over the 30 minutes of testing, we observed a slight light-induced degradation (LID) in the BA- and OA-inserted devices, which is a common phenomenon observed in perovskite solar cells with a normal device structure and can be attributed to photo-induced ion migration and trap formation within the perovskite layer. In contrast, the HA-inserted devices exhibit no LID and demonstrate a remarkably more stable photocurrent output. This advantage was further confirmed by an independent third-party certification center (SIMIT). A certified swept efficiency of 19.01% was confirmed before the maximum power point tracking (MPPT) test as shown in **Figure 5h and Figure 4-S35**. Following more than 30 minutes of MPPT, the efficiency gradually increased at a slow pace, resulting in a certified efficiency of 19.30% Finally, as illustrated in **Figure 4-5i**. No occurrence of LID during the 30-minute certification of MPPT, along with the extremely stable power output, verified the great stability of the unique 2D lattice enabled by the HA spacer cation.

Finally, we conducted a set of stability measurements on the FA-based 2D perovskite devices without encapsulation under different aging conditions. The long-term operational stability of the unencapsulated devices was measured by tracking the maximum power point under continuous one-sun illumination (**Figure 4-5j**). The initial efficiencies of HA-SENA, Control, and FAPbI₃ solar cells are 19.86%, 18.91%, and 23.12%, respectively. The target devices (HA-SENA) exhibited less than 1% efficiency degradation after 1000 hours, while the PCE of the FAPbI₃ devices decreased to approximately 30% of its original value. Additionally, the thermal stability of the photovoltaic devices was also conducted at 85 °C and 50% RH. As depicted in **Figure 4-S36(a)**, the HA-based perovskite devices exhibited an extremely low degradation rate, with a loss of approximately 8.9% after 720 hours of thermal aging. In contrast, the BA- and OA-based perovskite devices displayed higher degradation rates, experiencing losses of

approximately 19% and 25% of their initial values, respectively. Furthermore, the devices were subjected to cyclic temperature measurements to investigate their performance variation under cold-warm or other types of strain fatigue (-25°C and 85°C). As shown in **Figure 4-S36(b)**, after 50 cycles, the HA-inserted 2D perovskite solar cell maintains 90.3 % PCE, outperforming BA- and OA-inserted perovskite devices (maintaining 76.1% PCE and 54.1% PCE, respectively). These findings underscore the exceptional environmental stability of the HA-based perovskite devices, characterized by a relatively low decay rate of PCE resulting from the micro-strain-relaxed lattice distortion and SU additive strategy (**Table 4-S4**, stability comparison).

4.4 Conclusion

In conclusion, we have successfully demonstrated a new design and development of low-n FA-based 2D perovskite solar cells that exhibit both high efficiency and high stability. By implementing organic spacer cation engineering, we achieved micro-strain relaxed lattice distortion in the FA-based 2D perovskite lattice. This approach effectively reduced symmetry breaking alleviated carrier-lattice interactions, and significantly improved the stability of the perovskite lattice against photothermal aging stresses, particularly under extreme temperature variations. Moreover, we innovatively employed a SENA additive strategy to modulate the crystallization kinetics, forming intermediate phases through Lewis's base reactions, which suppressed the non-uniform nucleation and facilitated the vertical growth of the 2D perovskite. These strategies effectively inhibited non-radiative carrier recombination and greatly improved photovoltaic performance. The optimized PCE of the FA-based 2D photovoltaic devices reached 20.03% (certified efficiency of 19.30%), setting a new record for FA-based low-n 2D perovskite solar cells. Remarkably, the devices without encapsulation exhibited minimal efficiency degradation (less than 1%) after operating at the maximum power point for 1000 hours and maintaining 92.3% of their initial efficiency after 1000 hours of heating at 85°C, and 91.1% of their initial efficiency after 50 cycles of thermal cycling. Our work demonstrates a promising pathway to further improve the performance and stability of photovoltaic devices, advancing the commercialization of perovskite-based energy and optoelectronic devices.

4.5 Appendices

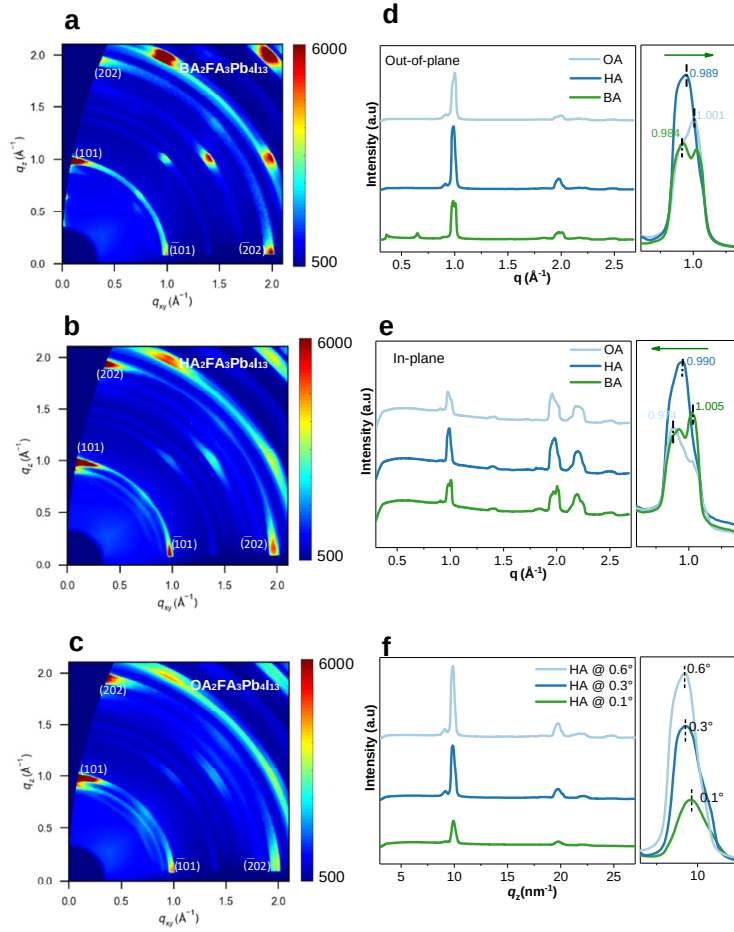


Figure 4-S1 Analysis of GIWAXS results. **(a-c)** GIWAXS patterns for the BA-, HA-, and OA-inserted perovskite films with the incident angle of 0.6°, respectively. **(d-e)** Corresponding intensity profiles along the q_z and q_{xy} direction from GIWAXS results with the incident angle of 0.6°, respectively. The peaks in the out-of-plane direction show a rightward movement and the opposite trend in the in-plane. **(f)** Intensity profiles along the q_z direction (out of plane) of HA-inserted perovskite film with incident angles from 0.1° to 0.6°.

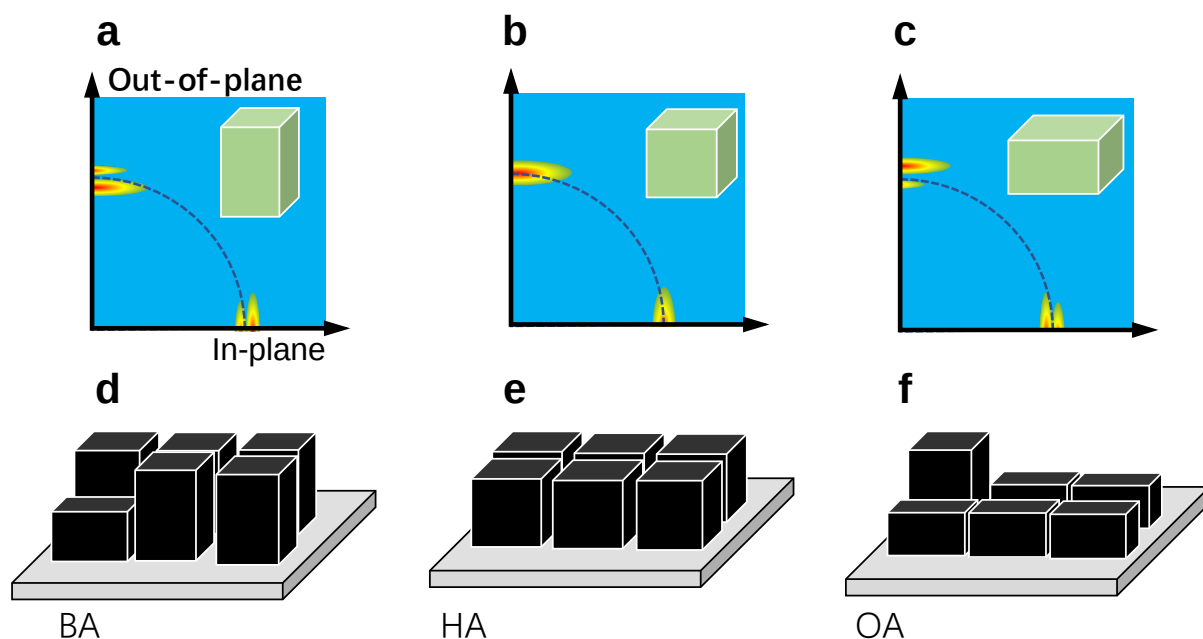


Figure 4-S2 Schematic of lattice distortion-based GIWAXS results.

No perturbations on the diffraction peak in the in-plane and out-of-plane directions, implying that lattices are closer to cubic are shown in **(b)**. The shift of the diffraction peak position means that the lattice spacing changes. For example, the larger q_z (narrower the spacing distance) in the out-of-plane direction, implies a compressive elongated lattice, as shown in **(a)**. The smaller q_z (wider the spacing distance d) in the out-of-plane direction, implies a stretched elongated lattice, as shown in **(c)**. Therefore, no splitting peaks of the (111) lattice plane in the in-plane and out-of-plane directions, implying that HA-inserted perovskite lattices are closer to cubic are shown in **(e)**. The splitting peak of the (111) lattice plane in the out-of-plane and in-plane direction infers the BA- and OA-inserted perovskite lattices are elongated lattices as shown in **(d)** and **(f)**.

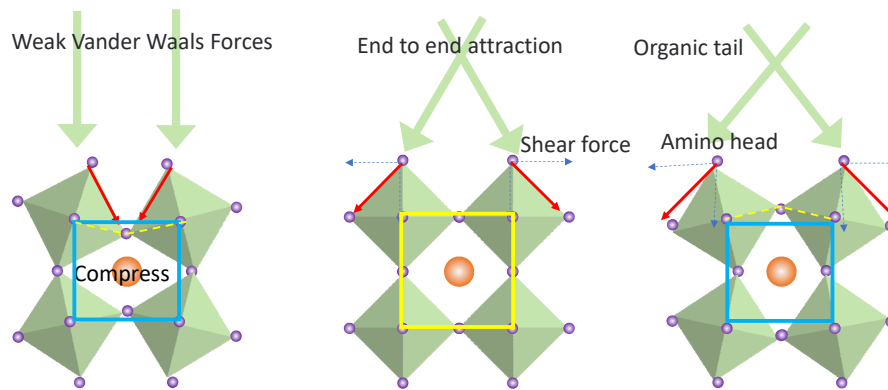


Figure 4-S3 Schematic of shear force. When the spacer cation is inserted along the (101) crystal plane of 3D perovskite to form 2D perovskite, it forms a weak Vander Waals force at one end and a strong hydrogen bonding at the other end. The lead-iodine octahedron possesses a cohesive force of inward compression. In 2D RP perovskite, organic spacer cations are staggered. The chain alkyl chain forms a shearing force because it is attracted end to end. When the shear force is small, the Pb-I octahedron still shows an inward cohesion force(**a**). Appropriate shear force can make the lattice close to the cube (**b**), while excessive shear force will form an outward cohesion force (**c**). The octahedron tilting also results in a smaller lattice constant.

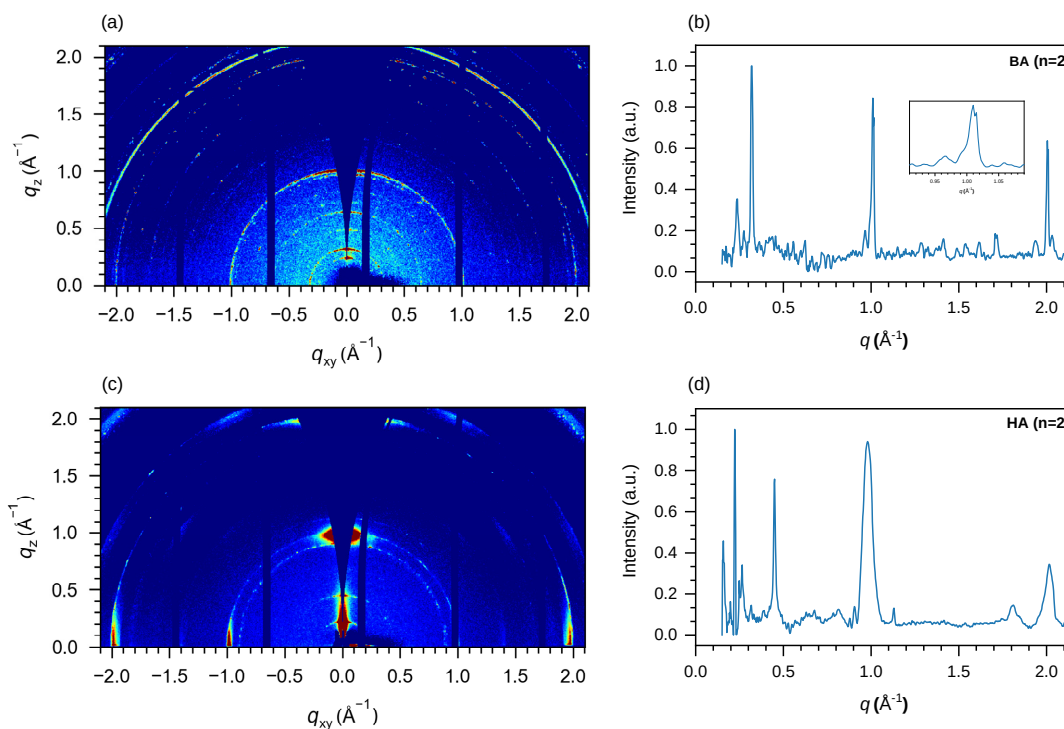


Figure 4-S4. (a-c) GIWAXS patterns for the BA-, and HA-inserted (n=2) 2D FA-based

perovskite films with the incident angle of 0.6°, respectively. **(b-d)** Corresponding intensity profiles along the out-of-plane direction from GIWAXS results.

Supplemental Note S3.

Quantification of the lattice distortion based on DFT.

We used representative n=4 (BA)₂FA₃Pb₄I₁₃, (HA)₂FA₃Pb₄I₁₃, and (OA)₂FA₃Pb₄I₁₃ structures for theoretical calculations to support the experimental results and the perovskite crystal data, and the structures are summarized in **Table S6**. The lattice distortions of the Pb-I framework can be divided into two main parts: one is the distortion of the Pb-I single octahedron, and another important structural distortion is the collective distortion between adjacent octahedra of perovskite layers (octahedral tilting). After structure optimization, we calculated the bond length quadratic elongation ($\langle\lambda\rangle$) and bond angle variance (σ), respectively, using VESTA software⁹⁻¹⁰.

$$\begin{aligned} \langle\lambda\rangle &= \frac{1}{n} \sum_{i=1}^n \left(\frac{l_i}{l_0}\right)^2 \\ \sigma^2 &= \frac{1}{m-1} \sum_{i=1}^m (\alpha_i - 180)^2 \end{aligned} \quad (1)$$

where l_i represents the Pb-Pb bond length, l_0 is the average Pb-Pb bond distance, and α_i is the octahedral Pb-I-Pb bond angle. Notably, the Pb-I-Pb bond angle deviates from the ideal 180°, respectively. DFT simulations were further used to reveal the lattice structure variations in these FA-based 2D perovskites. The octahedra distortion and tilting were calculated by their bond length quadratic elongation ($\langle\lambda\rangle$) and bond angle variance (σ) and the deduction was illustrated in Fig 1C. It can be inferred that larger $\langle\lambda\rangle$ and σ^2 values correspond to more distorted octahedrons and the Pb shifts deviated from the center. The tilting between adjacent octahedrons was considered using $\langle\lambda\rangle$ of neighboring Pb-Pb bond and σ^2 values of Pb-I-Pb. Statistical results show that the lowest octahedral tilting appears in HA-inserted perovskite ($\langle\lambda\rangle = 1.0066$, $\sigma = 37.7238$), as compared to both BA ($\langle\lambda\rangle = 1.0082$, $\sigma = 38.2069$) and OA-inserted perovskites ($\langle\lambda\rangle = 1.0117$, $\sigma = 39.9906$). DFT results further prove that the HA-inserted Pb-I framework obtains the lowest formation energy, meaning that fragile structures in the 2D lattice can be most stabilized with HA insertion in Fig. S5. These results indicate that the HA-inserted

lattice structure obtains a relatively lower degree of octahedra distortion and tilting deviated from the center, which can be beneficial to the stability performance of FA-based 2D perovskites.

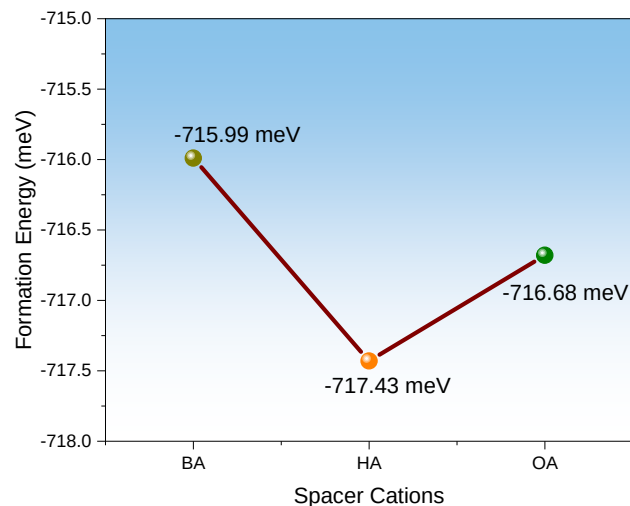


Figure 4-S5 The formation energy of the Pb-I Octahedral framework is based on DFT results of 2D FA-based perovskite with BA, HA, and OA organic spacers, respectively.

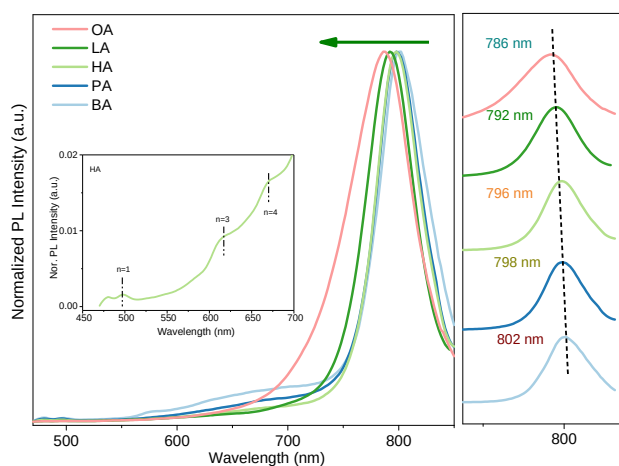


Figure 4-S6 The PL spectrum of different 2D FA-based perovskite films excited from the front side, the peak shows a clear blue shift as the increases of linear chain length.

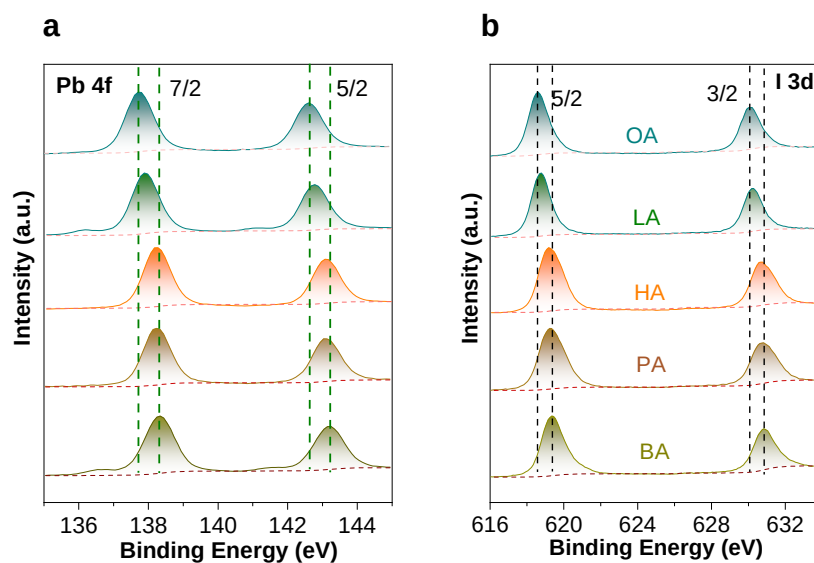
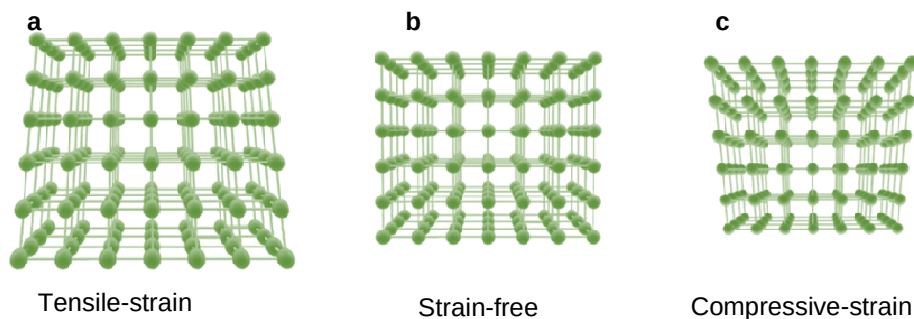


Figure 4-S7 (a) The Pb 4f and (b) I 3d core-level XPS spectra of distorted 2D FA perovskite films based on BA, PA, HA, LA, OA organic spacer cations, respectively, and the peaks of Pb 4f and I 3d orbitals both move towards lower binding energy.

Supplemental Note S4

Macrostrain:



Microstrain:

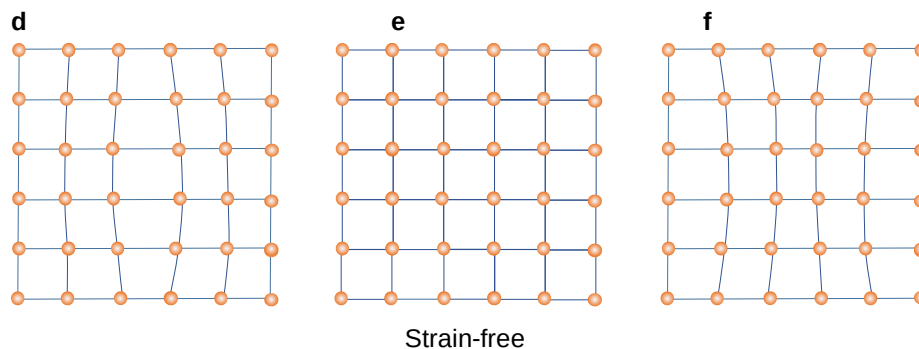


Figure 4-S8 Schematic of Macro- and microstrain.

(a-c) Macrostrain usually results in a uniform lattice distortion that is observed as a shift in the X-ray diffraction peaks. (d-e) Micro strain is caused by deviations from the ideal crystalline lattice (perfectly ordered crystalline array) and is often produced by residual stresses, dislocations, vacancies, grain boundaries, and any other defect that causes a nonuniform lattice distortion in the crystal. It results in a distribution of d -spacings that is observed as a broadening peak.

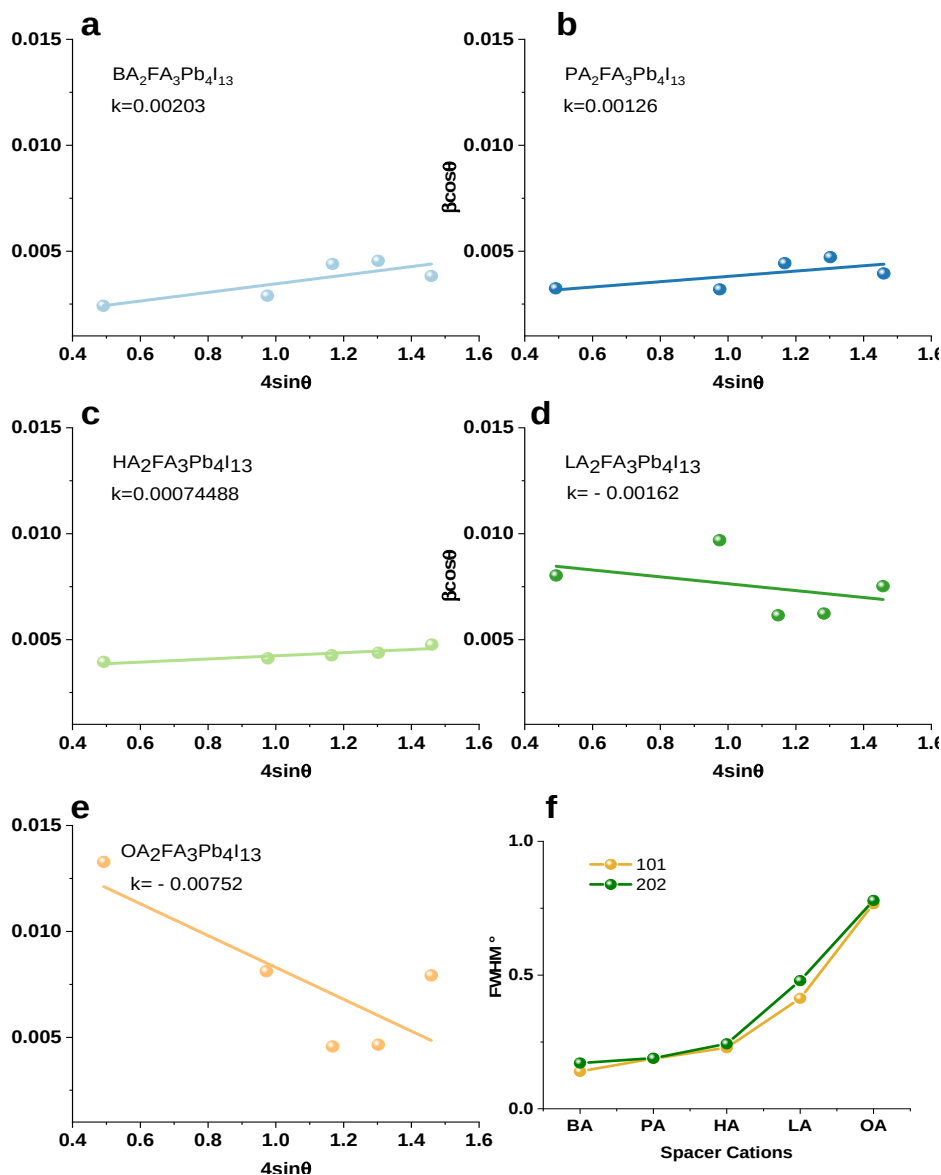


Figure 4-S9 (a-e) The slope of the fitting line extracted from XRD patterns of perovskites based on BA, PA, HA, LA, and OA spacer cations, respectively, according to Williamson–Hall analysis[236, 272], the slope k determines the lattice strain, where the positive value represents the tensile strain, and the negative value represents the compressive strain. **(f)** The FWHM of

(101) and (202) lattice plane when the spacer cations change from BA to OA.

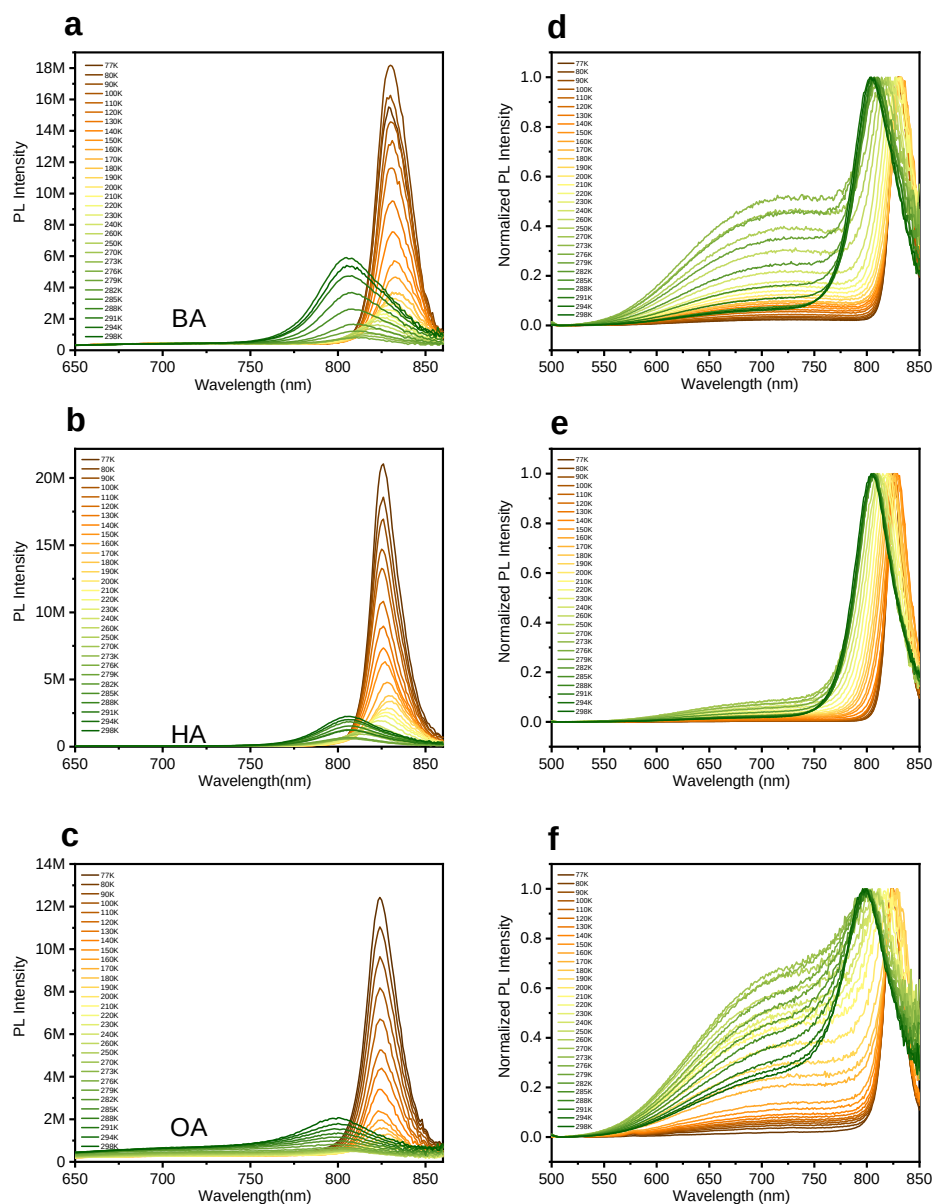


Figure 4-S10 (a-c) Original PL intensities result and (d-f) corresponding normalized PL intensities of quasi-2D FA-based perovskite films based on BA, HA, and OA organic spacers, respectively, in the temperature range from 77 K to 298K.

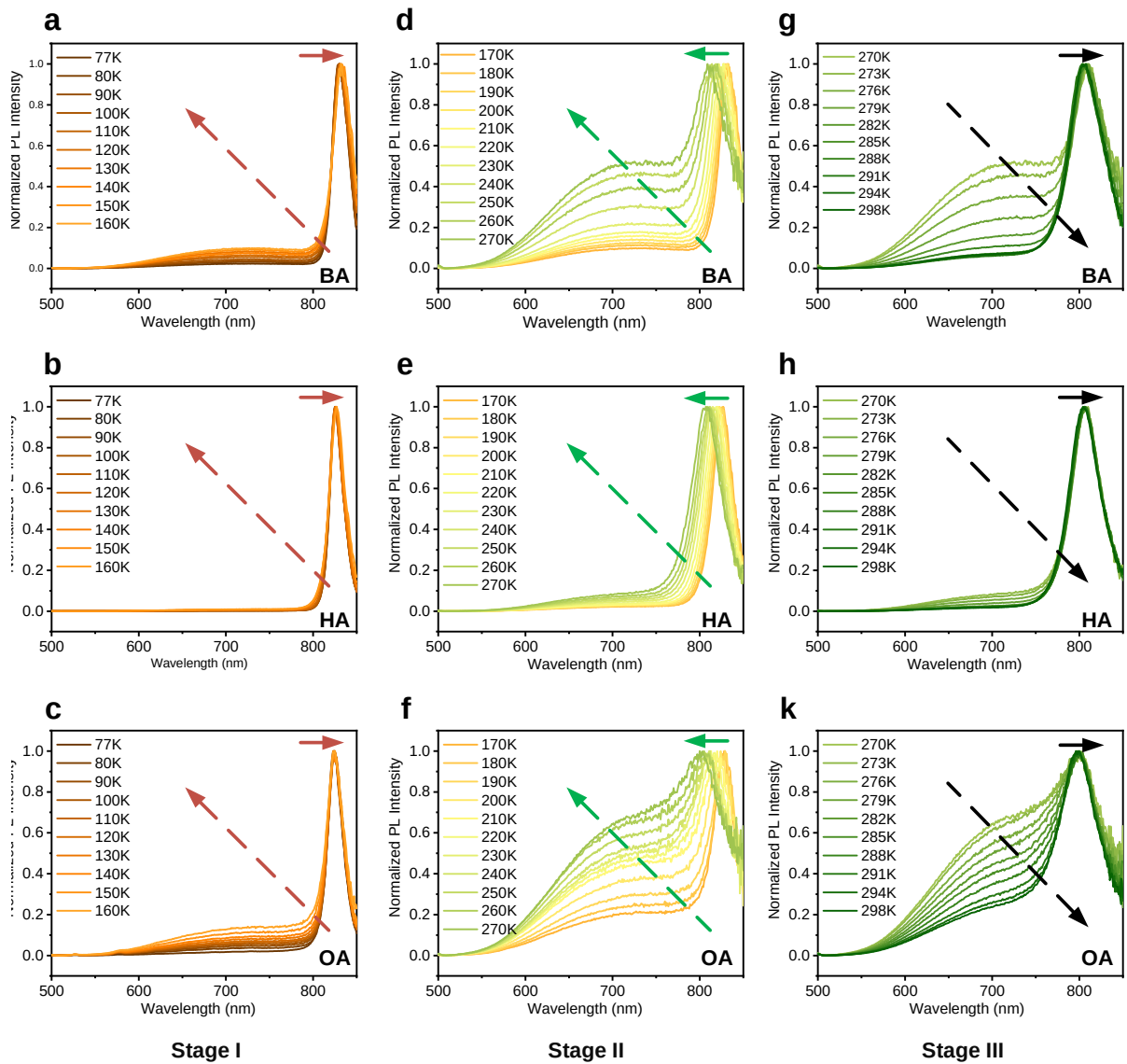


Figure 4-S11 Phase transition and carrier-lattice interaction. Normalized PL of 2D perovskites under different temperatures, showing three distinct stages. (a-c) The first stage ranges from 77 K to 160 K. (d-f) The second stage ranges from 170 K to 270 K, (g-k) The third stage ranges from 270 K to 298 K.

Supplemental Note S5.

Phase Transition and Carrier-Lattice Interaction

To further investigate the uneven peak broadening within the range of 600nm to 800nm, the normalized PL curves (**Figure 4-S10**) were divided into three distinct temperature segments separated at 160 K and 270 K, respectively, as depicted in **Figures 4-1F-H & Figure 4-S11**.

Specifically, for the first temperature segment (below 160 K), the PL peak positions are located at around 826 nm with a temperature range from 77 K to 150 K and undergo a slight red shift to around 828 nm within the temperature range of 150~160 K in **Figure 4-S11(a-c)**. This behavior can be explained that smaller bandgap in low temperatures is the typical behavior due to the positive temperature coefficient of bandgap in lead halide perovskites [260]. The slight redshift at low temperatures can be ascribed to the lattice contraction, short lead-iodine bonds resulting in more orbital overlapping, and adjusting the bonding and antibonding states, thereby reducing the energy bandgap.

For the second temperature part (170 K to 270 K), a pronounced and sudden blue shift of all the main PL peaks from 828 nm to 820 nm is observed in **Figure 4-S11(d-f)**. The obvious reverse shift that occurs at around 160 K-170K may be ascribed to the phase transition from low symmetry to higher symmetry of tetragonal phase structures[267], and the structural phase transition corresponds to a change of the perovskite octahedral tilting or distortion [266]. Furthermore, for the BA- and OA-inserted perovskite (**Figures 4-S11 (d&f)**), the PL peaks signal at a lower wavelength (PL peak positions are located at around 650-700 nm) shows a progressively upward intensity as the temperature rises. This can be attributed to the contribution of the low-*n* phase 2D perovskite components. Near 270 K, the PL intensities of low-*n* phase 2D perovskite reached the highest values, the increase of low-*n* phase 2D perovskite is the main reason for the non-uniform broadening of BA- and OA-inserted perovskite.

For the third temperature segment (270 K to 298 K), all the main PL peak positions exhibit a slight blue shift with a continuous trend in **Figures 4-S11(g-k)**. However, the proportion

related to the low-n phase of BA-and OA-inserted 2D perovskites began gradually decreasing with the increased temperatures. Notably, there is an apparent inverse increase in the maximum PL intensity around 270 K as shown in **Figure 4-S10**. Considering the variation at full-width of half maximum (FWHM) and the main peak position shifts with the temperature, we speculate that a phase transition from the quasi-tetragonal to the quasi-cubic phase occurs around 260-270 K for all the FA-based 2D perovskites [267]. Compared to HA-inserted perovskites, the BA- and OA-inserted 2D perovskites show higher sensitivity in the PL intensity as the temperature varied, further highlighting the superiority of the HA-inserted 2D perovskite in stabilizing the inorganic framework, particularly for the real-environment applications exposed to cold-warm cycles.

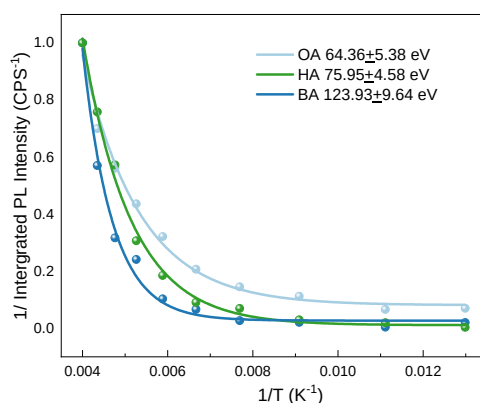


Figure 4-S12 Exciton binding energy determined by the integrated PL intensity versus different temperatures of FA-based 2D perovskite films. We extracted E_b values of the obtained FA-based 2D perovskites by fitting the temperature-dependent excitonic emission intensity.

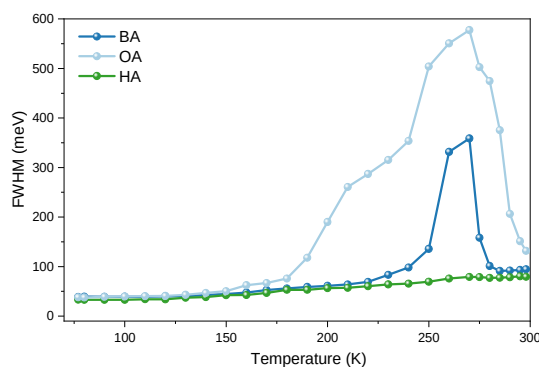


Figure 4-S13 FWHM versus temperature of FA-based 2D perovskite film with BA, HA, and OA organic spacers, respectively, indicating the intensity of carrier-lattice interaction.

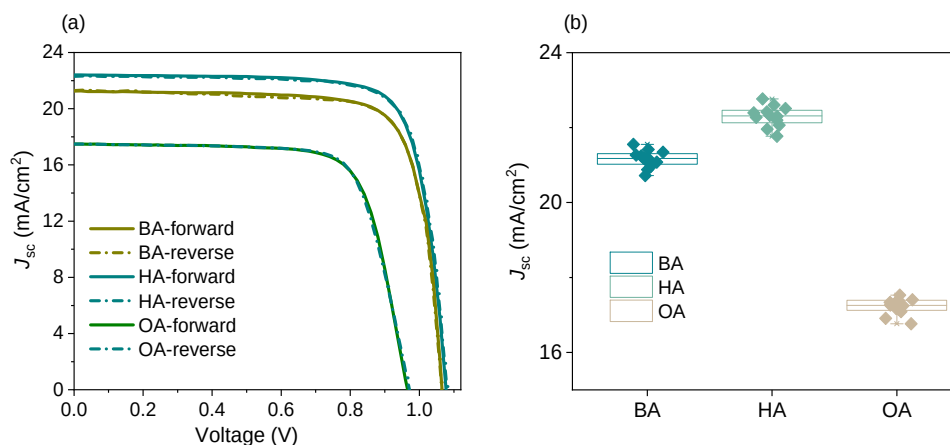


Fig. 4-S14 (a) J - V curves (under forward and reverse scanning direction) of the best devices based on various FA-based 2D perovskites with BA HA OA spacers. J_{sc} distribution for the different PSCs.

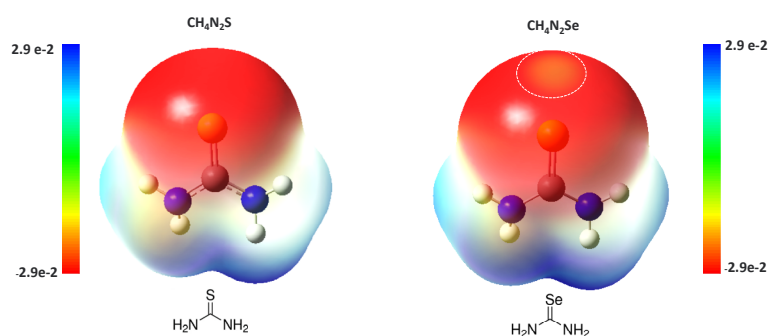


Figure 4-S15 Chemical structures and calculated electrostatic potential (ESP) mapping profiles of thiourea (TU), and selenourea (SENA), respectively. The ESP color bar ranges from -2.9e-2 to 2.9e-2 for clear comparison.

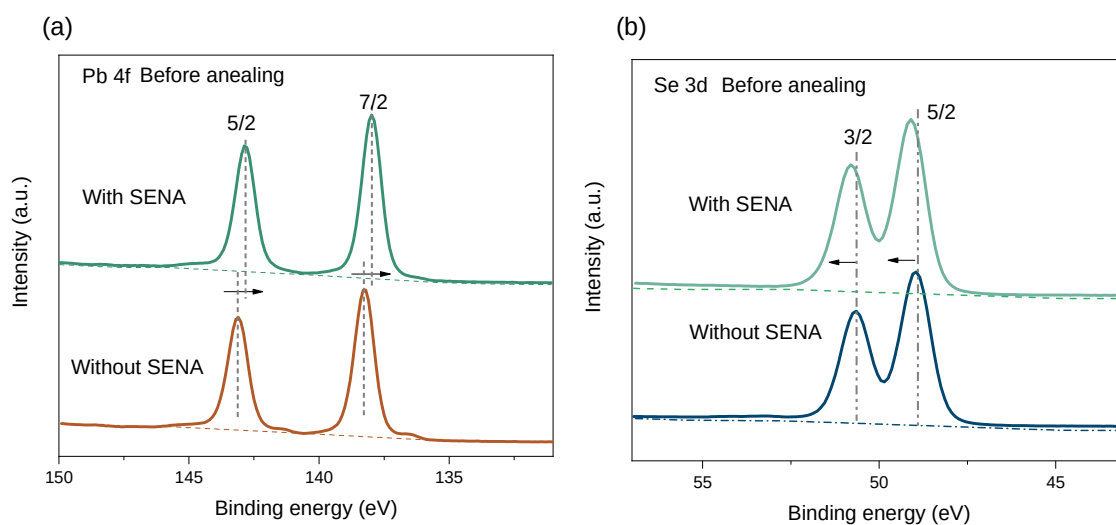


Figure 4-S16. (a) the Pb 4f core-level XPS spectra of the HA-inserted 2D FA perovskite films

with/no SENA additives before annealing, and the peaks of Pb 4f orbitals move towards lower binding energy. (b) the Se 3d core-level XPS spectra of the HA-inserted 2D FA perovskite films with/no SENA additives before annealing, and the peaks of Se 3d orbitals move towards higher binding energy.

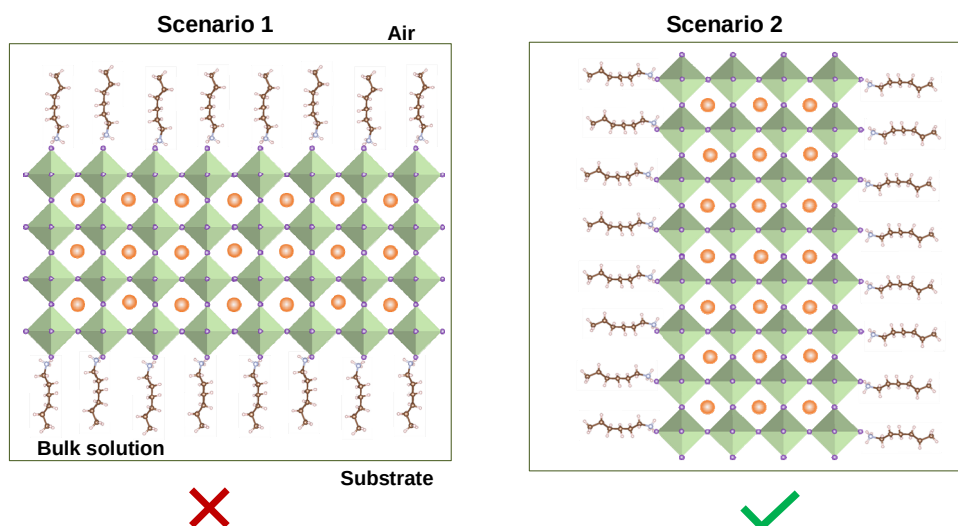


Figure 4-S17 Schematic of the 2D perovskite orientation. Scenarios 1 and 2 show two possible nuclear orientations for the anisotropic precursor to dissolve at the interface.

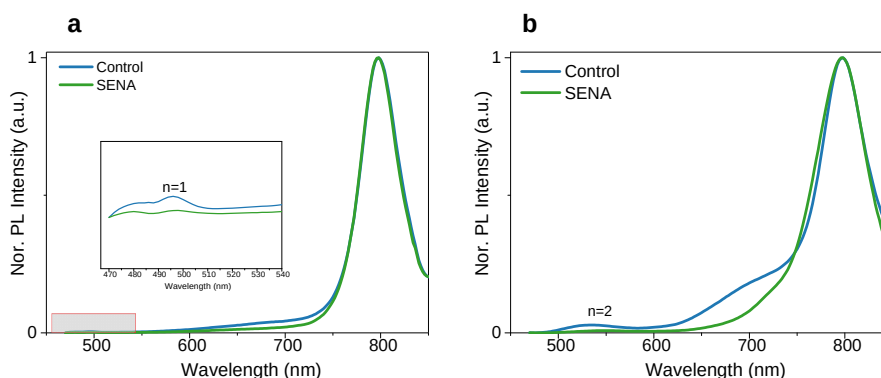


Figure 4-S18 (a) The PL intensities result from the front side (air/perovskite) and (b) backside (perovskite/glass substrate interface) and corresponding normalized PL intensities of control films and target 2D perovskite films with SENA additives.

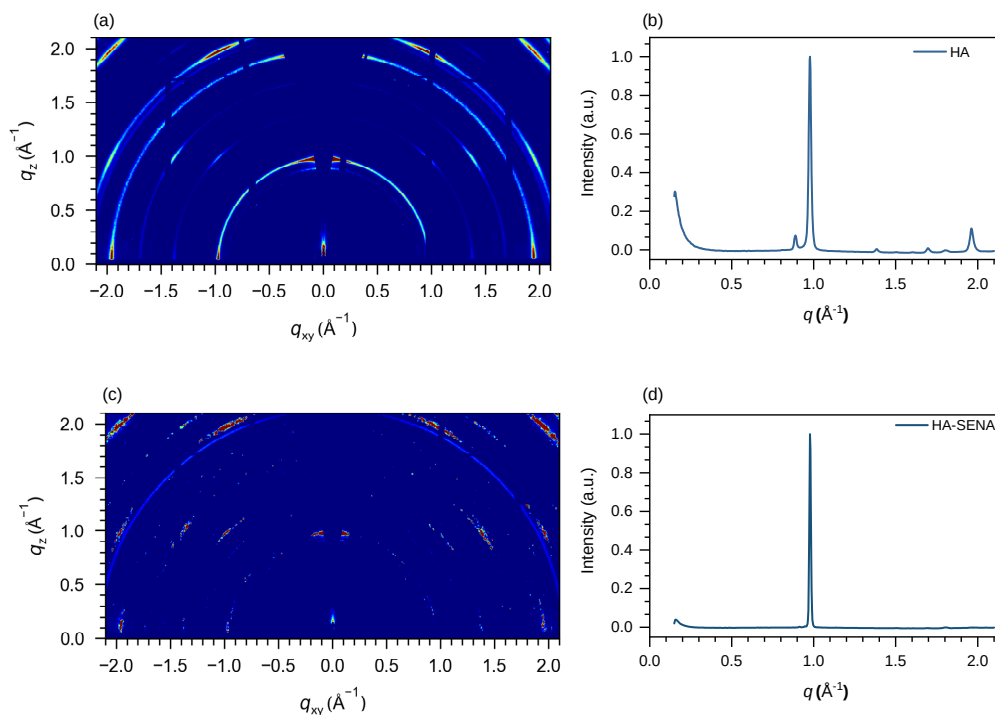


Figure 4-S19 (a-c) GIWAXS patterns for the HA-, and HA-SENA perovskite films with the incident angle of 0.6°, respectively. (b-d) Corresponding intensity profiles along the out-of-plane direction from GIWAXS results.

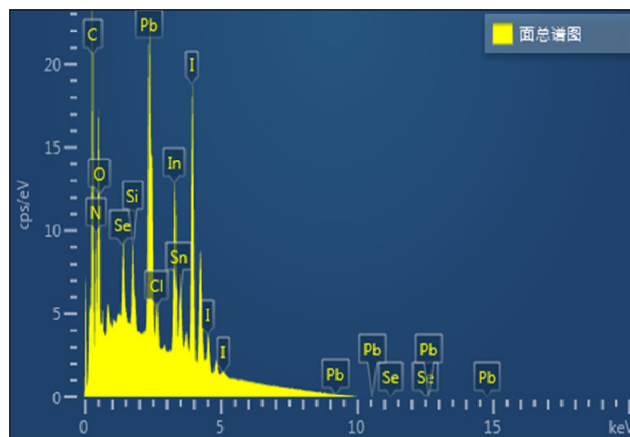


Figure 4-S20 EDS elemental signals for the HA-SU 2D perovskite before annealing, the total dispersive spectrum of EDS, showing a clear Se element signal.

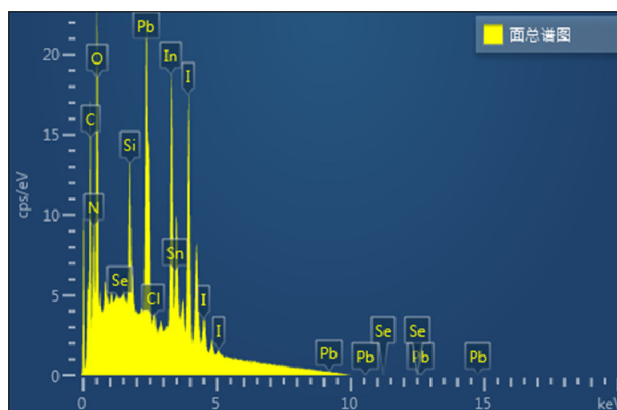


Figure 4-S21 EDS elemental signals for the HA-SU 2D perovskite after annealing, the total dispersive spectrum of EDS, indicating that SENA was removed after annealing.

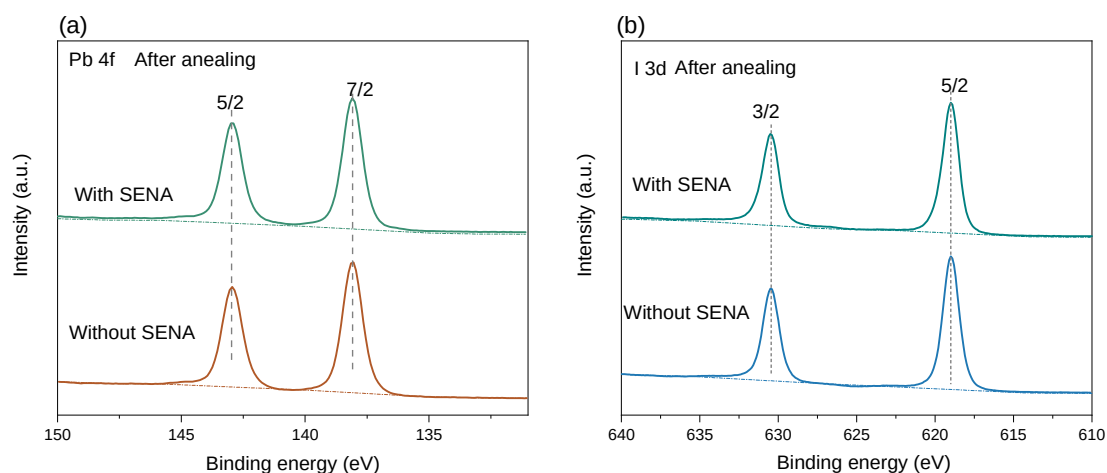


Figure 4-S22. (a) The Pb 4f and (b) I 3d core-level XPS spectra of FA-based 2D perovskite films with and without SENA additives, respectively, after annealing, and the peaks of Pb 4f and I 3d orbitals both negligible changes.

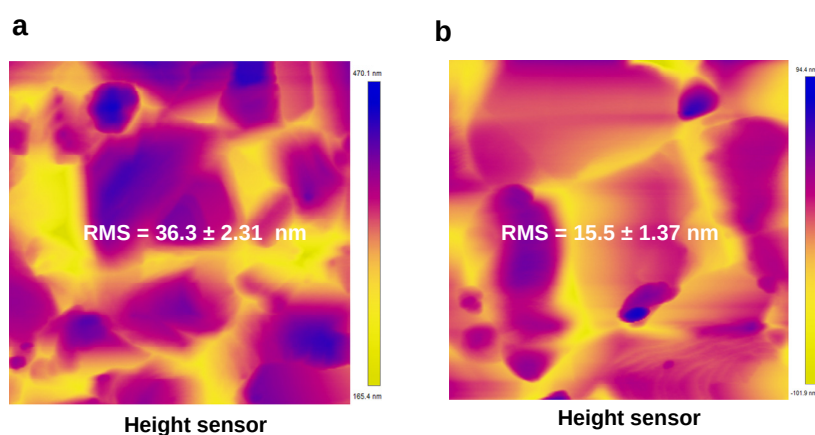


Fig. 4-S23 (a-b) AFM topography images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) and RMS surface roughness of FA-based 2D perovskite films treated without and with SENA additive, respectively.

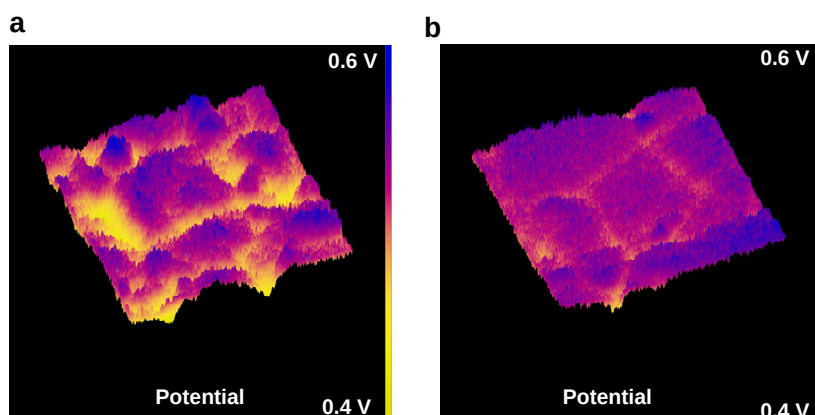


Figure 4-S24 (a-b) Surface potential 3D images of FA-based 2D perovskite films treated without and with SENA additive, respectively, at the same topography area measured by KPFM ($2\ \mu\text{m} \times 2\ \mu\text{m}$).

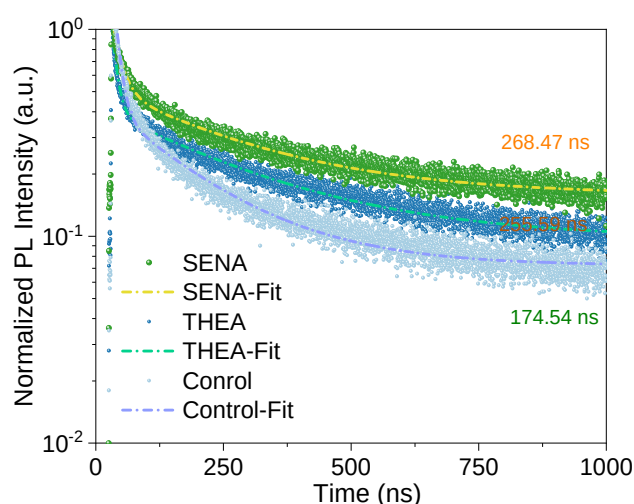


Figure 4-S25 TRPL analysis of control and target 2D FA perovskite films treated with thiourea (TU), and selenourea (SENA), respectively. The TRPL decays were fit by bi-exponential components using the equation $[Y=A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)]$, where A_1 and A_2 are the amplitudes, τ_1 , and τ_2 are the PL decay times. In general, the fast decay component (τ_1) originates from the quenching of charge carriers at the interface and nonradiative recombination induced by charge-trapping defect states, and the slow decay component (τ_2) is related to the bulk recombination of the charge carriers.

Conditions	τ_1 [ns]	τ_2 [ns]
------------	---------------	---------------

HA-THNA	17.55358	255.59161
HA- SENA	10.07269	268.47193
Control	11.33933	174.54773

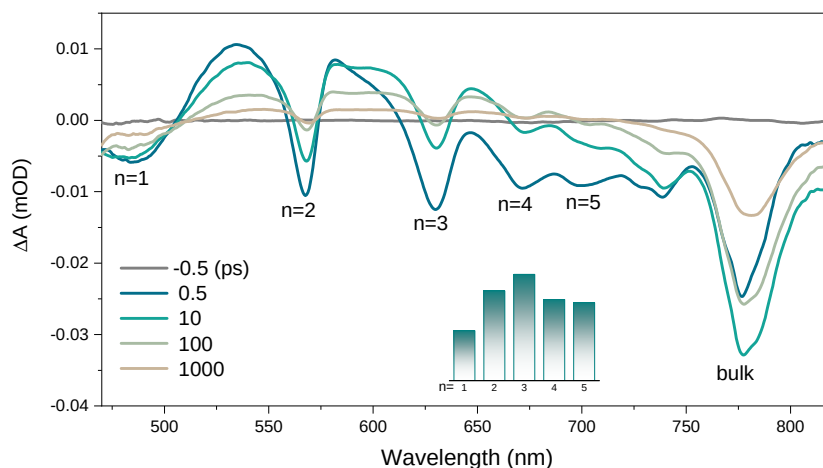


Figure 4-S26 (a) Transient absorption (TA) color maps of 2D perovskite films with HA spacer cations. The relative content of each phase was estimated from the intensities of the GSB peaks and shown in the embedded graph [214].

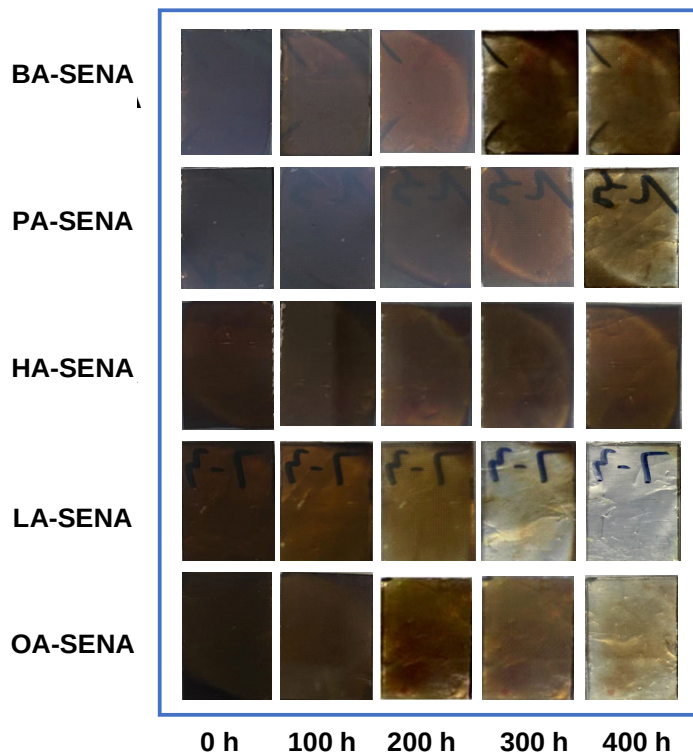


Figure 4-S27 Light stability measurements of various 2D FA-based perovskite films. Optical morphology images of various 2D FA-based perovskite films (based on BA, PA, HA, LA, and

OA organic spacers) showing their colors with time under light (AM 1.5G, 30-50% relative humidity, room temperature).

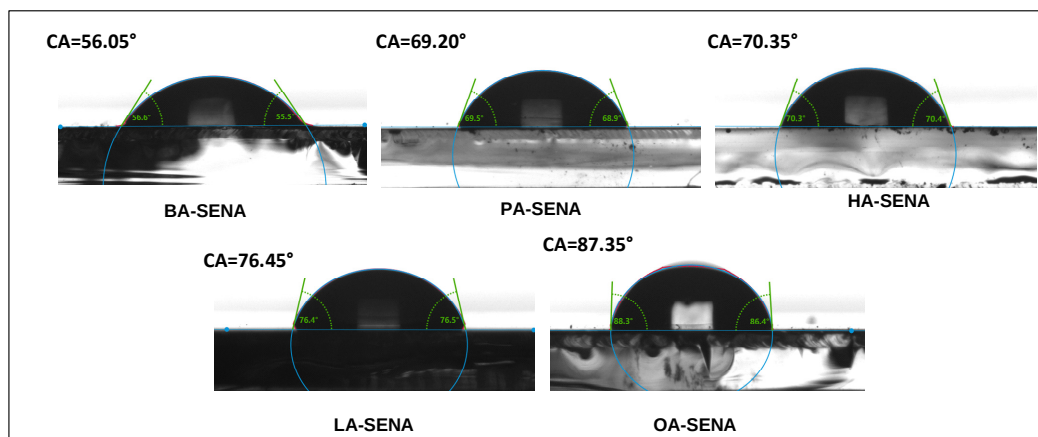


Fig. 4-S28 Surface water contact angle measurements for 2D RP perovskite films based on different organic spacers, respectively. The gradually increased contact angle indicates enhanced hydrophobicity, consistent with the hydrophobic property of the alkyl chain.

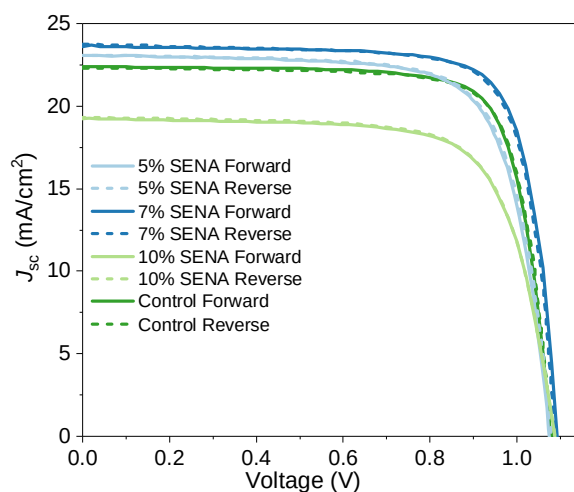


Figure 4-S29 *J-V* curves of the corresponding control and target 2D perovskite devices based on 5% SU, 7% SU, and 10% SENA, respectively. The main parameters (obtained in the forward scanning and reverse scanning) are summarized in Table S1.

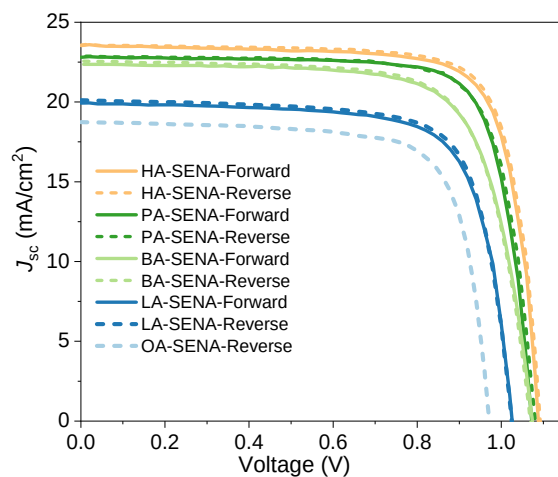


Figure 4-S30 *J*-*V* curves of the corresponding devices based on various FA-based 2D perovskites with BA, PA, HA, LA, and OA spacer cations after using the SENA additives. The main parameters (obtained in the forward scanning and reverse scanning) are summarized in Table S2.

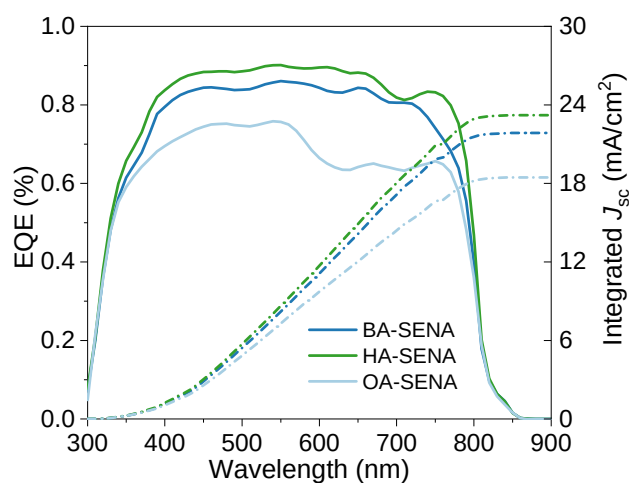


Figure 4-S31 The external quantum efficiency (EQE) spectra and integrated current densities are 23.21 mA/cm², 21.85 mA/cm², 18.45 mA/cm², for BA-, HA-, OA- SENA based 2D perovskite devices, respectively.

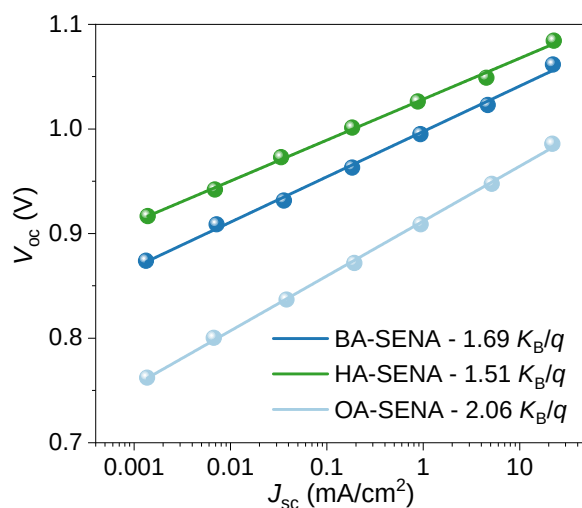


Figure 4-S32 The relationship of V_{oc} versus J_{sc} under a varied light intensity of 2D perovskite devices with SENA additives, the extracted ideal factors of BA-, HA-, and OA-SENA based 2D perovskites are $1.69 (k_B T/q)$, $1.51(k_B T/q)$, and $2.06(k_B T/q)$.

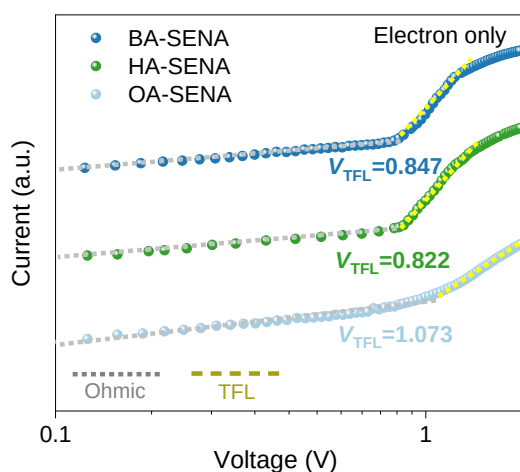


Figure 4-S33 SCLC of corresponding electron-only perovskite devices, the electron trap densities are calculated as $9.37 \times 10^{15} \text{ cm}^{-2}$ and $9.09 \times 10^{15} \text{ cm}^{-3}$, and $1.19 \times 10^{16} \text{ cm}^{-3}$ for BA-, HA-, and OA-inserted perovskites, respectively.

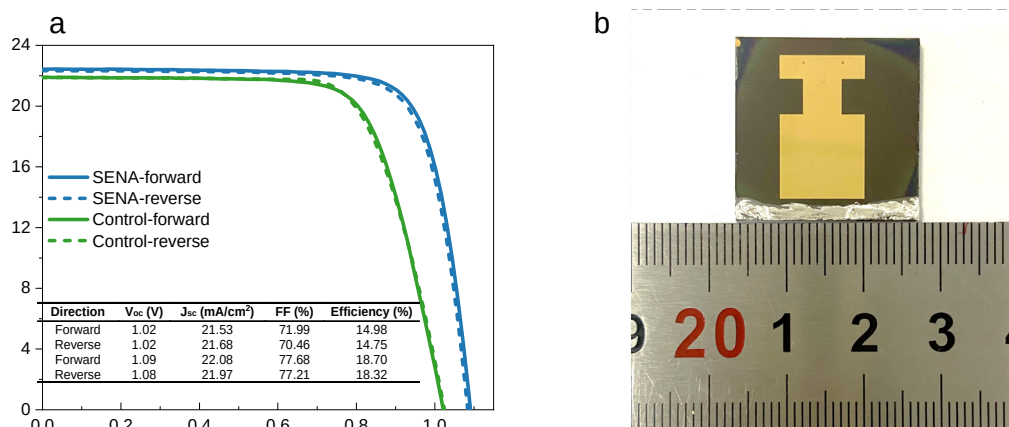


Figure 4-S34 (a) J-V curves and photovoltaic parameters of 1.02 cm² large area devices under forward and reverse scanning direction with and without SENA additives. **(b)** Optical photograph of the corresponding 1.02 cm² large area champion devices.

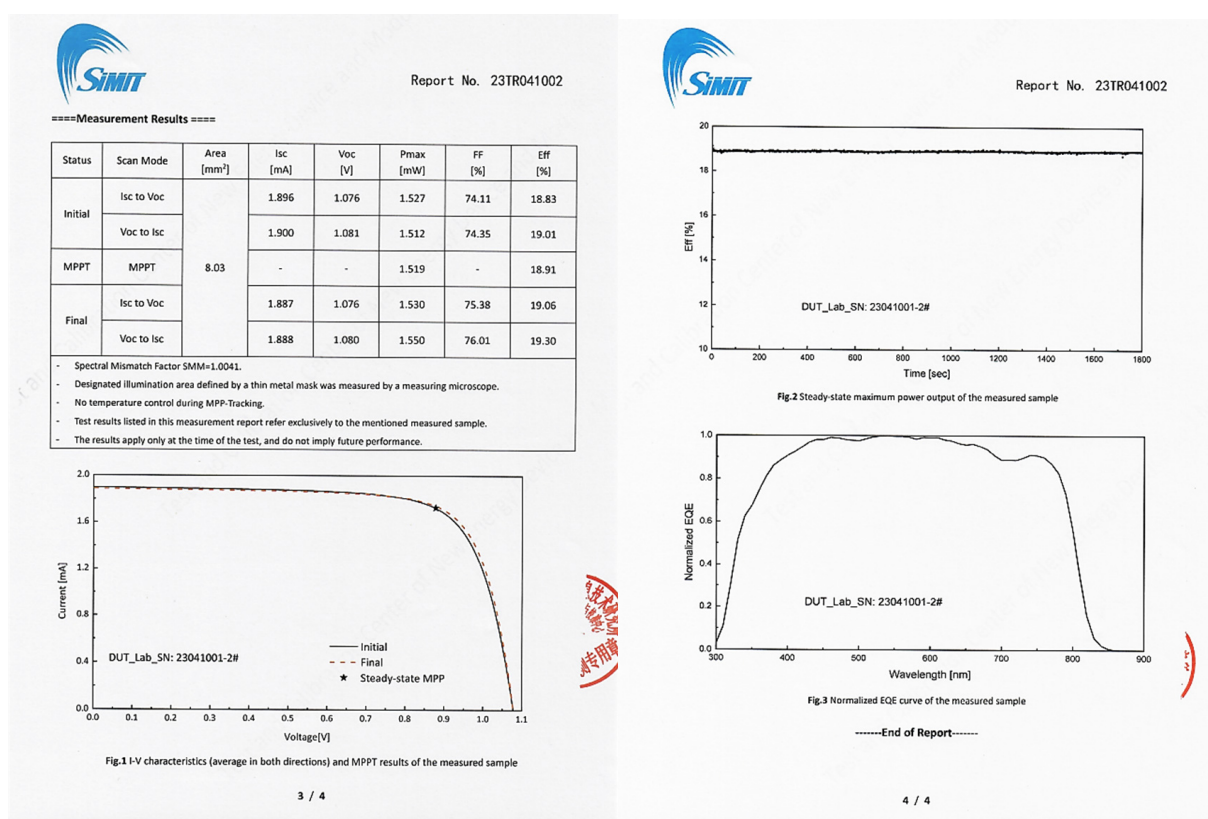


Figure 4-S35 (a) The initial and final PCE under the MPPT test certificated from Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Science (SIMIT) for the champion FA-based 2D PSCs. **(b)** The MPPT test and EQE measurements were certificated by the Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Science (SIMIT) for championing FA-based 2D PSCs.

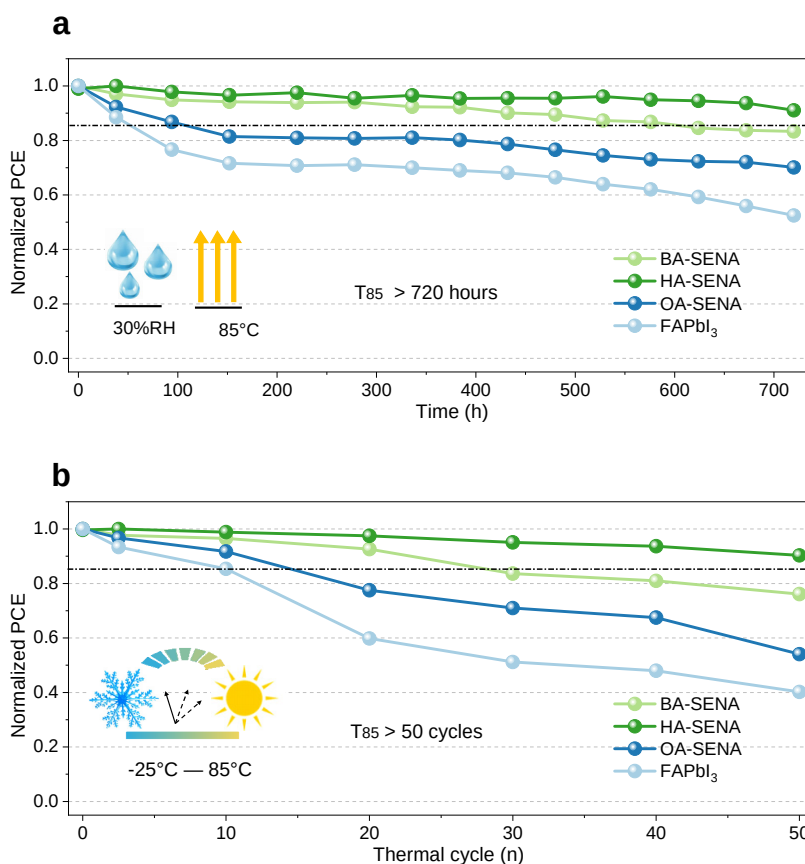


Figure 4-S36 Stability of PSCs (a-b) Stability for unencapsulated 2D and encapsulated 3D perovskite devices performed under (a) 85 °C (dark condition, RH~30±5%), and (b) cold (-25°C) and warm (85°C) alternating fatigues. The initial efficiencies of the BA-SENA, HA-SENA, OA-SENA, and FAPbI₃ solar cells are 17.93%, 19.56%, 13.58%, and 22.75%, respectively. After 720 hours of thermal aging for HA-SENA perovskite devices, the degradation rate is extremely low (losing ~8.9%). However, BA- and OA-SENA perovskite devices show much higher degradation rates, losing about 19% and 25% of their original values. Furthermore, to test the performance changes when encountering cold-warm or other types of strain fatigues, we also investigated the device performance under cycle shock measurements of cold (-25°C) and heat (85°C). The initial efficiencies of the BA-SENA, HA-SENA, OA-SENA, and FAPbI₃ solar cells in the cyclic temperature measurements are 17.51%, 19.62%, 13.29%, and 23.32%, respectively. As shown in (b), after 50 cycles, HA-inserted 2D perovskite solar cell maintains 90.3 % PCE, outperforming BA- and OA-inserted perovskite devices (just maintaining 76.1% PCE and 54.1% PCE after 50 cycles). These data indicate that HA-inserted perovskite devices exhibit excellent environmental stability with a relatively low decay rate of PCE.

Table 4-S1. Main parameters (obtained in the forward scanning and reverse scanning) of the best devices of various FA-based 2D perovskites based on 5% SENA, 7% SENA, and 10% SENA.

	Direction	V_{oc} (V)	J_{sc} (mA/cm²)	FF (%)	Efficiency (%)
Control	Forward	1.08	22.61	77.85	19.02
	Reverse	1.08	22.58	77.87	19.00
5% SENA	Forward	1.08	23.09	74.20	18.50
	Reverse	1.09	23.02	74.02	18.57
7% SENA	Forward	1.09	23.58	75.20	19.32
	Reverse	1.09	23.60	77.86	20.03
10% SENA	Forward	1.09	19.26	73.52	15.43
	Reverse	1.08	19.34	72.36	15.12

Table 4-S2. Main parameters (obtained in the forward scanning and reverse scanning) of the best 2D perovskites devices after being treated with SENA additives.

	Direction	V_{oc} (V)	J_{sc} (mA/cm²)	FF (%)	Efficiency (%)
BA- SENA	Forward	1.07	22.36	74.89	17.91
	Reverse	1.07	22.46	73.78	17.74
PA- SENA	Forward	1.08	22.57	77.85	18.97
	Reverse	1.08	22.86	77.18	19.05
HA- SENA	Forward	1.09	23.58	75.20	19.32
	Reverse	1.09	23.60	77.86	20.03
LA- SENA	Forward	1.02	20.06	73.76	15.01
	Reverse	1.02	20.10	74.36	15.24
OA- SENA	Forward	0.97	18.68	74.60	13.52
	Reverse	0.97	18.70	74.41	13.49

Table 4-S3. Main parameters comparison of 1.02 cm² large area devices under forward and reverse scanning direction with and without SENA additives.

	Direction	V_{oc} (V)	J_{sc} (mA/cm²)	FF (%)	Efficiency (%)
Control	Forward	1.02	21.53	71.99	14.98
	Reverse	1.02	21.68	70.46	14.75
SENA	Forward	1.09	22.08	77.68	18.70
	Reverse	1.08	21.97	77.21	18.32

Table 4-S4. Summary of the representative low-n 2D PSCs.

Perovskites	n _a	PCE (%)	Jsc (mA/c ²)	Method	Stability (Photostability/Moisture/Thermal)	Ref
BA ₂ MA ₃ Pb ₄ I ₁₃	4	11.10	14.2	Co-solvents	None	[273]
BA ₂ MA ₃ Pb ₄ I ₁₃	4	12.52	16.76	Hot casting	AM 1.5G RH=65% (T ₈₀ =2250 h); AM 1.5G (T ₇₀ =2050 h, T ₈₀ =200 h)	[274]
BA ₂ MA ₃ Pb ₄ I ₁₃	4	13.68	19.94	Cesium doping	Dark RH=30% (T ₈₉ =1400 h); RH=65% (T ₈₅ =36 h); RH85% (T ₈₁ =24 h); 80 °C (T ₈₅ =16 h)	[275]
BA ₂ MA ₃ Pb ₄ I ₁₃	4	17.26	19.86	Annealing	N ₂ (T ₉₆ =2000 h)	[276]
BA ₂ MA ₃ Pb ₄ I ₁₃	4	16.25	16.75	Additives	RH=65% (T ₉₄ =4680 h); 80 °C (T ₉₆ =558 h); AM 1.5G (T ₉₆ =1100 h)	[277]
BA ₂ MA ₃ Pb ₄ I ₁₃	4	16.48	18.67	Additives	AM 1.5G (MPPT) RH=55-60%, (T ₈₀ =3200 h); RH=55-60% (T ₈₉ =86 h); 85 °C (T ₉₂ =816 h)	[278]
BA ₂ MA ₃ Pb ₄ I ₁₃	4	17.10	17.56	Memory seeds	AM 1.5G (T ₉₈ =800 h)	[279]
(BA) _{1.6} (MA) _{3.4} Pb ₄ I ₁₃	4	16.29	20.44	Non-preheating	RH=65% ± 5%, (T ₁₀ =160 h); N ₂ (T ₉₇ =2040 h);	[280]
BEA ₂ MA ₃ Pb ₄ I ₁₃	4	16.10	20.63	Spacer cations	N ₂ (T ₈₃ =3500 h)	[281]
(3BBA) _{1.8} MA _{2.5} Pb ₃ I ₁₀	3 . 3	18.20	18.22	Hot casting	Room temperature RH=40% (T ₈₂ =2400h)	[282]
(ThMA) ₂ MA ₂ Pb ₃ I ₁₀	3	15.42	18.89	Additives	Dark with RH = 30 ± 10% (T ₉₀ =1000 h)	[283]
PEA ₂ FA ₃ Pb ₄ I ₁₃	4	11.30	14.70	Additives	RH=45% (T ₉₀ =720 h)	[284]
PEA ₂ MA ₃ Pb ₄ I ₁₃	4	18.48	18.52	Additives	RH=40% (T ₉₀ =1200 h); AM 1.5G (T ₉₅ =500 h) MPPT;	[285]
PEA ₂ MA ₃ Pb ₄ I ₁₃	4	17.03	18.47	Additives	RH=40% (T ₉₀ =150 h); 85 °C (T ₉₀ =1600 h)	[286]
FPEA ₂ MA ₃ Pb ₄ I ₁₃	4	15.20	13.70	Hydrothermal	RH=30 ± 5% (T ₈₃ =1510 h); RH=85% (T ₆₇ =530 h)	[287]
PEA _{0.2} BA _{1.8} MA ₃ Pb ₄ I ₁₃	4	15.81	16.51	Post-treatment	RH = 25 ± 5% (T ₉₀ =496 h); 50 ± 5% (T ₈₉ =496 h); 85 °C (T ₉₈ =1590 h)	[288]
(BM)(BA)MA ₃ Pb ₄ I ₁₃	4	17.30	19.80	Ionic Liquid	RH=30-60% (T ₉₀ =1000 h); RH=85% (T ₈₇ =100 h)	[289]
BDA ₂ MA ₃ Pb ₄ I ₁₃	4	14.38	19.90	Additives	RH=30-40% (T ₉₂ =1200 h); 80 °C (T ₈₂ =24h)	[290]
AA ₂ MA ₃ Pb ₄ I ₁₃	4	18.42	18.57	Post annealing	RH=65% (T ₉₉ >744 h); N ₂ (T ₉₉ >1848 h);	[291]
ThFA ₂ MA ₂ Pb ₃ I ₁₀	3	16.72	20.17	Anti-solvents	AM 1.5G (T ₉₀ =216 h); N ₂ (T ₉₉ =3000 h)	[292]
GAMA ₄ Pb ₄ I ₁₃	4	15.27	20.14	Additives	RH=50% (T ₇₅ =480 h); 42 °C and RH=50±5% (T ₆₂ =300 h); 85 °C (T ₆₀ =61 h)	[293]
(GA)(MA) ₃ Pb ₃ I ₁₀	3	18.48	22.26	Additives	RH=30-40% (T ₉₅ =3144 h); 80 °C (T ₇₉ =65 h); 55% RH and 60 °C (T ₅₇ =200 h) (MPPT)	[294]
(NpMA) ₂ MA ₃ Pb ₄ I ₁₃	4	17.25	20.89	Anti-solvents	RH=30 ± 5% (T ₈₉ =1000 h); N ₂ at 80 °C (T ₈₀ =600 h); N ₂ (T ₉₁ =4100 h);	[295]
F-PEA ₂ MA ₃ Pb ₄ I ₁₃	4	18.10	19.04	Additives	RH=40%-50% (T ₉₅ =720 h); 80 °C (T ₈₀ =720 h);	[296]
(PDMA)(MA) ₃ Pb ₄ I ₁₃	4	15.81	21.10	Hot casting	RH=30% (T ₉₃ =744 h); 80°C and RH=45% (T ₇₃ =12 h);	[297]
(MAMP)MA ₃ Pb ₄ I ₁₃	4	16.53	17.97	Additives	RH=40-50% (T ₉₂ =1000 h); 80°C (T ₉₀ =212 h); AM 1.5G (T ₉₀ =505 h)	[298]
(PPA) ₂ (Cs _{0.05} (FA _{0.88} MA _{0.12}) _{0.95}) ₃ -Pb ₄ (I _{0.88} Br _{0.12}) ₁₃	4	14.76	19.33	Space cations	85 °C and 85% (T ₉₄ =600 h)	[299]

(BA _{0.9} PEA _{0.1}) ₂ MA ₃ Pb ₄ I ₁₃	4	15.46	17.12	Space cations	AM 1.5G (T ₈₀ =700 h); N ₂ (T ₉₂ =7000 h); AM 1.5G (T ₉₅ =1200 h); 85°C (T ₈₀ =120 h);	[300]
(3AMP) (MA _{0.75} FA _{0.25}) ₃ Pb ₄ I ₁₃	4	18.67	19.51	Annealing	RH45 ± 5% T ₉₀ =1440 h; 85° T ₉₀ =480 h; T ₉₉ >50 thermal cycles;	[301]
(3AMP) (MA _{0.75} FA _{0.25}) ₃ Pb ₄ I ₁₃	4	16.25	17.91	Additives	RH25 ± 5% T ₈₀ =840 h; RH45 ± 5% T ₈₀ =840 h;	[302]
PDMA ₂ FA ₃ Pb ₄ I ₁₃	4	7.11	11.48	Space cations	RH=30-50% (T ₈₅ =1440 h); MPP AM 1.5G (T ₆₀ =500 h)	[303]
PDAFA ₃ Pb ₄ I ₁₃	4	13.80	17.30	Additives	RH=30-40% (T ₈₅ =540 h); 85°C and N ₂ (T ₈₆ =1000 h)	[251]
PDA _{0.9} PA _{0.2} FA ₃ Pb ₄ I ₁₃	4	16.00	17.60	Additives	85 °C (T ₉₀ =800 h)	[304]
BA ₂ FA ₃ Pb ₄ I ₁₃	4	18.14	21.62	Additives	RH=40% and 85 °C (T ₉₃ =720 h); AM 1.5G (T ₈₆ =720 h)	[305]
HA ₂ FA ₃ Pb ₄ I ₁₃	4	20.03	23.60	Additives	AM 1.5 G MPPT (T ₉₉ >1000 h); RH=30% 85 °C (T ₈₅ > 720 h); -25°C- 85°C (T ₈₅ > 50 cycles)	This work

^a Here n represents average n based on the initial composition.

Table 4-S5. Fitting parameters for the kinetics of HA and HA- SENA treated 2D FA-based films, τ_{et} represents the establishment of the bleaching peaks; τ_1 and τ_2 are the fast decay and slow decay components.

Spacer	Phase	τ_{et} [ps]	τ_1 [ps]	τ_2 [ps]
	n=3	\	0.6258	17.4826
HA	n=4	\	0.66166	7.38545
	Large n	0.86553	\	\
	n=3	\	0.28997	28.21
HA- SENA	n=4	\	0.3878	23.04
	Large n	0.547	\	\

Table 4-S6. Perovskite crystal data and structures.

Spacer	Layer	Crystal System	Space group	a	b	c
BA	n=4	Orthorhombic	Ccmm	9.02 Å	62.22 Å	8.71 Å
HA	n=4	Orthorhombic	Ccmm	9.53 Å	66.99 Å	7.85 Å
OA	n=4	Orthorhombic	Ccmm	9.29 Å	71.23 Å	8.22 Å

Chapter 5 Oriented Low-n Ruddlesden-Popper Formamidinium-based Perovskite for Efficient and Air-Stable Solar Cells

The sun's energy can be transformed into usable power
and the day will come when mankind will use
this inexhaustible resource more wisely

-----Charles Fritts

The relatively lower crystallinity and random orientation of quantum well structures hinder carrier transport and limit the performance of formamidinium (FA) based low-n 2D perovskite devices. In this work, the crystallization and quantum-well orientation were fine-tuned to achieve efficient low-n FA-based Ruddlesden-Popper perovskite solar cells. The effects of different ionic additives on the crystallization, orientation, and photovoltaic performance of FA-based low-n 2D perovskites were comparatively investigated. We found that NH_4^+ and SCN^- can significantly retard the heterogeneous crystallization of low-n phases in the intermediate state and drive the templated growth of the quantum well structure with vertical orientation. The optimized photovoltaic device based on $(\text{BA})_2(\text{FA})_3\text{Pb}_4\text{I}_{13}$ achieved a power conversion efficiency (PCE) of 18.14%, setting the highest record for FA-based low-n 2D perovskite solar cells as far as we know (average $n=4$). The unencapsulated device exhibited excellent stability and maintained 93.3% of its original PCE at 85°C, and 86.3% at 1 Sun illumination after 720 hours in humid ambient conditions.

5.1 Introduction

Layered two-dimensional (2D) Ruddlesden-Popper (RP) perovskites have attracted great attention for their use in photovoltaic devices due to their excellent optoelectronic properties[78, 277, 306-312]. Owing to efforts in composition control, crystallization optimization, grain growth, and passivation, the solar conversion efficiency and stability of 2D-based perovskite

solar cells (PSCs) have achieved rapid progress in recent years[313-319]. One of the attractive properties of 2D perovskite is its tunable wide bandgap[80, 320]. In general, reducing the layer number (n) of 2D perovskite layers can increase the optical bandgap via the quantum confinement effect[320, 321]. In comparison with the wide-bandgap 3D perovskites that suffer from low ambient stability and composition segregation, the low- n 2D perovskites show excellent stability owing to the successful passivation by hydrophobic spacer cations [322, 323]. Currently, the pure-FA-based high- n 2D perovskites enabled efficient PSCs reaching an efficiency of 21.07%[324]. However, the device efficiency of FA-based low- n 2D perovskites is still low (the highest recorded efficiency for $n=4$ is 16.0%) [251, 313].

Apart from the increased exciton binding energy due to the reduced quantum well thickness, the main obstacle to high efficiency is the relatively low crystallinity in low- n 2D perovskites as well as disorderly oriented layered structures that hinder carrier transport[313, 325]. The increased amount of spacer cations in lower- n phases can confine parallel growth and gain superiority in competition with smaller central organic cations which try to expand crystal growth outside the layers[326, 327]. To keep a vertically oriented layered structure while reducing n is significant for realizing efficient and stable single- and multi-junction solar cells. At present, although great progress has been achieved in MA-based 2D perovskites, there is a strong motivation to replace MA with FA because of the high thermal stability of FA-based perovskites. The crystallization of FA-based 2D perovskites is more complex in contrast to extensively studied MA-based analogs, including (i) disordered nucleation and growth either with corner-sharing or face-sharing structures, (ii) stronger interaction between FA cations and $[\text{PbI}_6]^{4-}$ octahedrons, (iii) various interaction between FA cations with the commonly used solvents to retard crystallization like dimethyl sulfoxide (DMSO) [251, 313, 324]. These factors could disorder the crystallization and result in randomly distributed layered structures. For low- n FA-based 2D perovskites, this effect would be exacerbated, as more spacer cations are involved in the crystallization process when n is reduced. Few efforts have been devoted to crystallographic studies of the growth and orientation of pure FA-based low- n 2D perovskite. Some solutions to tune the crystallinity and orientation have been investigated, like formamidinium chloride (FACl), hydrochloric acid (HCl), and thiourea (TU) [251, 328, 329]. However, the device efficiency is still limited and calls for a rational approach to precisely tune

the crystallization and orientation of FA-based low-n 2D crystals, thereby enabling charge transport along vertically aligned quantum well structures. In previous results, NH_4^+ , Cl^- and SCN^- ions have been used successfully to modulate crystallization in MA, Cs, or FA-MA-based perovskite solar cells. Nevertheless, a comprehensive understanding of the effects of these ionic additives on pure FA-based 2D perovskite films has yet to be achieved. Thus, it is of great interest to explore the roles of these ionic additives in low-n 2D FA perovskites to achieve efficient and stable perovskite solar cells.

Here, we report a way of tuning the crystallization and vertical growth of pure FA-based low-n 2D RP perovskites. We show that the synergistic effect of NH_4^+ and SCN^- additives is more beneficial to control the nucleation of pure FA-based compositions. The heterogeneous crystallization of low-n phases is inhibited on both bottom and top interfaces in the intermediate state, followed by templated growth of vertically orientated quantum well structures accompanied by the ionic exchange process. The resulting films exhibit excellent out-of-plane orientated layered structure, increased grain size with reduced trap density, and improved carrier lifetime. Finally, the optimized perovskite solar cell achieved a high-power conversion efficiency (PCE) of 18.14%, which is the highest to date for FA-based low-n 2D devices with an average $n=4$ to the best of our knowledge. The unencapsulated devices exhibited excellent stability and maintained 93.3% PCE at 85°C, and 86.3% at 1 Sun illumination after 720 hours in humid ambient conditions.

5.2 Experimental section

5.2.1 Materials

All the materials and chemicals in our work were used as received without further purification. Formamidinium iodide (FAI, 99.99%, Xi'an Polymer Light Technology Corp.). Lead iodide (PbI_2 , 99.99%, Xi'an Polymer Light Technology Corp.). n-Butylammonium iodide (BAI, 99.99%, Xi'an Polymer Light Technology Corp.) Ammonium rhodanate (NH_4SCN , 99.99%, Sigma-Aldrich), Ammonium chloride (NH_4Cl , 99.99%, Sigma-Aldrich), 2,2',7,7'-Tetrakis [N, N-di(4-methoxyphenyl) amino] -9,9'-spirobifluorene (Spiro-OMeTAD, 99.99%, Borun New Material Corp.). Bis (trifluoromethane) sulfonimide lithium salt (Li-TFSI, 99.99%, Sigma-

Aldrich), 4-tert-butyl-pyridine (tBP, 99.99%, Sigma-Aldrich), Tin dioxide (SnO_2 , colloidal dispersion (15%), Alfa Aesar). *N,N*-dimethylformamide (DMF, anhydrous, 99.7%, Sigma-Aldrich), dimethyl sulfoxide (DMSO, anhydrous, 99.7%, Sigma-Aldrich), and Isopropyl alcohol (IPA, anhydrous, 99.9%, Sigma-Aldrich).

5.2.2 Preparation of perovskite precursor solutions

The 1.0 M perovskite precursor solution of $(\text{BA})_2(\text{FA})_3\text{Pb}_4\text{I}_{13}$ was prepared by mixing a stoichiometric ratio of 2:3:4 for BAI, FAI, and PbI_2 in 900 μL DMF and 100 μL DMSO. The additives of NH_4SCN and NH_4Cl were then added to the precursors with designated molar ratios. All solutions were stirred overnight at room temperature before use.

5.2.3 Fabrication of solar cells

Perovskite solar cells were fabricated on pre-patterned FTO glass substrates. FTO substrates were etched with zinc powder and diluted hydrochloric acid (HCl) to produce the desired pattern and then washed with detergent, deionized water, ethanol, acetone under ultrasonic and then washed by UV-ozone, each step for 15 minutes, respectively. Then, the diluted SnO_2 colloid (15%, diluted by deionized water with a volume ratio of 1:5) is spin-coated onto FTO substrates at 3000 rpm for 30 s and annealed on a hot plate at 150 °C for 30 min. After cooling to room temperature, the FTO/ SnO_2 substrates were further treated with UV ozone for 15 minutes. The perovskite layer is spin-coated onto the FTO/ SnO_2 substrates by the one-step deposition method. The $(\text{BA})_2(\text{FA})_3\text{Pb}_4\text{I}_{13}$ perovskite films were obtained by spin-coating the precursor at 5000 rpm in the N_2 -filled glove box, at 15 s before the end, 300 μL of isopropanol was gently dropped onto the center of FTO/ SnO_2 substrate. After dripping the antisolvent, the substrate was followed by heating at 150 °C for 30 min in ambient conditions (with 30–40% relative humidity) to obtain the final perovskite films. After cooling down to room temperature, the hole-transport layer of the Spiro-OMeTAD layer was deposited on top of the perovskite films by spin-coating 80 μL of the precursor solution at 3000 rpm for 30 s. The Spiro-OMeTAD solution was prepared by dissolving 73mg Spiro-OMeTAD in 1ml CB with 17.5 μL Li-TFSI (520mg/ml, acetonitrile) and 28.8 μL tBP as dopants. For the stability tests, the hole transporting materials was replaced by PTAA, for which 20 mg ml^{-1} PTAA doped with ~1% 2,3,5,6-

Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) dissolved in toluene (preheated to avoid precipitates) was spin-coated at 2500 rpm for 30s. Finally, the devices were completed by thermal evaporation of a 60 nm Au electrode.

5.2.4 Characterization

GIWAXS measurements were performed at beamline BL14B1 at the Shanghai Synchrotron Radiation Facility (SSRF). SEM measurements for top view and cross-sectional samples were obtained by Tescan Maia3 Gmu (model 2016). AFM measurements data were measured on Dimension Fast Scan Bio Atomic Force Microscope. The XRD patterns were taken on the Rigaku Dmax 2600 diffractometer using Cu K α radiation with a Nickel filter. UV-vis Absorption Measurements of perovskite film were recorded by Shimadzu UV2450 spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on an AXIS Ultra DLD (Kratos) spectrometer. FTIR was conducted on a Thermo Scientific Nicolet 6700 Spectrometer. DLS was collected on NanoBrook Omni from Brookhaven Instruments. PL and TRPL measurements were obtained by using an FLS1000 spectrometer (Edinburgh Instruments) with 470 nm excitation wavelength and a 500nm optical filter. PL mapping was realized on the Leica TCS SP8 STED 3X super-resolution system. Current density-voltage curves (J-V curves) were collected using a Keithley 2400 source-meter under AM 1.5G 1sun illumination from a 3A simulator (Newport, Oriel® Sol3A™, 94023A), calibrated by standard silicon reference cell (Newport, Newport Oriel 91150-KG5). The cells were covered by a shadow mask with an aperture area of 0.08 cm². External quantum efficiency (EQE) measurements were conducted on SM-250 (Bunkoukeiki) using monochromatic incident light of 1×10¹⁶ photons cm⁻² with the alternating current mode. The device's stability was tested in a BIR-50 solar cell light resistance testing system. The operational stability tests were carried out at the MPP for the encapsulated devices under AM1.5G illumination (100 mW cm⁻²). For thermal stability, the tests were conducted on another aging chamber with a temperature controlled at 85±5 °C. The space charge limited current (SCLC) was measured by an electrochemical analysis instrument (Zahner, Germany). The static contact angle tests were characterized by a water droplet with a DSA100 instrument.

5.3 Results and discussion

5.3.1 Orientation and crystallization of 2D perovskites

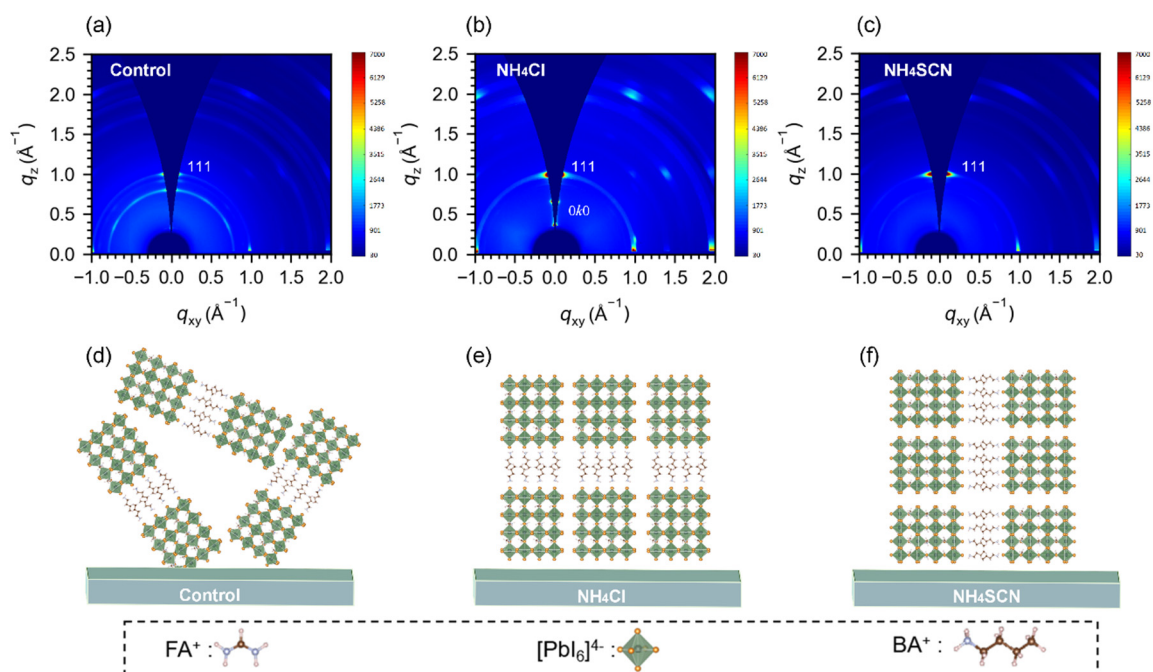


Figure 5-1. GIWAXS patterns of perovskite films treated by different additives. (a-c) GIWAXS patterns of the control (a), NH₄Cl (b), and NH₄SCN (c) treated perovskite films; (d-f) The schematic diagram of quantum-well orientations in perovskite films with random orientation (d), parallel orientation (e), vertical orientation (f) relative to the substrate.

We fabricated 2D FA-based perovskite thin films by the one-step spin coating method (**Figure 5-S1**). N-butylammonium iodide (BAI), formamidinium iodide (FAI), and lead iodide (PbI₂) were dissolved in a mixed solvent of DMF and DMSO with a molar ratio of 2:3:4 with a proper amount of additives. At the end of spin-coating, isopropanol (IPA) was used as an anti-solvent to extract excess solvents. Subsequently, the perovskite films with different additives were thermally annealed at 150 °C for 30 min under ambient conditions (30–40% relative humidity) to obtain dark brown 2D FA-based perovskite films.

Grazing-incidence wide-angle X-ray Scattering (GIWAXS) was used to investigate the orientation of 2D FA-based perovskite films. The GIWAXS patterns of the perovskite films treated with different additives are depicted in **Figures 5-1a-c**, and the corresponding

schematic diagram of quantum-well orientations is illustrated in Figures 5-(1d-f). The grazing incidence angle was set as 0.5° [314], in this regime, the detective X-ray can penetrate ~ 210 nm thickness of the film as calculated in **Figure 5-S2**. This depth is comparable to the resulting perovskite film thickness according to cross-sectional SEM results mentioned later. As shown in **Figure 5-1a**, the control film shows Debye-Scherrer diffraction rings with relatively lower diffraction intensity, especially at the higher q range ($q > 1.7 \text{ \AA}^{-1}$), indicating that a substantial portion of the film possesses randomly oriented grains. The diffraction rings at 0.78 and $0.9 \text{ \AA}^{-1}$ could be ascribed to hexagonal δ and PbI_2 phases at the surface, respectively, which may relate to incomplete transformation to perovskite phases and can be avoided after additive treatment. In **Figure 5-1b**, the film treated with NH_4Cl has a higher diffraction intensity, indicating the well-crystallized property of the film. However, obvious diffraction spots appeared at a low q range along the out-of-plane (q_z) direction (**Figure 5-S3**), which can correspond to the $(0k0)$ planes of low- n layered phases, indicating the in-plane orientation of 2D quantum wells (**Figure 5-1e**) that will hinder the charge transfer and reduce the device performance [330]. In contrast, the film with NH_4SCN additives exhibited sharp and discrete Bragg spots, implying that the perovskite films have a more ordered orientation. Meanwhile, the absence of diffraction along q_z lower than $1 \text{ \AA}^{-1}$ indicates the out-of-plane orientation of 2D quantum wells[326] (**Figure 5-1f**). The integrated results along the out-of-plane and in-plane directions manifest the preferred orientation of NH_4SCN treated film (**Figure 5-S3**). These results demonstrate that the NH_4SCN additive can inhibit the in-plane growth of 2D FA perovskite and drive the growth of highly oriented layered structures perpendicular to the substrate, which can act as continuous charge transport channels for effective charge transport and further extraction.

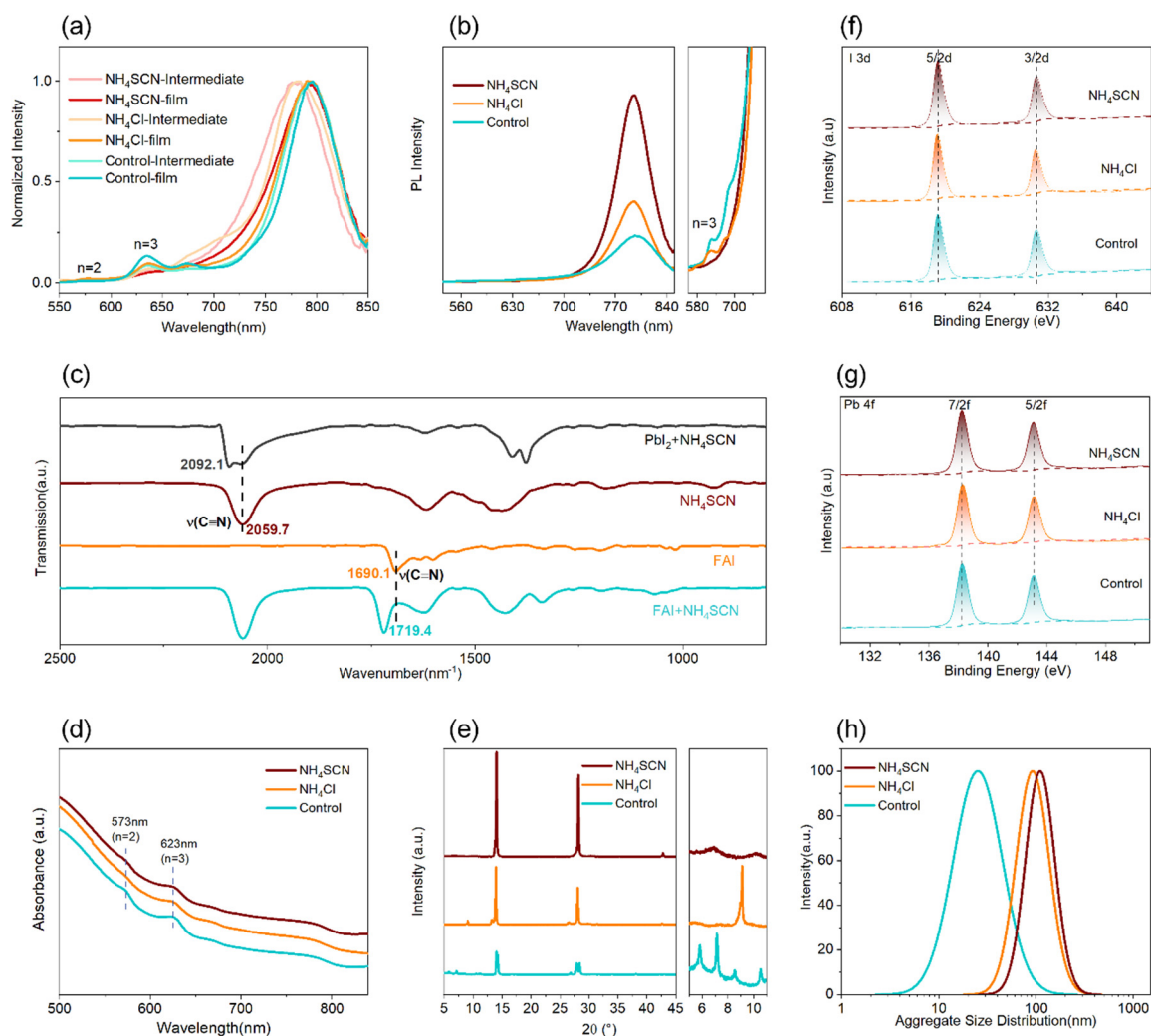


Figure 5-2. Crystallization and film property of 2D perovskites. (a-b) Steady-state PL spectra from bottom (a) and top side (b) of as-prepared films; (c) FTIR of different compositions; (d-e) UV-Vis (d) and XRD (e) patterns of additives treated films; (f-g) Pb 4f and I 3d core level XPS for additives treated films; (h) DLS of perovskite precursors.

The crystallization with different additives was then characterized. The photoluminescence (PL) of intermediate and annealed films was detected from the bottom (glass) side [251]. As shown in **Figure 5-2a**, the NH₄SCN-treated intermediate film significantly inhibited the formation of lower-n ($n < 4$) phases at the bottom, which are always conducive to parallel growth of 2D layered structures[326]. After annealing, both control and NH₄Cl-treated films showed enhanced low-n phases, indicating the growth of layered structures at the film/substrate interface in these cases. In the case of NH₄SCN, the low-n phases in the annealed film exhibited

similar PL intensity with that in the intermediate, demonstrating inhibited growth of these phases during the following annealing process. This can be attributed to the strong retardation of SCN^- in the crystallization process, which can strongly coordinate with Pb^{2+} and organic ions. It shows that NH_4Cl can also inhibit the formation of low- n phases in the intermediate state, but the intensities of these phases were still enhanced after annealing, probably because of the weaker interaction of Cl^- with Pb^{2+} or with organic ions compared to SCN^- . After annealing, the main peak positions of NH_4Cl or NH_4SCN treated films also showed a red shift compared with the intermediates. This can relate to ionic exchange from Cl^- or SCN^- mediated phases to full I^- phases, and/or replacement of NH_4^+ by FA^+ ions after annealing. Thus, it can be inferred that retarded crystallization occurred after the treatment with ionic additives, and SCN^- has a stronger ability in reducing the heterogeneous nucleation of low- n phases than Cl^- , consequently inhibiting the parallel growth of layered structures. The photoluminescent property from the top (film) side was also confirmed. As shown in **Figure 5-2b**, after annealing, the emission peak of NH_4SCN treated film is the strongest at 796 nm with the narrowest half peak width compared with the control and NH_4Cl treated films, suggesting well crystallinity of the NH_4SCN treated film with lower carrier traps. The exciton peak distribution of the spectrum further proves that the NH_4SCN additive can also effectively suppress the growth of the low- n phases near the film surface, avoiding templated parallel growth of layered structures that is not conducive to the carrier transport in the device[331]. These results are consistent with that from GIWAXS, indicating SCN^- had a strong retarding property on crystallization, and inhibited heterogeneous nucleation at both top and bottom interfaces, favoring vertically oriented growth of 2D layered structure.

FTIR results in **Figure 5-2c** manifest the strong interaction of SCN^- with Pb and FA cations. the $\text{C}\equiv\text{N}$ stretching vibration of NH_4SCN significantly shifted from 2059.7 to 2092.1 cm^{-1} after interacted with PbI_2 , and the symmetric stretching of $\text{C}\equiv\text{N}$ in NH_4SCN at 1435 cm^{-1} also split into peaks at 1410.6 and 1377.7 cm^{-1} , respectively. These changed vibrational signals can be seen as the loss of vibrational degeneracy since the interaction between electron acceptor Pb^{2+} with electron donor SCN^- . Interaction between FA^+ and SCN^- was also investigated. FAI has a symmetric stretching vibration of $\text{C}=\text{N}$ mainly at 1690.1 cm^{-1} , obviously shifted to 1719.4 cm^{-1}

¹ when interacting with NH₄SCN. This can be caused by changed hydrogen binding interactions between these species.

The UV-Vis results in **Figure 5-2d** showed relatively reduced exciton absorption peaks of low-*n* phases after treatment by NH₄Cl and NH₄SCN, with clear absorption structures of 2D layered perovskites. X-ray diffraction (XRD) results in **Figure 5-2e** further revealed improved crystallinity and orientation. Higher intensity diffraction peaks and smaller FWHMs demonstrate the effectiveness of the additives, corresponding to enhanced crystallinity and enlarged grain sizes. The diffraction peaks at about 14.1° and 28.3° represent the (111) and (202) diffractions of 2D perovskite, respectively. Compared to the additives-treated films, the control film has more chaotic diffraction peaks within 10° which can correlate to (0*k*0) planes of low-*n* phases, indicating randomly grown layered 2D phases [327]. The NH₄Cl-treated film depicts a diffraction peak in the magnified XRD patterns at 9.1°, which can correspond to the (0*k*0) diffraction peaks of the low-*n* phase of 2D FA perovskite. For NH₄SCN-treated film, few of these peaks in the XRD pattern imply that the 2D perovskite sheets in the film are oriented mainly perpendicular to the substrate, which can facilitate efficient charge transport [252]. The increased $I_{(202)}/I_{(111)}$ intensity also indicates a higher degree of vertical orientation of NH₄SCN-treated films (**Figure 5-S4**) [332]. It can be inferred that the additives neither entered the perovskite lattice nor distorted the Pb-I framework, but only played a role in tuning the crystallization of the perovskite films. The X-ray photoelectron spectroscopy (XPS) results in **Figures 5-2f,g** revealed unchanged binding states of Pb 4f and I 3d core level after additive treatment. The absence of a sulfur signal in the XPS result and the absence of characteristic vibration peaks of SCN⁻ in FTIR curves (**Figure 5-S5**) suggest that SCN⁻ does not exist in the lattice of perovskite films.

The morphology evolutions of perovskite films treated with additives were also investigated. According to Ostwald ripening theory, enhancing the colloidal size in the precursor should assist in grain growth[105, 316]. We measured the colloidal size in the precursor by the characterization of Dynamic Light Scattering (DLS). The result in **Figure 5-2h** shows that the precursor added with NH₄SCN exhibited an enlarged colloidal size (average 110.9 nm) compared to the control (25.2 nm) and NH₄Cl (93.6 nm) added solution. This tendency is consistent with that of grain sizes from SEM results as shown in **Figures 5-3a-c**. When NH₄Cl

and NH_4SCN additives are introduced, the crystal size of perovskite films becomes larger compared with the film without additives. Especially for the perovskite prepared with NH_4SCN additive, a reduction of the void's generation and formation of larger grains in the film was observed. The SEM and XRD results of different concentrations in **Figures 5-S6,7** showed an optimized value of 7.5%. The lattice strains of NH_4SCN treated films were also calculated[313, 333], the corresponding result showed tensile strains in the range of 0.00128-0.00157, as shown in **Figure 5-S7**. This level is lower than previously reported MA-based 2D perovskites[333]. Atomic Force Microscope (AFM) images in **Figures 5-3d-f** and **Figure 5-S8** further confirmed these results, where the NH_4SCN treated film surface shows larger grains and well-defined grain boundaries, accompanied by flatter surface potential distribution (**Figure 5-S9**). As previously mentioned, the morphological difference could be attributed to the stronger interaction of SCN^- with the perovskite components than Cl^- , resulting in more regular and enlarged crystal grains[332].

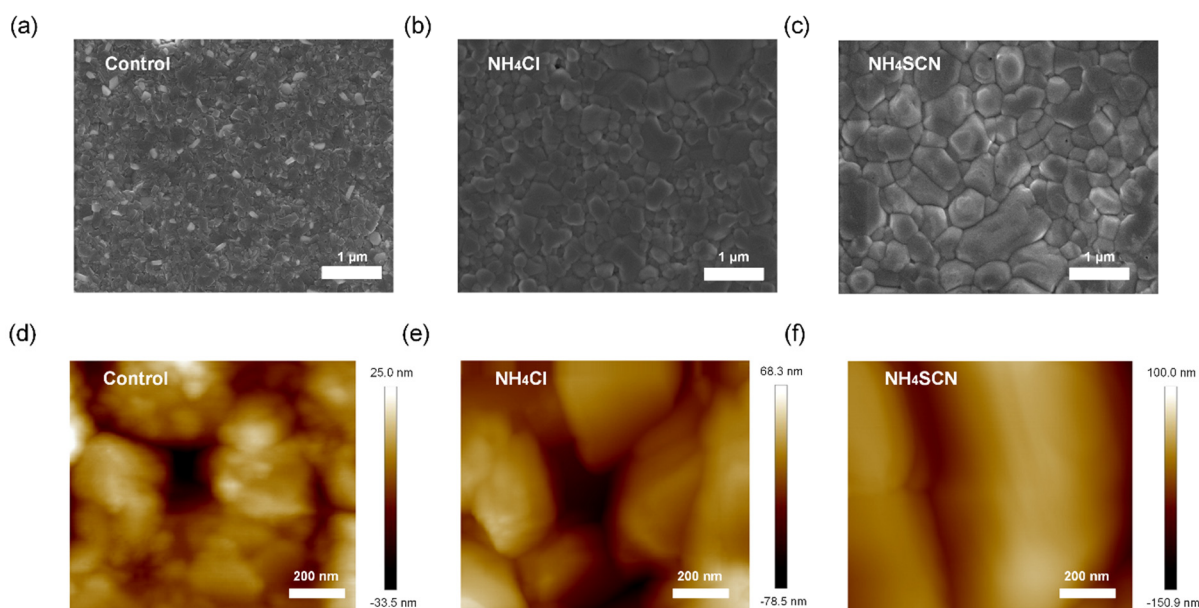


Figure 5-3. The morphology evolutions of perovskite films. Top-view SEM (a-c) and AFM (d-f) images of perovskite films treated with no additives (a, d), NH_4Cl additives (b, e), and NH_4SCN additives (c, f).

Time-resolved photoluminescence (TRPL, **Figure 5-S10**) was used to further characterize the properties of NH_4SCN -treated film. The band edge carrier lifetime was extracted using a double exponential decay function that fits the spectral data[292, 334]:

$$Y = A_1 \exp(-\frac{t}{\tau_1}) + A_2 \exp(-\frac{t}{\tau_2}) + \gamma_0$$

Where τ_1 corresponds to the rapid non-radiative recombination caused by defects or impurities in grains, τ_2 represents the slow recombination of charge carriers [335, 336]. The calculated average charge carrier lifetimes for the control and films treated with NH_4Cl and NH_4SCN additive are 61.8ns, 94.1ns, and 144.3ns, respectively. The significant increase in the carrier lifetime indicates a marked improvement in charge transport and reduced non-radiative recombination in the NH_4SCN -treated film, which can be due to the improved film properties with lower lattice defects.

Based on these results, it can be concluded that NH_4SCN additives in perovskite precursor solutions can significantly suppress low-n-phases formation and drive the vertical growth of pure FA-based low-n 2D perovskites, thereby facilitating carrier transport and reducing non-radiative carrier recombination. These properties are of vital importance for efficient and stable perovskite solar cells. The NH_4SCN additive can significantly improve the crystallization and orientation of pure FA-based 2D perovskite films, which could be attributed to the following reasons according to our results: (i) The smaller NH_4^+ anions can easily diffuse into the $[\text{PbI}_x]$ octahedron and enhance the saturation solubility of Pb-I plumbate, thereby inhibiting the homogeneous nucleation in the liquid film; (ii) SCN^- possesses linear Lewis structure, and lone pair electrons from S and N atoms which can strongly coordinate with Pb^{2+} ions and FA^+ cations in precursor solution, thus forming more stable intermediate structure before crystallization (Supplementary note 1). These factors benefit stable aligned crystallization along the 3D-like templates which prefer to form at the top surface after anti-solvent extraction, thus enhancing the vertical orientation of the layered structures[326]. Importantly, during the high-temperature annealing process, SCN^- is more prone to exchange with I^- compared to Cl^- . Because SCN^- has a more matched effective ionic radius than Cl^- ($\text{SCN}^- = 217$ pm, $\text{Cl}^- = 181$ pm, $\text{I}^- = 220$ pm), the utilization of this ion can avoid structure destruction and material defects [337, 338]. It was also demonstrated previously that SCN^- ions can drive and stabilize the formation of corner-sharing structures of FAPbI_3 , which can avoid the generation of undesirable phase-sharing structures during the crystallization process[339]. Therefore, we

consider that the synergistic effect between ions in NH_4SCN is beneficial to regulating the nucleation and growth of 2D grains, significantly increasing the grain size improving the quantum well orientation, and reducing the defects in films.

5.3.2 Photovoltaic performance and stability of devices

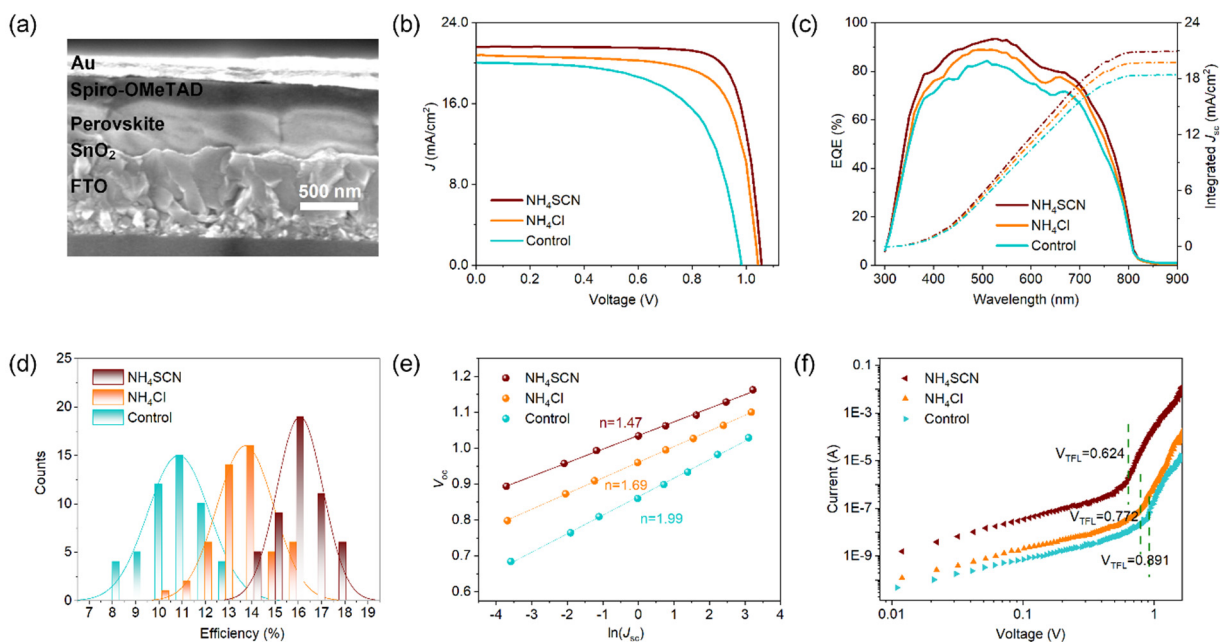


Figure 5-4. Photovoltaic performance of devices. Cross-sectional SEM images of NH_4SCN treated PSC; (b-c) J–V curves (b), EQE (c) curves and integrated photocurrent for different additives treated devices; (d) Statistical PCE histogram of 50 devices based on different additives treated perovskites; (e) Ideality factor for different additives treated devices; (f) SCLC of electron-only devices.

We further evaluate the performance of low-n 2D FA-based PSCs treated with additives. All fabricated perovskite solar cells adopted the device structure of FTO/SnO₂/Perovskite/Spiro-OMeTAD/Au, and the corresponding cross-sectional SEM images are illustrated in **Figure 5-4a** and **Figure 5-S11**. The grain size of the control perovskite is too small to penetrate the entire film, and the grain boundary will hinder carrier transport. In contrast, NH_4SCN -treated perovskite film was dense, uniform, and had larger grains (approaching μm grade) which are comparable to the film thickness. The optimized concentration of NH_4SCN was determined as 7.5% (molar ratio), as its pin-hole free property of the films and the most enhanced crystallinity

(**Figures 5-S6,7**), consistent with that of device performance (**Table 5-S1**). The optimized concentration of NH_4Cl was also determined as 15% based on the device performance (**Table 5-S2**). Representative current density-voltage characteristics (J - V) of different additive-treated PSCs with average $n=4$ are shown in **Figure 5-4b**, and all the extracted photovoltaic parameters are summarized in **Table 5-S3**. Among all the devices, the champion PSC with NH_4SCN additive achieves a maximum PCE of 18.14%, combined with V_{oc} of 1.062 V, J_{sc} of $21.62 \text{ mA}\cdot\text{cm}^{-2}$, and FF of 78.96%. Compared with control and NH_4Cl treated devices, the increase of PCE after NH_4SCN treatment was primarily due to the increase of short-circuit current density (J_{sc}) and fill factor (FF), which could be attributed to larger grains and optimized orientation of quantum well structures. The integrated current densities calculated from external quantum efficiency (EQE) spectra of control, NH_4Cl , and NH_4SCN additive-treated devices (**Figure 5-4c**) were 18.42 mA cm^2 , 19.73 mA cm^2 , 20.92 mA cm^2 , which matched well with J_{sc} values obtained from the J - V curve. **Figure 5-4d** shows the statistical distribution of PCE for a batch of 50 PSCs, the PCE significantly improved while maintaining good reproducibility with the assistance of the NH_4SCN additive. The IV performance of 2D FA-based PSCs with average $n=3$ was also tested as shown in **Figure 5-S12**. The device efficiency shows enhancement from 5.96 to 8.78% after treatment of NH_4SCN . This PCE value is also comparable to the highest reported values for $n=3$ (**Table 5-S4**), verifying the unique advantages of NH_4SCN in enhancing the performance of low- n 2D FA-based perovskites.

To evaluate the carrier transport and recombination of the devices, the relationship between V_{oc} and photocurrent under different illumination intensities was used (**Figure 5-4e**), according to the formula [340]: $\partial(V_{oc})/\partial(\ln I_{ph}) = nk_B T/q$, where I_{ph} is the light intensity, k_B is the Boltzmann constant, T is the absolute temperature, q is the elementary charge, and n is the ideality factor. The curves slope of control and that treated with NH_4Cl and NH_4SCN additives were 1.99 ($k_B T/q$), 1.69 ($k_B T/q$) and 1.47 ($k_B T/q$), respectively. The higher ideality factor of the devices confirms that the 2D perovskite with NH_4SCN additive is more conducive to efficient charge transport and reduced recombination. We further performed space charge-limited current (SCLC) measurements to investigate the defect density of corresponding films (**Figure 5-4f**). The trap density was determined by the following equation [341, 342]: $N_t = (2\epsilon_0\epsilon_r V_{TFL})/(qL^2)$,

where V_{TFL} is the trap filling limited voltage, L is the thickness of the perovskite film, ϵ_r is the relative permittivity of perovskite [275], ϵ_0 is the vacuum permittivity ($8.854 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$). The V_{TFL} of the control, NH_4Cl , and NH_4SCN treated devices in the trap-filling confinement region were determined to be 0.89 V, 0.77 V, and 0.62V, respectively, and the corresponding electron trap densities were calculated to be $9.80 \times 10^{15} \text{ cm}^{-3}$, $8.54 \times 10^{15} \text{ cm}^{-3}$ and $6.90 \times 10^{15} \text{ cm}^{-3}$, respectively. The SCLC results show that the perovskite films treated with NH_4SCN additive can effectively reduce the electron traps, thereby significantly eliminating the trap-assisted non-radiative recombination loss, consistent with that from TRPL results.

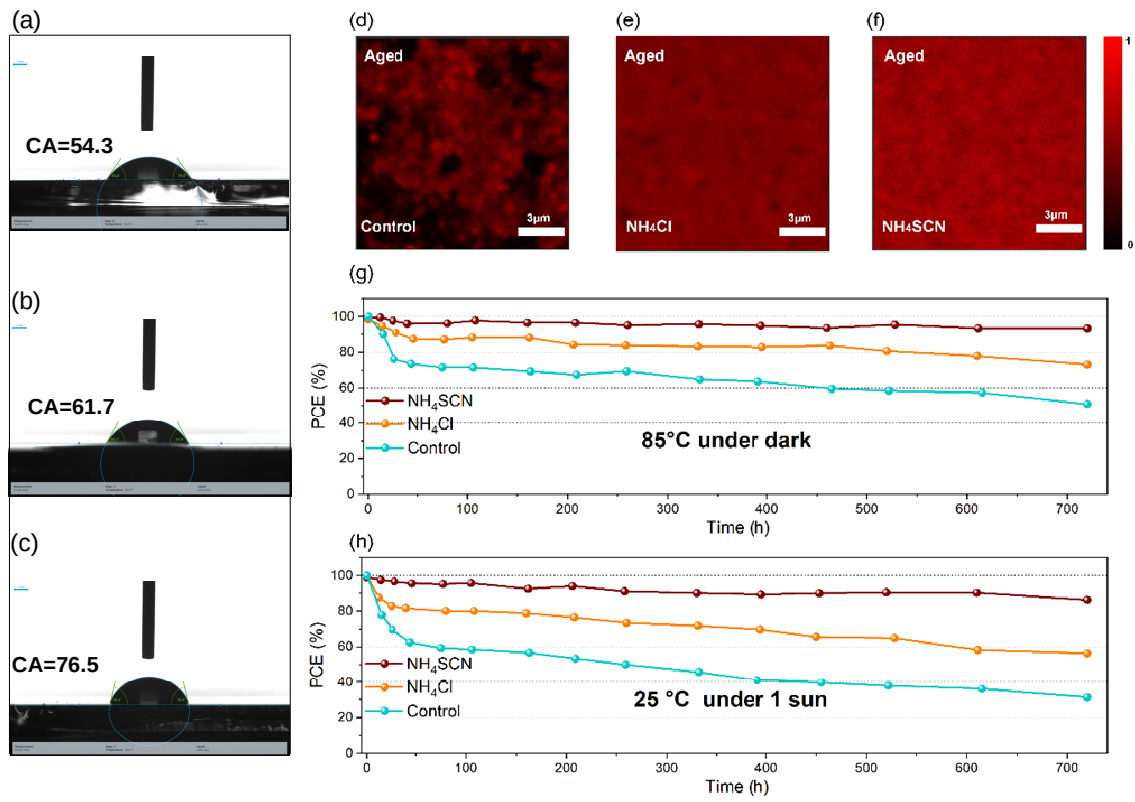


Figure 5-5. Stability of perovskite films and devices. Contact angle measurement of a water droplet on control (a), NH_4Cl (b), and NH_4SCN (c) treated FA-based low-n 2D perovskite films. PL Mapping for 200 hours aged (d-f) 2D FA perovskite films treated by different additives, tested under 1sun illumination in air with 40% relative humidity; (g) Thermal stability of the unencapsulated PSCs at 85°C in air with 40% relative humidity; (h) Operational stability of the unencapsulated PSCs under 1sun illumination (AM 1.5G) in air with 40% relative humidity at room temperature.

Although 2D perovskites with reduced n commonly possess better stability due to increased hydrophobic spacer cations, issues like undesirable phase distribution and crystallization also influence related performance. We further evaluated the stability of pure-FA-based low- n 2D perovskite films and devices treated with different additives. Firstly, water contact angle (CA) measurements were used to study the hydrophobic characteristics of films (**Figure 5-5a**). The contact angles of the control, NH_4Cl , and NH_4SCN -treated films are 54° , 61° , and 76° , respectively, indicating that the NH_4SCN -treated perovskite films have increased hydrophobicity. This may be related to the reduced grain boundaries and well crystallinity of NH_4SCN -treated film. The hydrophobic character was further investigated by an aging test under 1 Sunlight illumination in air with 40% relative humidity. In this test, the fresh and aged films after 200 hours were characterized by PL Mapping (**Figure 5-5d-f**). The obvious degraded region can be observed for the control film after the aging test. The NH_4Cl -treated film also showed a significant intensity decrease in the whole mapping region. For comparison, the NH_4SCN -treated film showed good stability with slightly changed fluorescence intensity. It should be noted that we didn't observe the generation of 1D δ phase or another polytype after illumination [343] (**Figure 5-S13**), indicating superior phase stability of well-crystallized low- n 2D FA perovskites. These results suggest enhanced film stability under both outer moisture ingress and light illumination with NH_4SCN treatment, which will be beneficial for enhancing the ambient operational stability of corresponding devices.

We then investigated the stability of devices under high temperatures and operational conditions. **Figure 5-5g** shows the PCE evolution for unencapsulated devices under 85°C with 40% relative humidity. The NH_4SCN -treated device exhibited the best thermal stability, retaining around 93.3% of initial efficiency after 720 hours, while for the control and NH_4Cl -treated devices, this value turned to 73.2% and 50.9%, respectively. The operational stability under 1 Sun illumination at ambient conditions was then evaluated. The NH_4SCN -treated device maintained 86.3% after continuous illumination for 720 hours (**Figure 5-5h**), better than the control and NH_4Cl -treated devices which degraded by 68.2% and 43.2% after the same operation. These results suggest an air-stable FA-based low- n 2D perovskite could be realized by NH_4SCN treatment, paving the way for realizing highly efficient and air-stable perovskite

solar cells.

5.4 Conclusion

In conclusion, we demonstrated an ionic NH_4SCN additive to drive the crystallization and orientation of FA-based low- n 2D Ruddlesden-Popper perovskites. The combination of NH_4^+ and SCN^- can strongly retard the crystallization and inhibit heterogeneous crystallization of low- n phases in the intermediate state. The subsequent templated growth of the quantum well structure is accompanied by an ionic exchange process. As for the stronger interaction of SCN^- with perovskite composition, and more matched ionic radius with I^- , the films treated by NH_4SCN showed better crystallinity, orientation, grain sizes, and reduced material defects than commonly used NH_4Cl . The resulting $\text{BA}_2\text{FA}_3\text{Pb}_4\text{I}_{13}$ film exhibited a prolonged carrier lifetime and reduced trap density. Finally, the optimized device achieved a champion PCE of 18.14%, which is the most efficient 2D pure FA-based PSC to date with an average of $n=4$ (**Table 5-S4**). Importantly, the unencapsulated 2D PSCs showed excellent air stability and maintained 93.3% PCE at 85°C , and over 86.3% under 1 Sun illumination after 720 hours in ambient condition with a relative humidity of 40%. Our findings thus provide new insights into understanding the effects of ionic additive on FA-based low- n 2D perovskite, which is yet to be exploited and make sense for efficient and stable single- and multi-junction perovskite solar cells.

5.5 Appendices

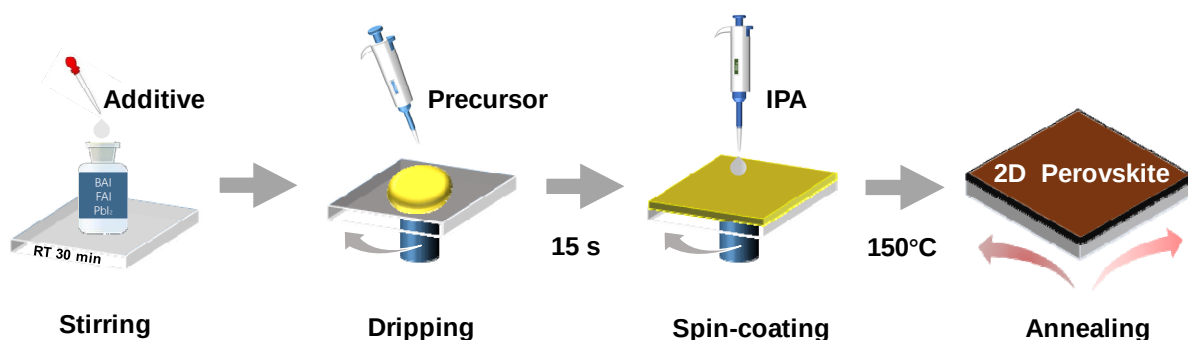
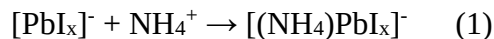


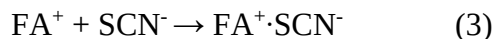
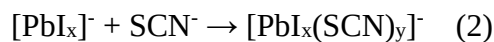
Figure 5-S1. Schematic diagram of the fabrication process of FA-based low- n 2D perovskite films by one-step spin coating method.

Supplementary note 5-1: We illustrate chemical equations below to demonstrate the crystallization process with the involvement of NH_4SCN :

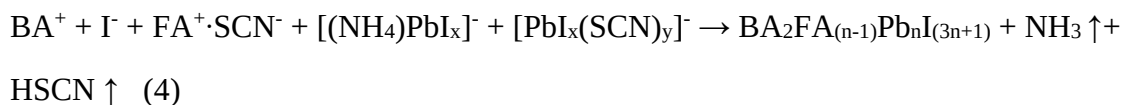
1. NH_4^+ diffuse into the $[\text{PbI}_x]^-$ octahedron:



2. SCN^- coordinate with Pb^{2+} ions and FA^+ cations:



3. Formation of 2D perovskites upon annealing companies with ion exchange process:



Supplementary note 5-2. Calculation of X-ray penetration depth vs incident angle

For an ideally flat surface, the value of X-ray penetration depth can be calculated from expression, where the intensity is reduced to $1/e$ of the original intensity [344].

$$\Lambda = \frac{\lambda}{2\sqrt{2}\pi} \frac{1}{\sqrt{\sqrt{(\alpha_i^2 - \alpha_c^2)^2 + 4\beta^2} - (\alpha_i^2 - \alpha_c^2)}}$$

Where α_i is the incident angle, λ is the X-ray wavelength, $\alpha_c = \sqrt{2\delta}$ is the critical angle of total reflection and β the imaginary part of the index of refraction.

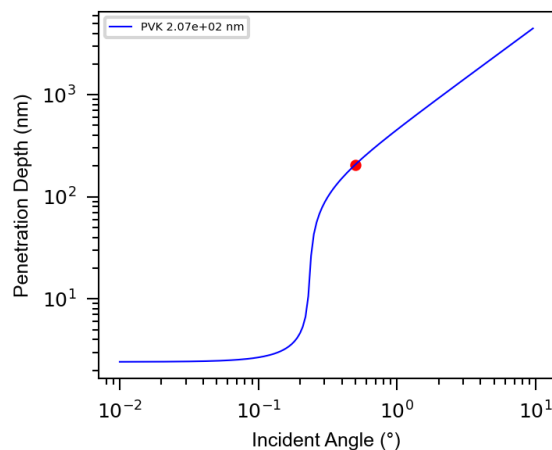


Figure 5-S2. Calculated X-ray incident depth as incident angle. The red dot represents the specific value in the GIWAXS measurement of this work, where the grazing incidence angle was set as 0.5° .

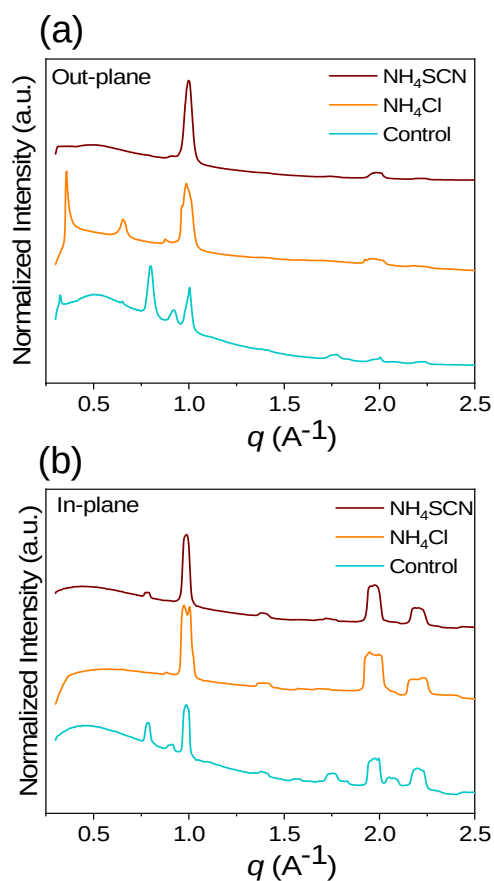


Figure 5-S3. The out-plane (a) and in-plane (b) integrated profiles from GIWAXS patterns of FA-based low-n 2D perovskite films treated with different additives.

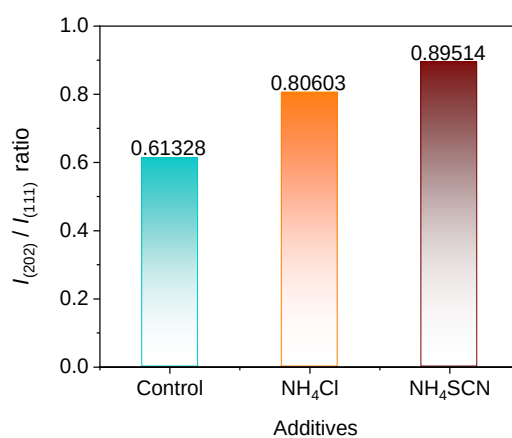


Figure 5-S4. $I_{(202)} / I_{(111)}$ ratio of FA-based low-n 2D perovskite films treated with different additives.

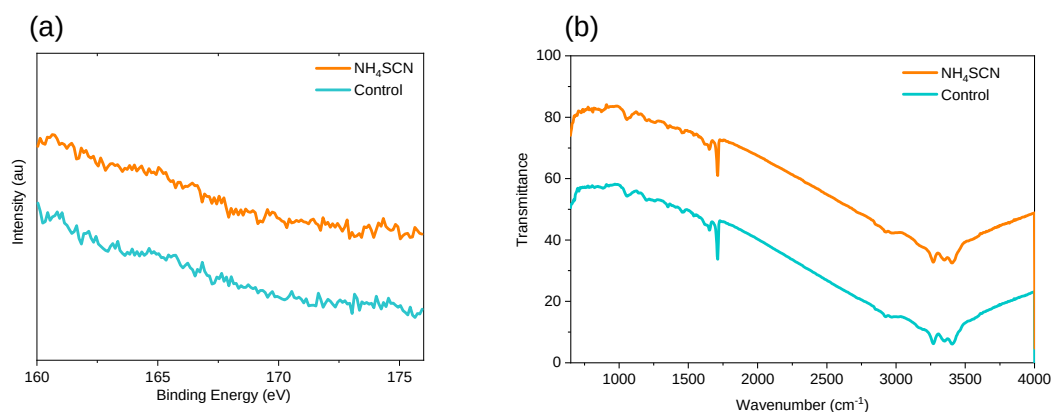


Figure 5-S5. (a)XPS spectra for the sulfur signal of 2D perovskite films with and without NH₄SCN additives. (b) FTIR curve of the films with and without NH₄SCN additives.

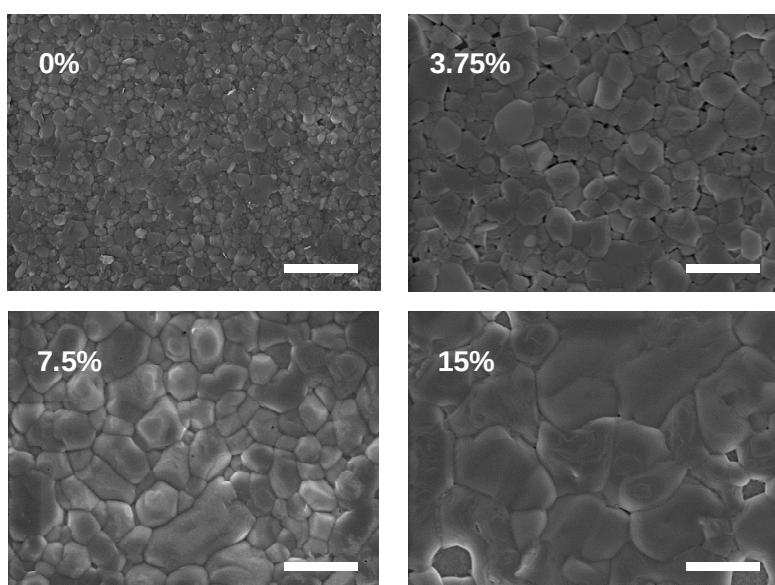


Figure 5-S6. SEM images of FA-based low-n 2D perovskite films treated with different concentrations of NH₄SCN (scale bar: 1μm).

Strain calculation through Williamson-Hall plot:

Williamson–Hall plots were applied to calculate the residual strain in perovskite films using Equation : [345]

$$\beta \cos \theta = \epsilon (4 \sin \theta) + \frac{k \lambda}{D}$$

Where β is the total broadening of XRD peaks, defined as FWHM, θ is diffraction angle, ϵ is residual strain, K is Scherrer constant, λ is the wavelength of X-ray (1.5418 Å), and D is crystal size of perovskite film. In our work, the XRD peaks located at 14°, 28°, and 43° were used to

calculate the residual strain. The β and θ are extracted from XRD patterns and need to be converted from degrees to radians before the linear fit.

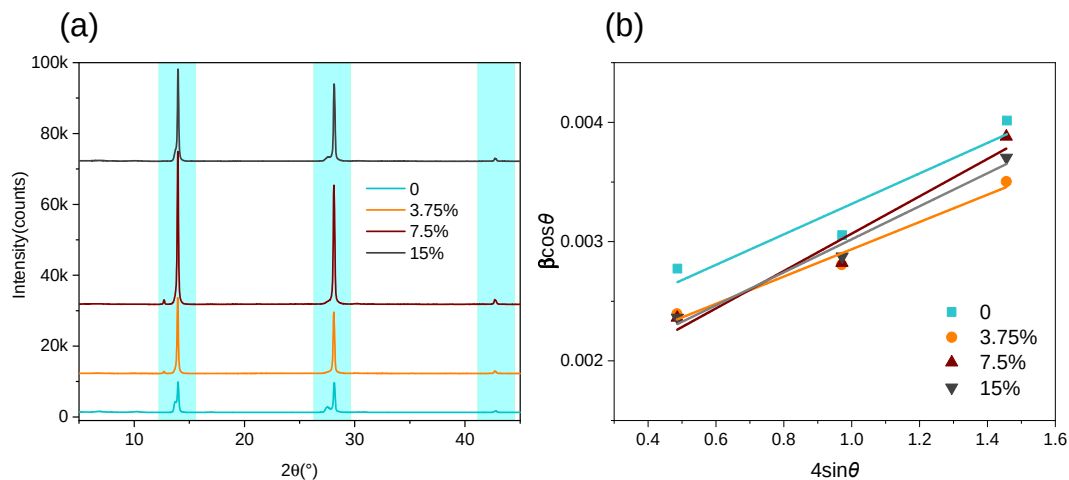


Figure 5-S7. XRD results and Williamson–Hall plots fitting of perovskite films treated with different concentrations of NH_4SCN .

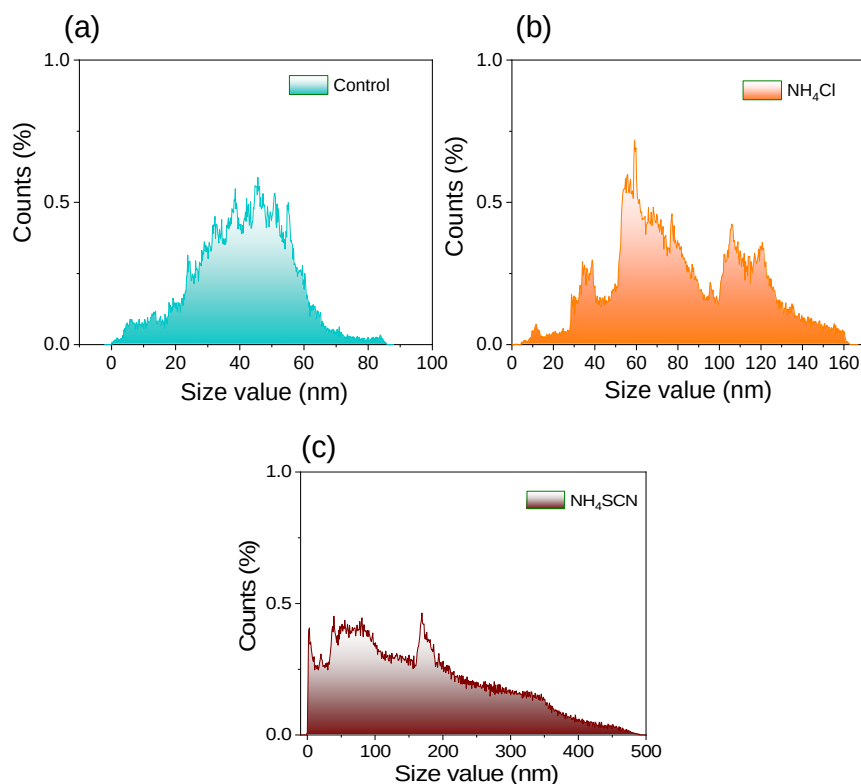


Figure 5-S8. The distribution of grain sizes of FA-based low-n 2D perovskite films treated with (a) no additives (b) NH_4Cl additives, and (c) NH_4SCN additives.

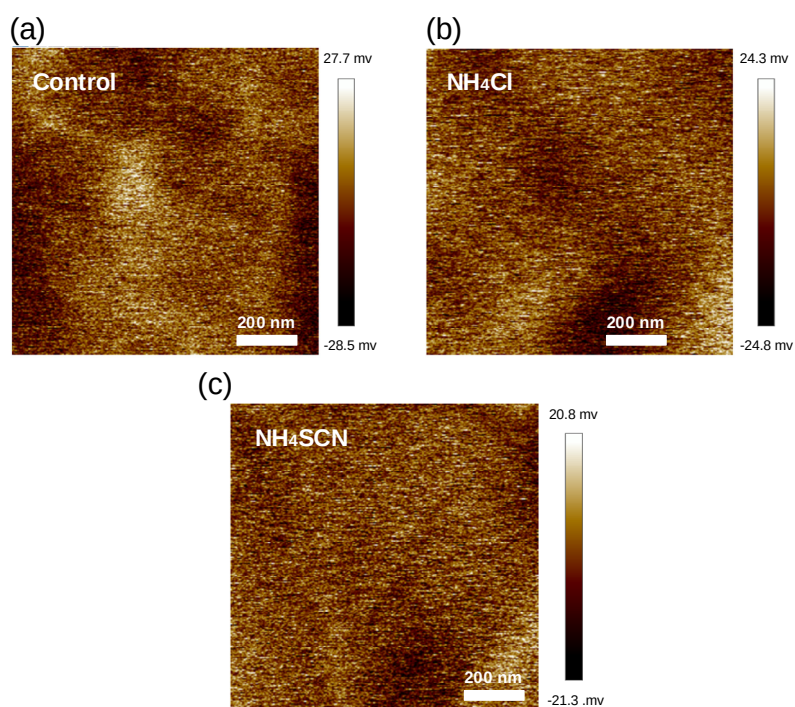


Figure 5-S9. The surface potential distribution of FA-based low-n 2D perovskite films treated with (a) no additives (b) NH_4Cl additives, and (c) NH_4SCN additives.

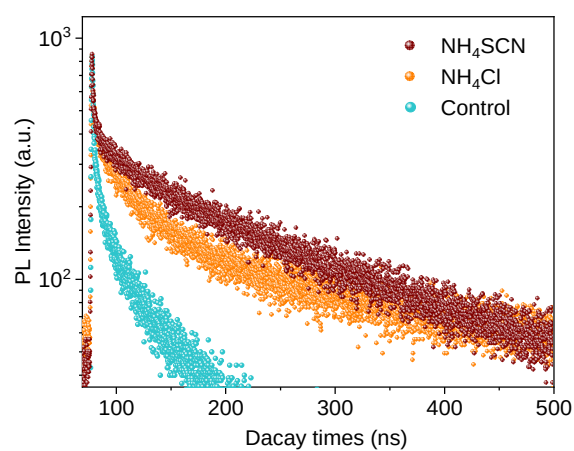


Figure 5-S10. TRPL spectra of FA-based low-n 2D films treated with different additives.

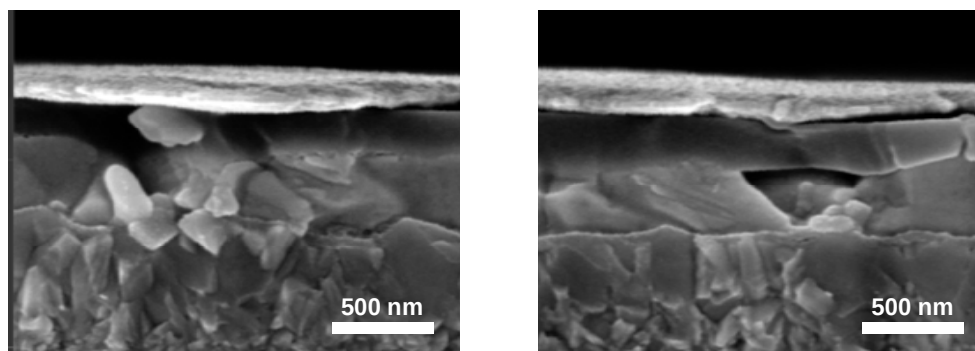


Figure 5-S11. Cross-sectional SEM images of FA-based low-n 2D PSCs based on control (left) and NH₄Cl-treated (right) perovskites.

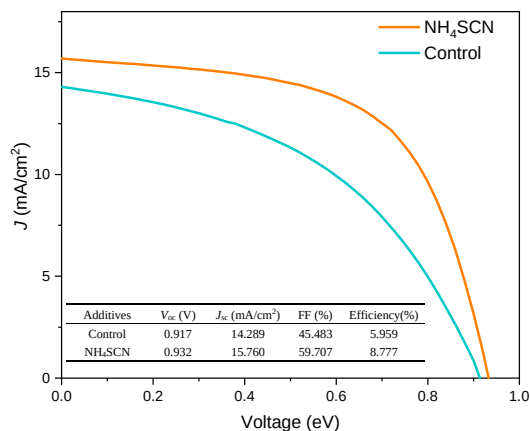


Figure 5-S12. IV curves of FA-based 2D perovskite solar cells with average n=3 before and after NH₄SCN treated, the device adopted the device structure of FTO/SnO₂/Perovskite/Spiro-OMeTAD/Au.

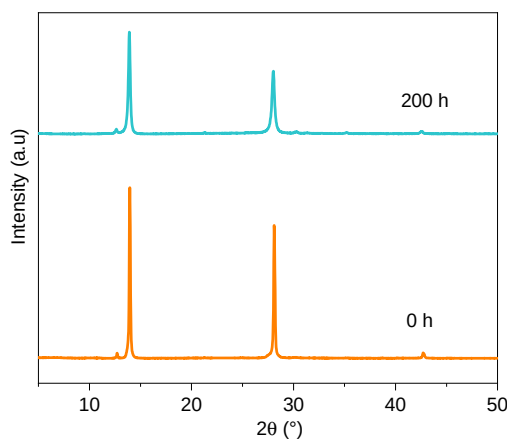


Figure 5-S13. XRD of NH₄SCN treated FA-based 2D perovskites before and after 1 Sun illumination in air.

Table 5-S1. Main parameters (obtained in the forward scanning and reverse scanning) of the best devices based on NH₄SCN treated perovskites with different concentrations.

Concentration	Direction	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Efficiency (%)
0	Forward	0.975	19.36	63.89	12.06
	Reverse	0.984	19.15	66.55	12.54
3.75%	Forward	1.025	20.38	72.88	15.22
	Reverse	1.028	20.46	73.26	15.41
7.5%	Forward	1.059	21.56	78.23	17.86

11.25%	Reverse	1.063	21.63	77.99	17.93
	Forward	1.042	21.35	75.39	16.77
15%	Reverse	1.038	21.42	76.02	16.90
	Forward	1.012	21.03	70.32	14.97
	Reverse	0.995	20.95	71.69	14.94

Table 5-S2. Main parameters (obtained in the forward scanning and reverse scanning) of the best devices based on NH₄Cl treated perovskites with different concentrations.

Concentration	Direction	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	Efficiency (%)
0	Forward	0.968	19.52	62.18	11.75
	Reverse	0.976	19.68	64.06	12.31
7.5%	Forward	1.043	20.85	69.86	15.19
	Reverse	1.051	20.66	70.43	15.30
15%	Forward	1.035	20.67	71.99	15.40
	Reverse	1.047	20.65	73.05	15.79
22.5%	Forward	1.017	19.15	64.85	12.63
	Reverse	1.041	19.63	67.99	13.89

Table 5-S3. Main parameters (obtained in the forward scanning and reverse scanning) of the best devices based on FA-based low-n 2D perovskites with different additives.

Additives	Direction	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	Efficiency (%)
NH ₄ SCN	Forward	1.062	21.62	78.96	18.14
	Reverse	1.067	21.61	78.66	18.14
NH ₄ Cl	Forward	1.044	20.75	73.64	15.95
	Reverse	1.044	20.86	73.21	15.94
Control	Forward	0.982	19.76	65.90	12.79
	Reverse	0.993	19.22	66.41	12.68

Table 5-S4. Summary of the representative FA-based 2D PSCs.

Additives	n ^a	Perovskites	PCE (%)	Year	Ref
HCl	9	BE ₂ FA ₈ Pb ₉ I ₂₈	17.4	2018	[346]
HCl	9	BA ₂ FA ₈ Pb ₉ I ₂₈	13.16	2020	[347]
MAI	4	PEA ₂ FA ₃ Pb ₄ I ₁₃	11.3	2018	[348]
MAI	5	(ThMA) ₂ FA ₄ Pb ₅ I ₁₆	19.06	2020	[349]
MAI&PbCl ₂	5	(4F-PEA) ₂ FA ₄ Pb ₅ I ₁₆	21.07	2022	[324]
FAI	4	PDAFA ₃ Pb ₄ I ₁₃	13.8	2021	[251]
FAI	4	PDA _{0.9} PA _{0.2} FA ₃ Pb ₄ I ₁₃	16.0	2021	[313]
Thiourea	3	BA ₂ FA ₂ Pb ₃ I ₁₀	7.33	2021	[325]
NH ₄ SCN	4	BA ₂ FA ₃ Pb ₄ I ₁₃	18.14	2022	This wor

^a Here n represents average n based on the initial composition.

Chapter 6 De-templated Crystallization in 2D Perovskites for Enhanced Photovoltaic Efficiency

The energy of the sun,
though immense and incomprehensible,
is but a fraction of what we see in the universe.
yet even this fraction holds the power
to revolutionize our world
-----Oliver Lodge

2D metal halide perovskites are renowned for tunable optoelectronic properties and superior stability compared to their 3D counterparts. However, their efficiency in photovoltaic devices has been hampered due to the disordered alignment of quantum wells and a tendency for in-plane growth. Herein, we proposed a de-templated crystallization strategy to control the crystallization kinetics of 2D perovskites via developing a stable intermediate phase in two-step deposition. By precisely adjusting the chemical interactions in the precursor solutions and driving the crystallization process, we successfully eliminate the templated in-plane growth near the liquid-air interface and promote the formation of highly out-of-plane orientated crystals, with the grain size exceeding 5 μm and carrier lifetime increased by four folds. The optimized 2D perovskite solar cell achieves a PCE of 21.16% and a J_{sc} of 23.71 mA cm^{-2} . Additionally, the devices demonstrate remarkable stability, with a PCE decrease of less than 5% after exposure to 65 $\pm$ 10% humidity for 1100 hours, heated at 85°C for 1077 hours, or continuous illumination for 1045 hours.

6.1 Introduction

2D metal halide perovskites have garnered significant research interest for the development of long-term stable PSCs due to their robust stability [274, 350-354]. Unlike their three-dimensional (3D) counterparts, 2D perovskites incorporate long-chain hydrophobic organic cations as spacers within the perovskite lattice, forming unique quantum-well (QW) structures[78, 327, 355]. The hydrophobicity of these organic spacer cations, dictated by the stoichiometric ratio, protects 2D perovskites from external corrosion and stabilizes their structure. However, QWs with fewer layers prefer to grow parallel to the substrates[356] (known as in-plane orientations), which limits the charge carrier transport and mobility across the layers, resulting in unideal photocurrent and PCE of the resulting PSCs [357, 358]. To improve the efficiency of 2D PSCs toward that of 3D PSCs, it is essential to adjust the layered structure from an in-plane to an out-of-plane orientation (perpendicular to the substrate) and enhance charge transport in 2D perovskites.

The in-plane orientation of the layered 2D perovskite structure is easily initiated by specific species or substrates due to the Van der Waals force or electrostatic induction[127, 359]. So far, various strategies to control the crystallization kinetics, such as additive-assisted engineering[151, 360], solvent vapor modulated crystallization [361], and temperature-controlled hot casting processing[274], typically implemented in a one-step method and mixed all the compositions in a precursor. The hardly controlled hydrophobic organic spacer cations tend to segregate and form a monolayer at the air-liquid interface, reducing surface energy and readily serving as nucleation sites for in-plane growth of the layered structure[128, 362-365]. Methods based on traditional two-step sequential deposition also confront serious segregation of organic spacer cations[257], as the large steric hindrance hinders their downward diffusion and further molecular exchange. Thus, it is critical to eliminate the in-plane templated growth induced by segregated spacer cations and to initiate new nucleation sites for out-of-plane crystallization of layered perovskites.

Herein, we present a de-templated crystallization strategy to realize controlled crystallization kinetics and highly out-of-plane orientation of 2D perovskite QWs. This method involves a

strategically preponed deposition of organic spacer cations along with lead iodide (PbI₂) and a molecular additive in the first step, which forms a stable intermediate phase. This intermediate phase effectively disrupts the typical in-plane templated growth (de-templated) induced by spacer cations. Subsequently, the deposition of formamidinium iodide (FAI) at a high surface concentration in the second step introduces new nucleation sites, significantly reducing the formation energy required for out-of-plane oriented QWs. This method promotes homogeneous ion interdiffusion and orderly crystal growth, leading to grain sizes exceeding 5 μm , and a nearly fourfold increase in carrier lifetime. Consequently, the optimized 2D PSC achieved a notable PCE of up to 21.16%, with the highest reported photocurrent of 23.71 mA/cm^2 in 2D Ruddlesden-Popper PSCs. Moreover, these PSCs demonstrate excellent stability, with less than 5% decrease in PCE after exposure to $65\pm 10\%$ humidity for 1100 hours, operation at 85°C for 1077 hours, or continuous illumination under 1 Sun solar light for 1045 hours.

6.2 Experimental section

6.2.1 Materials

Lead iodide (PbI₂, 99.99%), Formamidinium iodide (FAI, 99.99%), Hexylamine Hydroiodide (HAI), phenylethylammonium iodide (PEAI), and thiourea (TU) were sourced from TCI. Bis-(trifluoromethane) sulfonimide lithium salt (Li-TFSI) and 4-tert-butyl-pyridine (tBP) were supplied by Sigma-Aldrich. Methylammonium chloride (MACl), and 2,2',7,7'-Tetrakis [N, N-di(4-methoxyphenyl) amino]-9,9'-spirobifluorene (Spiro-OMeTAD) was sourced from Borun New Material Corp. chlorobenzene (CB), N, N'-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), were sourced from Sigma-Aldrich. A colloidal dispersion of tin (IV) oxide (SnO₂) was sourced from Alfa Aesar. ITO glass and FTO glass were purchased from Advanced Election Technology Co., Ltd.

6.2.2 Perovskite precursor solution

For the conventional two-step method (TTSD), the PbI₂ (1.0 mol) was dissolved in a solvent mixture of DMF and DMSO solution, while the FAI, HAI, and MACl (6 mg/ml) were dissolved in the IPA solution. The modified TTSD method with TU in the first step was defined in ATSD.

The modified TTSD with HAI preponed to the first step was defined in STSD. In the SATD spin-coating method, a mixture containing HAI, FAI, and PbI₂ at the same stoichiometric ratio of $n=4$, HAI and PbI₂ were prepared, and TU added to the PbI₂ precursors at concentrations ratio of PbI₂: TU=1:1 1:1.5, and 1:2 in the DMF and DMSO solutions, respectively. The FAI and MACl (6 mg/ml) were dissolved in the IPA solution. PEAi and ThDMA-based 2D FA perovskite films were prepared by dissolving these compounds along with TU and PbI₂ in mixed solvents of DMF and DMSO. FAI and MACl (6 mg/ml) were dissolved in IPA solution, maintaining a stoichiometric ratio of 2:3:4 ($n=4$). HA-based 2D FA perovskite films with different layers ($n=2$ and $n=3$) were prepared by a stoichiometric ratio of 2:1:2 ($n=2$), and 2:2:3 ($n=3$), by dissolving HAI, TU, and PbI₂ in mixed solvents of DMF and DMSO. Similarly, FAI and MACl were dissolved in IPA solution, respectively.

6.2.3 Device fabrication

First, patterned ITO glass substrates were prepared by a series of ultrasonic baths in detergent, deionized water, ethanol, and acetone, followed by UV ozone treatment. Each was conducted for 15 minutes. SnO₂ colloidal dispersion was then spin-coated at a speed of 3000 rpm for 30 seconds onto the prepared substrates, followed by an annealing process at 150°C for 30 minutes. The one-step method for 2D perovskite films deposited the precursor solution onto the substrate via spin-coating at 4000 rpm for 30 seconds, with 300 μ L of CB being used as an antisolvent 15 seconds before the end of the process. The two-step method consists of first rotating coating a metal halide precursor solution at 3000 rpm for 30 seconds, followed by rotating coating an organic cationic solution in IPA for 30 seconds at 5000 rpm. Then, the perovskite layers were annealed on a hotplate at 150°C for 30 minutes. Afterward, a Spiro-OMeTAD solution, acting as the hole-transport layer, was spin-coated at 3000 rpm for 30 seconds. This solution was prepared by dissolving 73 mg of Spiro-OMeTAD in 1 ml of CB to which 17.5 μ L of Li-TFSI (520 mg/ml in acetonitrile) and 28.8 μ L of 4-tBP were added as dopants. Finally, gold electrodes, 60 nm in thickness, were thermally evaporated onto the device to ensure good electrical contact.

6.2.4 Characterization of perovskite films

X-ray diffraction (XRD) data were obtained using Rigaku Dmax 2600 diffractometer using Cu $K\alpha$ radiation with a Nickel filter. Grazing incidence wide-angle X-ray scattering (GIWAXS) data were performed at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) with X-rays of 1.2398 Å wavelength. X-ray photoelectron spectroscopy (XPS) was conducted on the AXIS Ultra DLD spectrometer from Kratos. UV-Vis absorption spectra of perovskite films were conducted using a Shimadzu UV 2450 spectrometer. Transmission Electron Microscopic (TEM) was used FEI Themis-Z Double-corrected 60-300Kv S/TEM. The perovskite films were scratched off from the substrate and dispersed in toluene by sonication for 10 min, followed by being dropped on a Cu grid for characterization. For perovskite samples, both top-view and cross-sectional images were captured using a Tescan Maia3 Gmu (model 2016) scanning electron microscope (SEM). Kelvin probe force microscopy (KPFM) data were collected with a Dimension Fast Scan Bio Atomic Force Microscope. Photoluminescence (PL) Measurements were carried out with an FLS1000 spectrometer (Edinburgh Instruments), using a 470 nm excitation source, while the PL mapping was collected using a Leica TCS SP8 STED 3X super-resolution system. Time-resolved photoluminescence spectra (TRPL) were also performed on the same spectrometer as that for steady PL tests. For perovskite samples, both top-view and cross-sectional images were captured using a Tescan.

6.2.5 Device characterization and Stability measurement

J-V curves were recorded using a Keithley 2400 source-meter under AM 1.5G 1-sun illumination provided by a Newport Oriel® Sol3A™ 3A simulator (model 94023A). The light source calibration was performed with a standard silicon reference cell (Newport Oriel 91150-KG5). Measurements with active areas of 0.08 cm² and 1.02 cm² were used for the measurements. IPCE spectra measurements were measured using monochromatic light with an intensity of 1×10^{16} photons cm⁻² in alternating current mode. Accelerated aging experiments were conducted at 25° and a relative humidity (RH) of 50-60%. To assess thermal stability, non-encapsulated PSCs were placed on a hotplate inside an aging box set at 85°C, and PCE

evolution was tracked using periodic J - V measurements. Operational stability over the long term was evaluated with a Model BIR-50 system designed for solar cell light resistance testing. The performance of the unencapsulated devices was examined under continuous 1-sun illumination within a nitrogen-filled glovebox. All stability assessments involved a modified hole transport layer incorporating ion-exchanged PTAA, with further details available in earlier studies [1].

6.2.6 Computational method

All first-principles calculations are based on DFT calculations [366] and carried out using the VASP [367]. To account for van der Waals (vdW) forces, the DFT-D3 scheme of Grimme was adopted [368]. Projector-augmented wave (PAW) pseudopotentials are applied to simulate the valence states and the core-valence electron interactions [369]. For exchange and correlation effects, the Perdew-Burke-Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA)[370] was used, with spin-orbit coupling (SOC) taken into consideration. Plane-wave functions were expanded with a 500-eV energy cutoff, and a 4*4*4 Monkhorst–Pack k-point grid was used to Brillouin zone. The atomic geometries were fully optimized and ensured that forces on each atom were reduced to less than 0.01 eV/Å.

6.3 Results and discussion

Traditional two-step sequential deposition (TTSD) of 2D perovskite films generally separates the inorganic metal halides (PbI_2) and the mixture of organic species (FAI and HAI in this case) in a sequence, where the PbI_2 were first deposited onto a substrate, and subsequently a solution of FAI and HAI dissolved in isopropyl alcohol (IPA) is dynamically drop cast to react with PbI_2 and form perovskites, as illustrated in **Figure 6-1**. Due to its large steric hindrance and hydrophobicity, the organic spacer cations (HAI) are generally hard to diffuse and then template the in-plane crystallization of layered structure with low layer numbers, inferior for charge transport of low-dimensional PSCs.

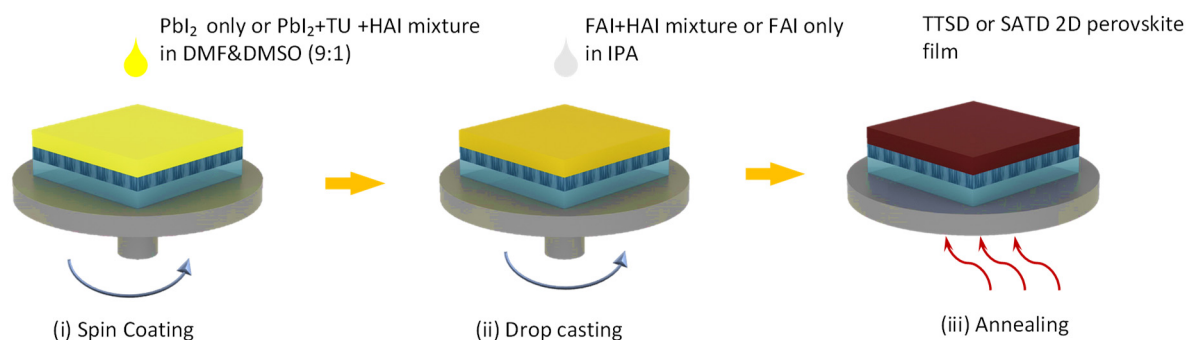


Figure 6-1. Fabrication flowchart of 2D perovskite films using various two-step deposition techniques.

Traditional two-step sequential deposition (TTSD) involves an initial deposition of PbI₂, followed by a secondary step of depositing a mixture of formamidinium iodide (FAI) and methylammonium iodide (HAI); Spacer-cation-preponed and additive-stabilized two-step deposition (SATD) method includes spin-coating of a mixture of PbI₂, Thiourea (TU) and HAI in the first step, followed by the deposition of FAI at the second step.

To mitigate the templating effect of the segregated organic spacer cations on the surface, we strategically preponed the deposition of organic spacer cations (HAI) and introduced them into the PbI₂ precursor in the first step. Additionally, we incorporated molecular additives (here we chose thiourea, TU) into the mixture, which was widely reported to retard the direct reactions between spacers and PbI₂[371-373]. In the second step, the FAI solution was spin-coated onto the wet film of the mixture. Given the high surface content of FAI, we expect it to generate a quasi-3D surface at the initial crystallization stage and facilitate out-of-plane crystallization of the layered structures. We refer to this method as the spacer-cation-preponed and additive-stabilized two-step deposition (SATD), the process flow and complete experimental design are detailed in **Fig. 6-S1**.

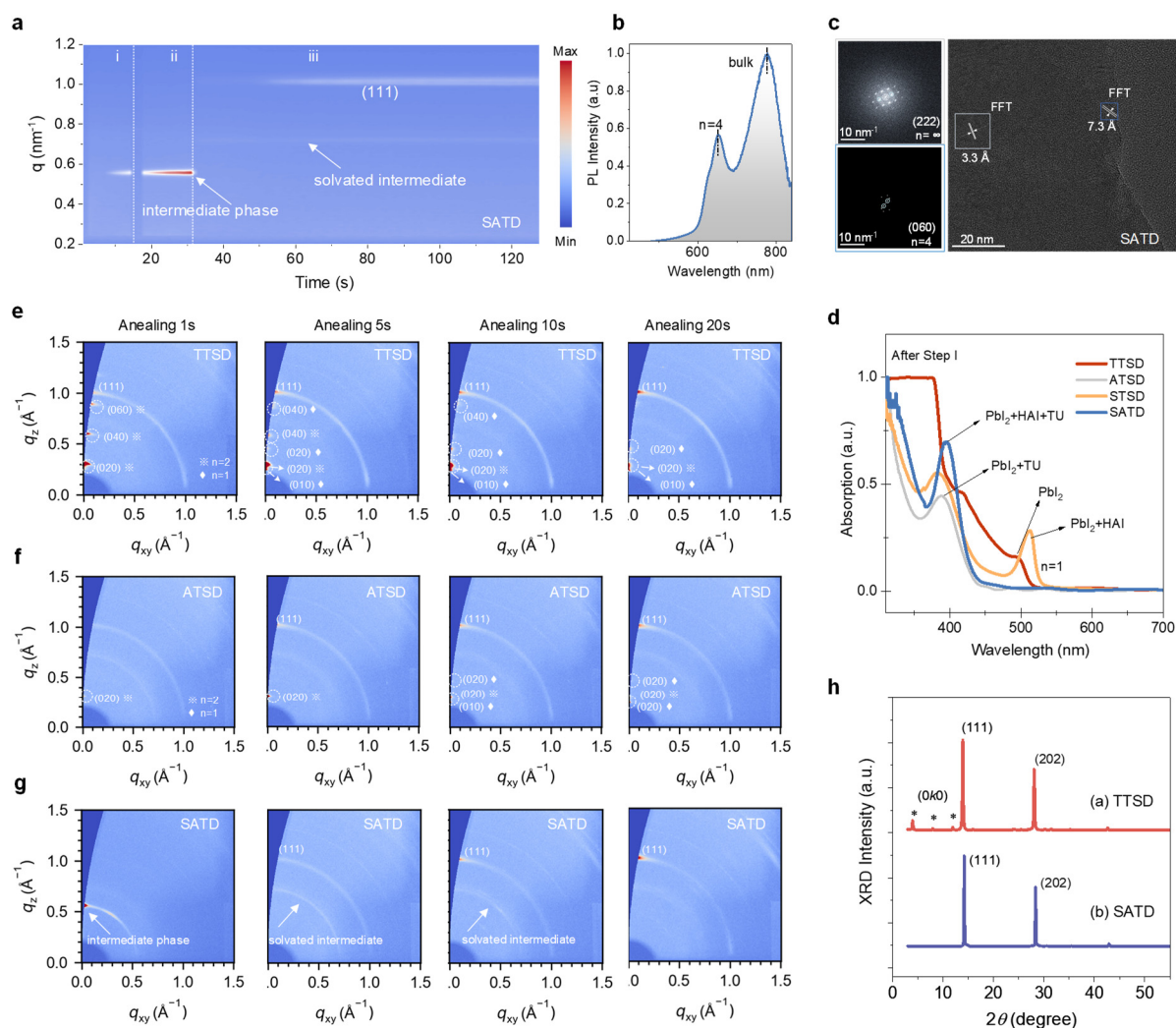


Figure 6-2. De-templated crystallization of 2D perovskite via SATD strategy. (a) Crystallization evolution of the target SATD films recorded by in-situ GIWAXS. (b) PL spectra of the resulted from SATD film excited from the glass side. (c) HRTEM images and corresponding FFT results of the resulted SATD film. (d) UV-Vis absorption spectra of the as-fabricated films after first-step deposition using different methods. (e-g) In-situ GIWAXS which tracks phase evolution from nucleation to crystallization during annealing for different samples (TTSD, ATSD, and SATD methods). (h) XRD patterns of the perovskite films employing SATD and TTSD, respectively.

To evaluate the de-templated effect of our new method, we first monitored the crystallization kinetics near the surface of SATD films by *in-situ* grazing incidence wide-angle X-ray scattering (GIWAXS) measurement, as illustrated in **Figure 6-2a**. The *in-situ* GIWAXS

patterns clearly show three distinct crystallization stages of the SATD film. First (0-15 s), the initially deposited PbI₂-TU-HAI mixture gradually formed an intermediate gel state ($q = 0.55 \text{ \AA}^{-1}$) [374] during spin-coating, indicating a progressive structural ordering. After the deposition of FAI (~15-30s), the gel state exhibits significant enhancement of diffraction, this could be attributed to the extraction of residual solvent by spin-casted IPA and possible molecular exchange between FA and TU. We regard the gel state in this stage as a stable intermediate phase, as no additional phase (even the solvated phases[375, 376]) was observed, and this intermediate phase remains stable during the whole process before annealing[377]. Upon annealing, the diffraction of the intermediate phase disappeared immediately, which could correspond to the thermal evaporation of most TU molecules. Simultaneously, a marked increase of (111) diffraction ($q = 1.0 \text{ \AA}^{-1}$) indicates the immediate formation of the bulk phase of perovskite at the surface, and no diffraction corresponding to the low- n phase could be detected. This could be attributed to the higher surface content of FAI salts preferentially reacting with PbI₂, providing new nucleation along out-of-plane [378]. Additional diffraction signals at $q = 0.7 \text{ \AA}^{-1}$ were noted, which could correspond to the generated solvated phases as the chemical interaction between solvent (like DMF/DMSO) and perovskite compositions[375, 376]. Finally, a perovskite with highly out-of-plane orientation, dominated by $n = 4$ phase[129], was confirmed after annealing for 30 minutes, as demonstrated by the steady-state photoluminescence (PL, **Figure 6-2b**) spectra excited from the back side of the film, and high-resolution transmission electron microscopy (HRTEM) image (**Figure 2c**).

The direct formation of the bulk phase upon annealing in the SATD sample is largely distinctive from that in the TTSD sample, where a set of in-plane oriented low- n 2D phases was initially generated upon annealing (**Figure 6-2e**). This indicates the templated in-plane growth of 2D phases was largely inhibited through the SATD strategy. We infer that the intermediate phase, which stably traps spacer cations and easily converts to the perovskite phase upon annealing, is vital to avoid in-plane growth. When combined with subsequently deposited FAI at a high surface concentration, this intermediate provides novel nucleation and promotes the highly out-of-plane orientated 2D perovskite[374].

To verify the importance of the intermediate phase, we compared the crystallization process of

the SATD method with the TTSD method. Additionally, two optimizations based on TTSD were investigated, as detailed in **Figure 6-S1**. These methods either lack TU or do not prepone the deposition of spacer cations. Specifically, we analyzed the additive-assisted two-step sequential deposition (ATSD) method, which incorporates TU in the first step to regulate crystallization without altering the deposition of HAI salt; and the spacer-cation-preponed two-step sequential deposition (STSD) method, where HAI salts were preponed to the first step, but without TU additives. Notably, the solubility of TU in IPA solutions is relatively low when introduced in the second step.

The ultraviolet-visible absorption spectra (UV-Vis, **Figure 6-2d**), recorded immediately after the first-step deposition, clearly illustrated the absorption differences of the resulting phases. The distinct absorption edge at 500 nm, corresponding to the 2.48 eV optical bandgap of PbI_2 , indicated rapid nucleation and initial crystallization of PbI_2 in the TTSD method. In contrast, the target mixture of PbI_2 , TU, and HAI of the SATD sample displayed an absorption peak at 400 nm, markedly distinct from the crystallized PbI_2 and $n=1$ phase (HA_2PbI_4). Additionally, the as-prepared film also appeared nearly colorless compared to the yellow PbI_2 films (**Fig. 6-S2**), indicating the formation of a unique intermediate phase [155]. Notably, the addition of TU could promote the formation of the intermediate phase (PbI_2/TU in solvent), which will be explored in detail below (ATSD). However, the preponed introduction of HAI alone but without TU (PbI_2/HAI in solvent) in the STSD method directly leads to the formation of the $n=1$ phase of 2D perovskite, which then easily templates the parallel growth of perovskites, as demonstrated in **Fig. 6-S3**.

The GIWAXS characterization monitored the crystallization of different films after the second step of deposition. For comparison, we captured the patterns after annealing for 1 s, 5 s, 10 s, and 20 s, respectively. For the TTSD methods, the uncontrolled reaction between PbI_2 and HAI/FAI triggers multiple- n valued phases ($q = 0.47 \text{ \AA}^{-1}$, $0.52 \text{ \AA}^{-1}$, and $0.66 \text{ \AA}^{-1}$) immediately after annealing for 1 s, with the $n = 1$ phase predominating. This indicates that the diffusion of spacer cations was impeded, causing them to remain at the surface and react with PbI_2 to form low- n phases. The diffraction attenuation of the $n = 6$ phase and intensification of the $n = 2$ phase indicate complex crystallization competition (**Fig. 6-S4**), which could be attributed to

the minor differences in the formation energy of these various n -valued phases. Ultimately, the TTSD-processed film prominently exhibits low- n phases with in-plane orientations, consistent with the X-ray diffraction (XRD) results in **Figure 6-4h**. **Figure 6-2f** shows the crystallization of the ATSD sample. Despite the TU can retard the crystallization of PbI_2 , the resulting film still displayed minor parallel orientation. This could be attributed to insufficient diffusion of HAI during the second step, due to the large steric hindrance of HAI cations. Thus, merely incorporating TU into the first step as an additive is not sufficient to fully inhibit the in-plane crystallization in two-step deposited films. In contrast, for the SATD method, the film was crystallized from the intermediate phase at the initial annealing stage, avoiding the templated low- n phases. Since the spacer cations HAI was pre-deposited, the secondly deposited FAI with a high surface content could promote the formation of bulk-phase, thereby reducing the formation barrier for out-of-plane orientated crystals [374]. Finally, the resulting film exhibited sharp and bright Bragg spots along the out-of-plane direction (**Figure 6-2g**), indicating a highly out-of-plane orientated 2D phase [129]. The XRD patterns in **Figure 6-2h** and **Fig. 6-S4** also confirmed the inhibition of parallel low- n phases in SATD films.

To reveal the underlying mechanism and the formation of stable intermediate in the SATD method, we employed Proton Nuclear Magnetic Resonance (^1H NMR) to distinguish the chemical interactions between perovskite compositions and TU molecules. As shown in **Figure 6-3c**, the addition of TU molecules resulted in the broadening and downfield shifting of the resonance signals attributed to the amino group of HA^+ and FA^+ (N-H protons, marked with an asterisk *), with $\Delta\delta$ values of 0.03 and 0.01 ppm, respectively. This indicates that TU can interact with these organic cations with a stronger binding with the HA^+ cation [379, 380]. Density Functional Theory (DFT) calculations, depicted in **Figure 6-3e**, confirmed the thermodynamical stability of HAI/TU and FAI/TU complexes, with HAI/TU exhibiting notably lower binding energy (-1.186 eV vs -0.799 eV). Consequently, it could be inferred that during intermediate formation, the FA^+ cations may be largely excluded and the high content of FA^+ could initiate a quasi-3D perovskite surface. The shift of the C=N stretching peak from 1618 cm^{-1} to 1659 cm^{-1} , observed in Fourier-transform infrared spectroscopy (FTIR) spectra (**Fig. 6-S5**), further indicates the enhanced hydrogen binding between TU and HA^+ .

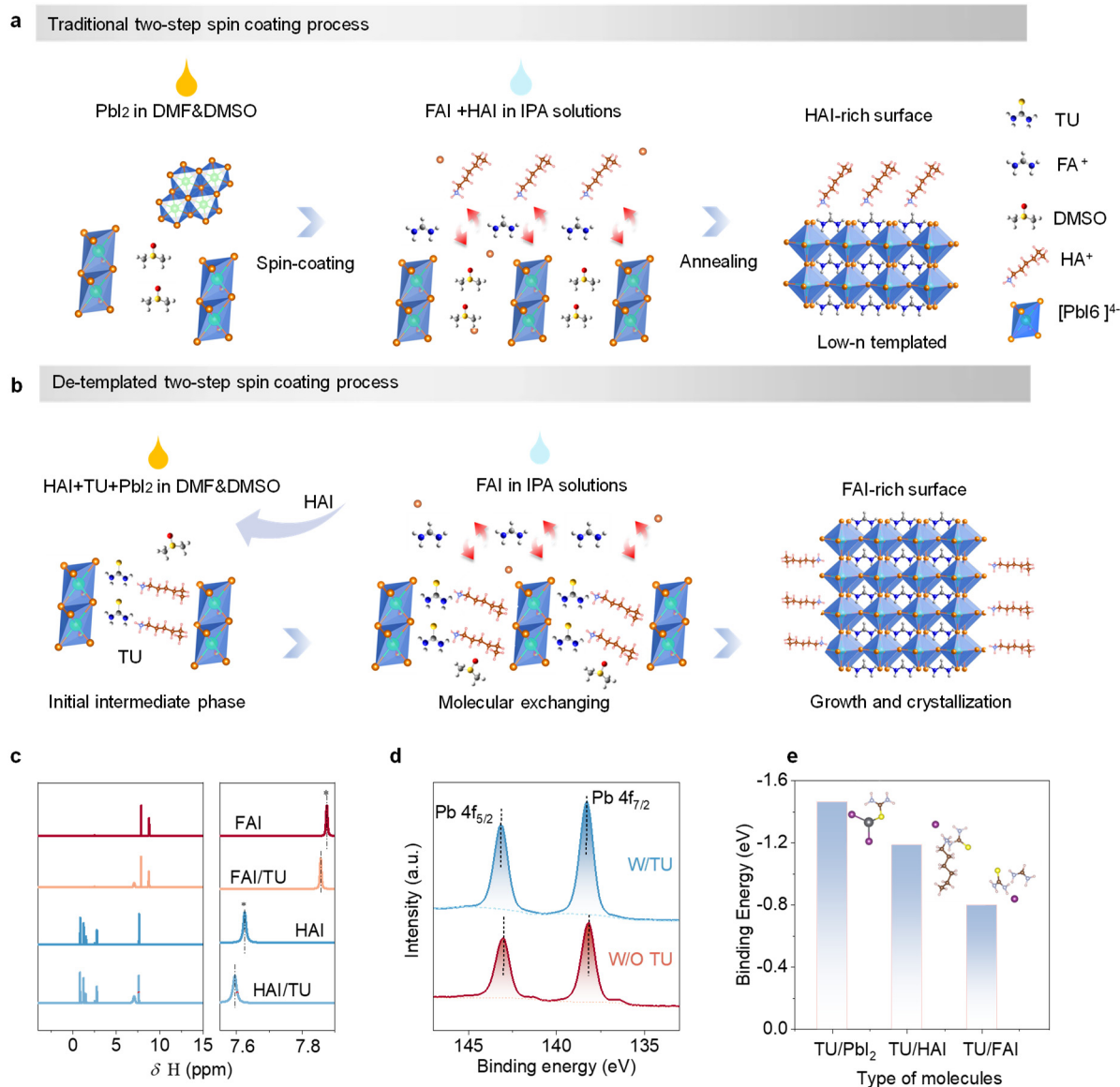


Figure 6-3. Mechanistic illustration of de-templated crystallization. (a-b) Schematic illustration of crystallization kinetics using TTSD and SATD strategy. (c) ^1H NMR spectra of organic salts before and after the interaction with TU. (d) Lead (Pb) 4f core-level XPS spectra of first-step films with and without TU addition. (e) Optimized structures and calculated binding energies of TU-involved molecular-ion complexes.

FTIR results further demonstrated an interaction between TU and PbI_2 . The C=N stretching vibrations are enhanced from 1618 cm^{-1} to 1654 cm^{-1} , while the C-N bending vibrations weakened from 1404 cm^{-1} to 1390 cm^{-1} . These changes could be attributed to the formation of strong bonds between the Pb ions and the electron-donating sulfur (S) atoms in TU molecules.

X-ray photoelectron spectroscopy (XPS) results further confirm the interactions between TU molecules and the $[\text{PbI}_6]^{4-}$ octahedral structures, as evidenced by the shift in the characteristic peaks of Pb^{2+} ($\text{Pb } 4f_{5/2}$ and $\text{Pb } 4f_{7/2}$), which move towards the higher binding energies after TU addition (**Figure 6-3d**). DFT calculations as illustrated in **Figure 6-3e** and **Fig. 6-S6**, quantified the interactions. The results also revealed a strong binding between TU and PbI_2 (-1.465 eV), which exceeds that between PbI_2 and HAI (-1.106 eV), PbI_2 and FAI (-0.852 eV), and also that between PbI_2 and dimethyl sulfoxide (DMSO) (-1.01 eV) [381]. These results are consistent with the Electrostatic Potential (ESP) analyses in **Fig. 6-S7**.

Based on the experimental and computational results, we infer that the added TU molecules can interact simultaneously with both organic spacer cations HAI and inorganic PbI_2 . This interaction effectively traps the spacer cations, establishing a dual-site regulation that facilitates the formation of stable intermediates. These stable intermediates inhibit the templated in-plane crystallization of low- n 2D perovskite phases in the first step and retard the rapid reactions between FAI and PbI_2 components in the subsequent step. Upon depositing organic FAI solutions, the high surface content of FAI in the second step generates an akin quasi-3D perovskite phase at the air-liquid surface, significantly reducing the formation energy required for out-of-plane oriented QWs[128][129]. Additionally, the thermal evaporation of TU also facilitates the downward diffusion of FAI, enhancing the compositional homogeneity in the out-of-plane direction of the 2D perovskite films [382]. This mechanism is illustrated in **Figures 6-3a and 3b**.

Kelvin probe force microscopy (KPFM) measurements were conducted to probe the photoelectronic properties of the SATD 2D perovskite films. As depicted in **Figures 6-4a and 4b**, the grain sizes of the SATD film increase by an order of magnitude to 5 μm compared to the TTSD film, significantly reducing the grain boundary proliferation and non-radiative recombination pathways. The TTSD film exhibits higher contact potential difference (CPD) and uneven surface potential distribution (**Figure 6-4c**). This could be related to rough surface texture with an extensive pinhole accumulation at the grain boundaries as confirmed by scanning electron microscopy (SEM) images in **Fig. 6-S8**. PL intensity mapping and time-resolved PL (TRPL) mapping results, presented in **Figures 6-4d-4g**, further reveal superior

homogeneity and reduced non-radiative recombination in the SATD film, even after 200 hours of light soaking. Conversely, the TTSD film displays conspicuous black spots at grain boundaries, accompanied by a corresponding decrease in PL intensity (**Figure 6-4d**), indicative of localized defects that could potentially initiate photodegradation[383]. Notably, the SATD film exhibits significantly enhanced carrier transport, with a TRPL carrier lifetime increased by nearly four-fold, as detailed in **Fig. 6-S9 and Table S6-1**.

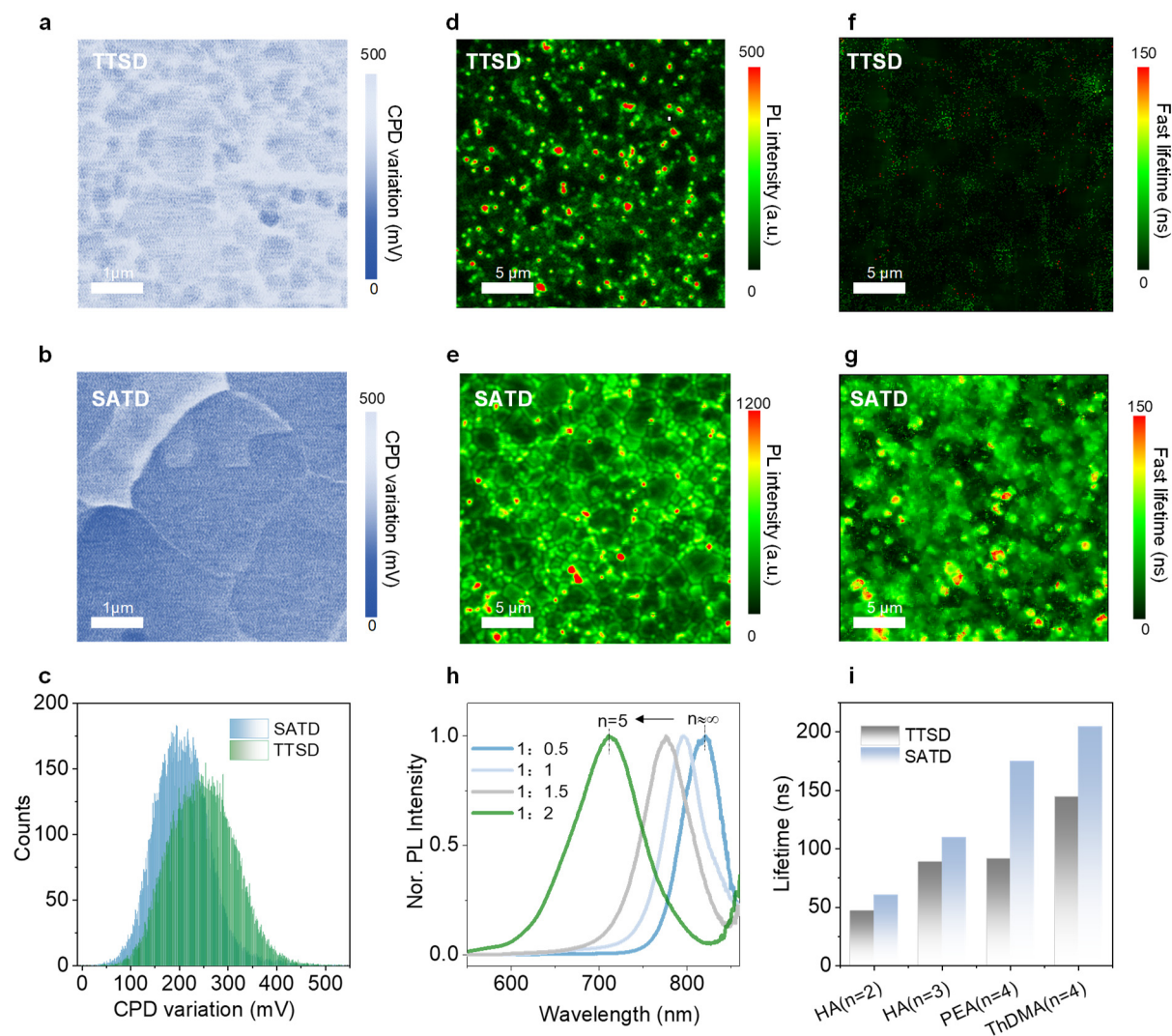


Figure 6-4. Photoelectronic properties of perovskite films. (a-b) Surface potential mapping and (c) the distribution of CPD variation of the TTSD and SATD perovskite films, respectively. (d-e) Confocal PL and (f-g) carrier lifetime mapping of the TTSD and the SATD perovskite films, respectively, after 200 hours of AM-1.5G illumination. (h) PL evolution of the fabricated SATD films as the increased ratios of TU (PbI₂: TU = 1:0.5, 1:1, 1:1.5, and 1:2). (i) Carrier

lifetimes of HA-based 2D perovskite films with different thicknesses of QWs ($n = 2$ and $n = 3$), and that adopting either RP or DJ type spacer cations (i.e., PEA, ThDMA), respectively.

Furthermore, we observed that in the HA-inserted 2D perovskite film (designated $n = 4$), increasing concentrations of TU led to a significant blue shift in the PL emission peak from 821 nm to 712 nm, as illustrated in **Figure 6-4h** and **Fig. 6-S10**. This shift to a higher energy bandgap indicates strengthened quantum confinement in corresponding films[80]. Additionally, the broadening of the PL emission peaks was also observed[384]. These observations may correlate with the purer 2D phase in the SATD film as the increase of TU molecules, brings the final film compositions closer to the initial stoichiometric ratios. Therefore, in the SATD method, strategic modulation of TU concentration in the first step may enable precise control over the phase distribution and photoluminescent properties of 2D perovskites, thereby paving a new way for enhancing the performance of related photovoltaic and optoelectronic devices.

We validate the versatility of the SATD method by applying it to a variety of 2D perovskites with different layer numbers (n) or incorporating various types of organic spacer cations. Specifically, we investigated HA-inserted 2D perovskites with layer numbers of $n=2$ and $n=3$. Lower- n -phase 2D perovskites typically present more challenges in altering the in-plane orientation of the perovskite films. The XRD results in **Fig. 6-S11** confirm that the SATD method effectively inhibits the in-plane growth in low- n perovskites. Furthermore, we adopted different types of organic spacer cations including Ruddlesden-Popper (RP) type 2-phenylethylammonium (PEA) and Dion-Jacobson (DJ) type 2,5-thiophene dimethylammonium (ThDMA)[385], to synthesize corresponding 2D perovskites using the SATD approach. Notably, the SATD method significantly enhances the carrier lifetimes of various types of 2D perovskite films as compared to the TTSD, as evidenced by TRPL results in **Figure 6-4h** and **Fig. 6-S12**.

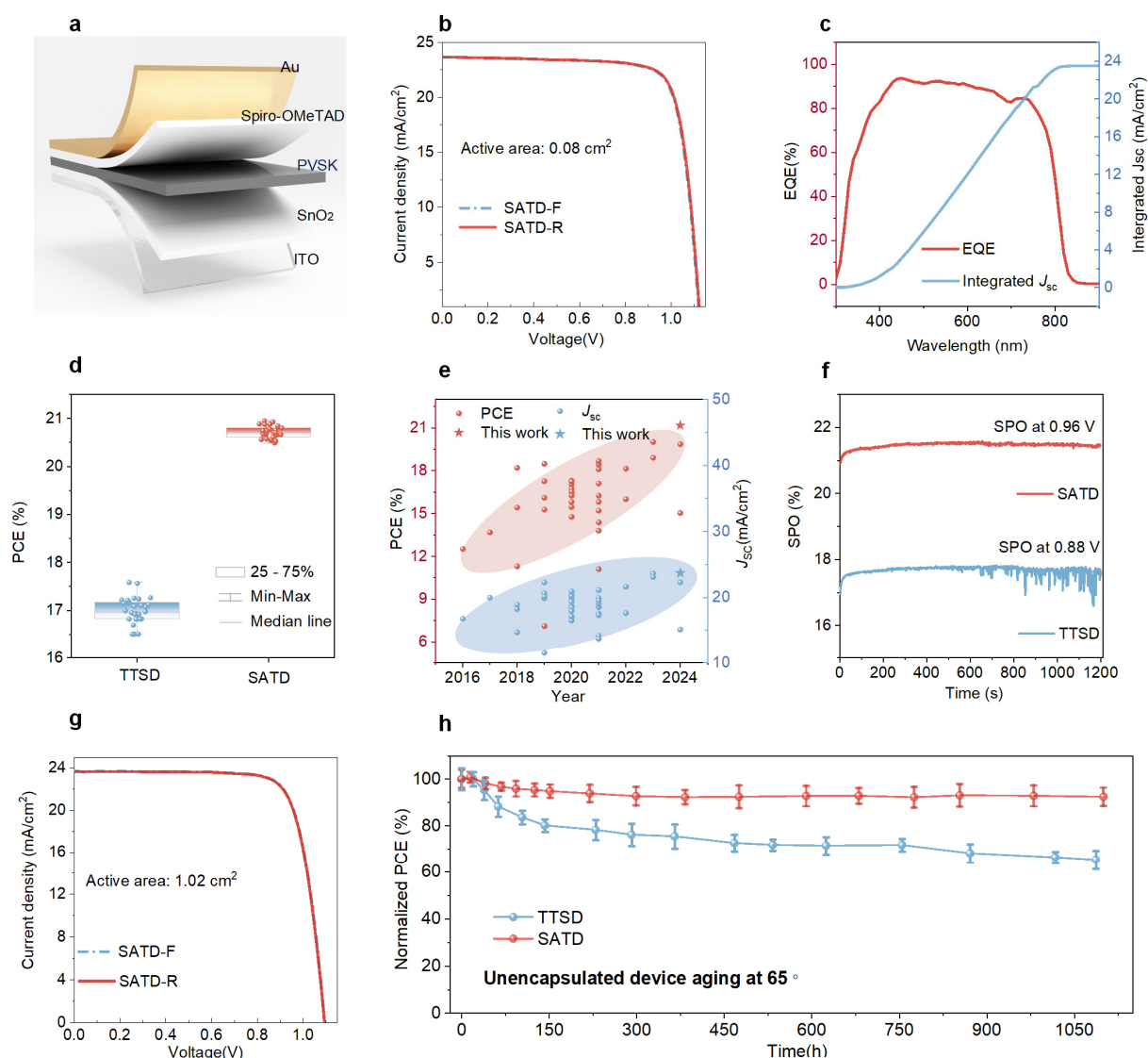


Figure 6-5. Device performance and stability. (a) The illustration of stacking structure of 2D PSCs. (b-c) J–V, and EQE curves of the target PSCs based on SATD. (d) Statistical distribution of PCEs for TTSD and SATD PSCs in the same batch. (e) Summary of PCE and Jsc evolutions of the representative 2D PSCs reported in the related literature (more details in Table 6-S2). (f) Steady-state power outputs (SPO) of the corresponding PSCs. (g) J–V curves of the SATD-based large-area (1.02 cm²) 2D PSCs. (h) Thermal stability of the unencapsulated 2D PSCs.

We further fabricated the PSCs by using the 2D perovskite active films through different methods as obtained above and then evaluated their photovoltaic device performance. The devices are with the structure of ITO/SnO₂/perovskite/Spiro-OMeTAD/Au, as schematically

depicted in **Figure 6-5a and Fig. 6-S13**. The optimized photovoltaic device based on the SATD perovskite layer, with an aperture area of 0.08 cm², achieves a high PCE of 21.16% (**Figures 5b, d**), outperforming TTSD device of 17.58% (**Figure 6-S14 and Table 6-S2**), ranking among the highest efficiencies reported for 2D Ruddlesden–Popper perovskite devices (**Figure 6-5e and Table 6-S3**). Such the impressive efficiency surge in the SATD PSCs can be primarily credited to the markedly increased short-circuit current density (J_{sc}), reaching up to 23.71 mA/cm², as corroborated by the corresponding values from the external quantum efficiency (EQE) results (**Figure 6-5c**). The high J_{sc} is a direct result of the highly out-of-plane orientation of the layered perovskites. Additionally, it represents the highest reported J_{sc} values among 2D PSCs to date (**Table 6-S3**). We also measured the steady-state power output (SPO) of the best-performing device for 1200 seconds at a fixed voltage near the maximum power point (MPP). An SPO of 21.45% was achieved in the SATD-processed device, surpassing the 17.67% of the TTSD-based device (**Figure 6-5f**). To verify the uniformity of the SATD-processed perovskite film on a large scale, we fabricated PSCs with an active area reaching up to 1.02 cm², which achieves a high PCE of 20.00 %, with a V_{oc} of 1.09 V and a J_{sc} of 23.53 mA cm⁻² (certified efficiency of 19.50%) (**Figure 6-5g and Fig. 6-S15&S16**). To the best of our knowledge, this represents the highest reported certified PCE for 2D PSCs with large areas up to 1 cm² (**Tables 6-S4,5**).

We further evaluated the stability of the resulting 2D PSCs under accelerated aging conditions. The unencapsulated SATD-processed device shows minimal PCE degradation (< 5%) after 1100 hours of exposure to a humid atmosphere (RH ~ 50-60%, 25°C), in stark contrast to the TTSD-based device, which experiences nearly a 30% reduction over the same period (**Figure 6-5h**). Further thermal stability tests at 85°C (**Fig. 6-S17**) indicate that the SATD device retains 95.4% of its initial efficiency after 1077 hours, significantly outperforming the TTSD-based device, which drops to 41.12% after 873 hours. Additionally, we assessed the long-term operational stability of the unencapsulated SATD-processed devices under continuous one-sun illumination (AM 1.5 G) in an N₂-filled glove box, with the devices operating at the maximum power point (MPPT) (**Fig. 6-S17**). The SATD-processed device retains approximately 95% of its initial PCE after 1045 hours, whereas the TTSD-based device falls to about 30% of its

original value. These improvements in device stability can be attributed to the improved film morphology and crystallinity achieved through the SATD strategy.

6.4 Conclusions and outlook

In summary, we demonstrated a de-templated crystallization strategy for producing high-quality 2D perovskite thin films with highly ordered out-of-plane orientations. This approach establishes a stable intermediate state, which effectively inhibits the in-plane nucleation of QWs and retards crystallization. The subsequent deposition of FAI in a high surface content promotes the desired out-of-plane-oriented crystallization. Consequently, we successfully achieved an impressive PCE of 21.16% and greatly improved device durability in the resultant 2D PSCs. Moreover, we showcase the high versatility of this approach for producing a range of out-of-plane oriented 2D perovskite films with different organic spacer cations and varying layer numbers. This universal and facile synthesis method for diverse 2D perovskite thin films also provides insights into developing additives to selectively anchor the perovskite compositions and presents a promising route for producing highly stable and efficient 2D PSCs.

6.5 Appendices

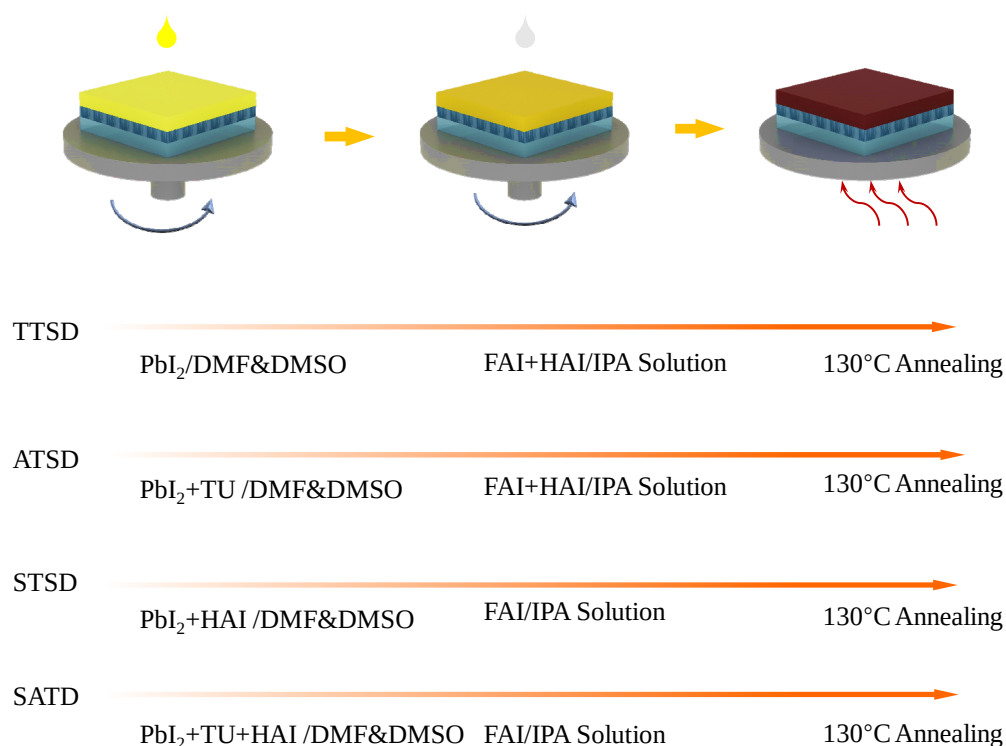


Figure 6-S1. Fabrication flowchart of 2D perovskite films based on different two-step deposition methods. **a)** traditional two-step sequential deposition method as defined in TTSD method (PbI_2 ; FAI+HAI), **b)** a modified additive-assisted two-step sequential deposition as defined in ATSD method (PbI_2 +TU; FAI+HAI). **c)** a modified spacer-cation-preponed two-step sequential deposition as defined in STSD method (PbI_2 +HAI; FAI+HAI), **d)** Target spacer-cation-preponed additive-stabilized two-step deposition (SATD) method (PbI_2 +TU+HAI; FAI), respectively.

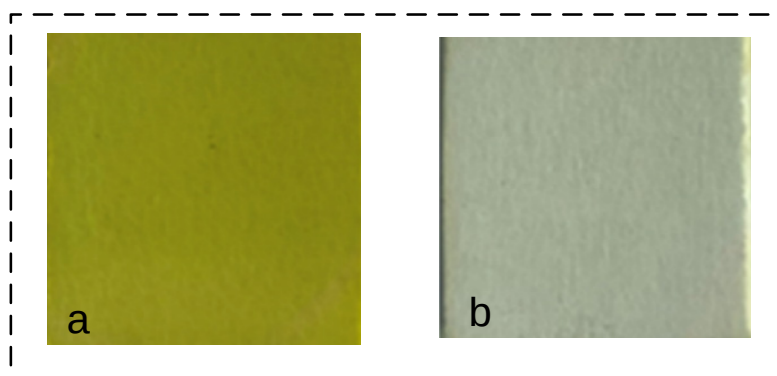


Figure 6-S2 Optical photo of wet perovskite film after the first deposition step using a) TTSD method and b) target SATD method, the SATD sample exhibited nearly colorless compared to the yellow PbI_2 films.

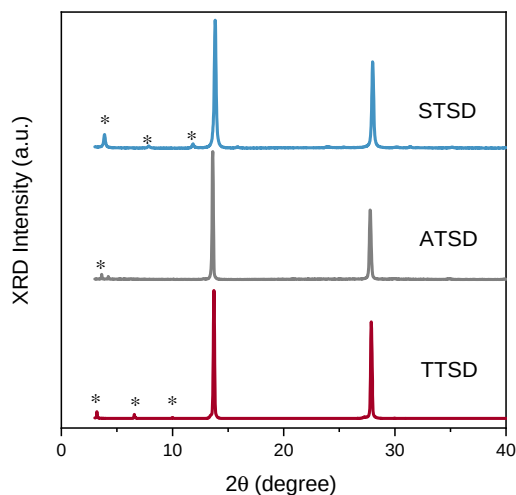


Figure 6-S3. XRD patterns of 2D FA-based perovskite films after annealing, with different deposition methods as shown in Supplementary Fig. 1 (the asterisk * represents the $0k0$ crystal plane).

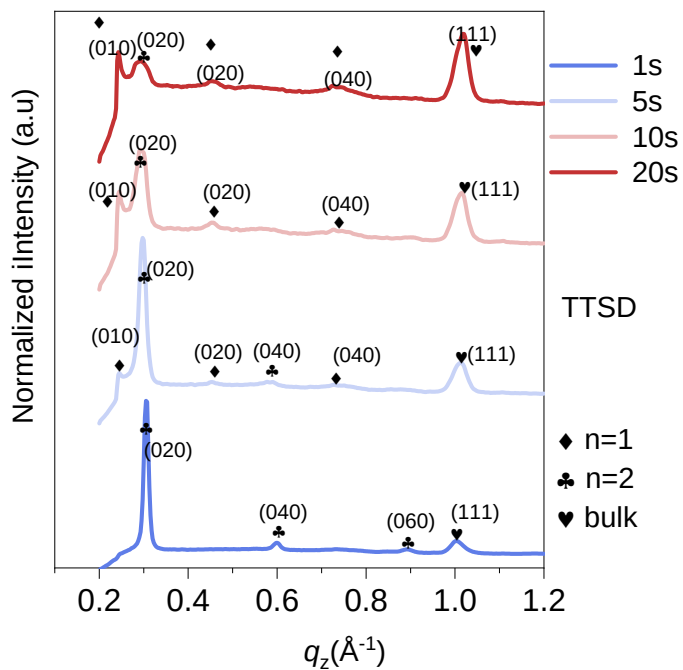


Figure 6-S4. Integrated diffraction intensity along the out-of-plane direction of GIWAXS patterns for the TTSD 2D perovskite films. The calibration of diffraction peaks is based on the literature [151, 361, 386].

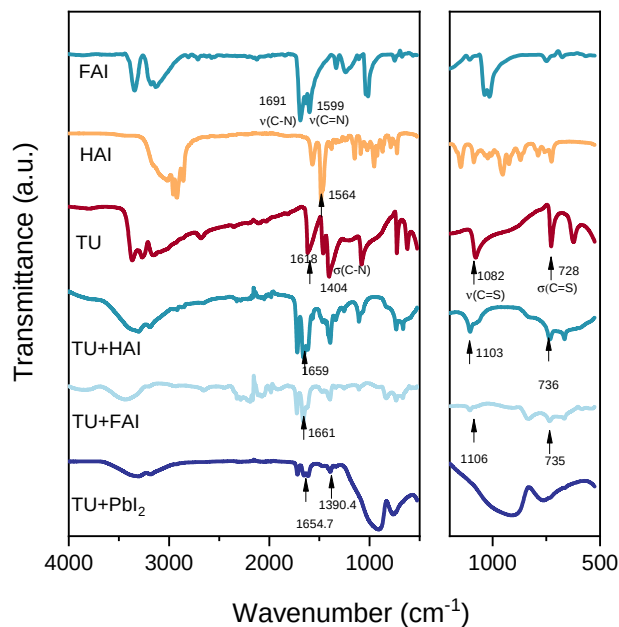


Figure 6-S5. FTIR spectra of the TU and that interacted with different perovskite components (FAI, HAI, and PbI₂), respectively.

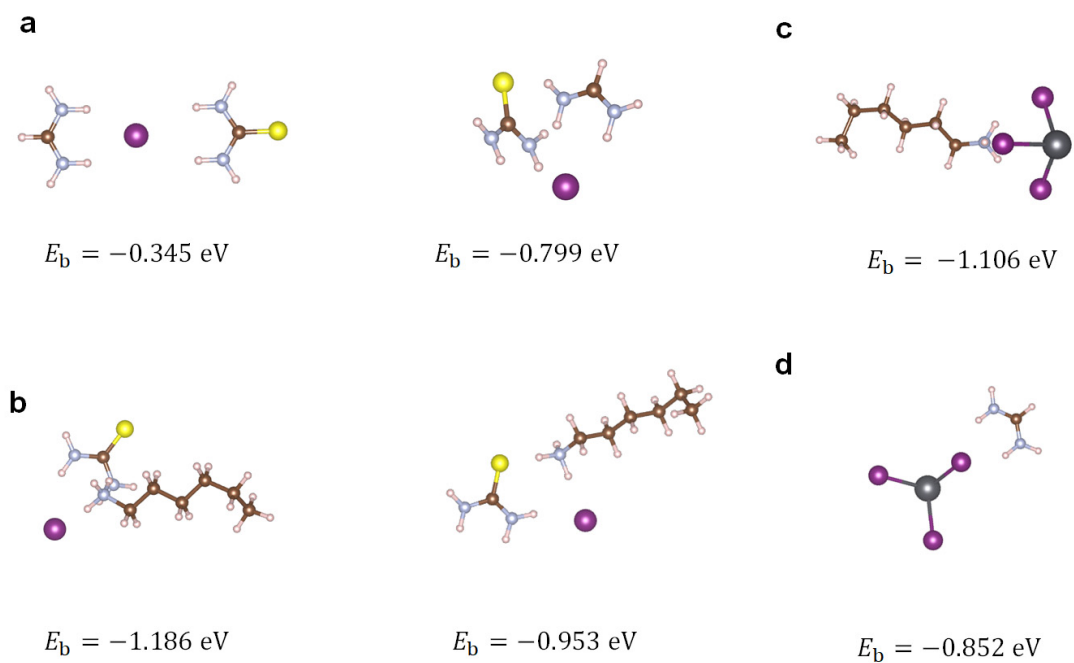


Figure 6-S6. FTIR spectra of the TU that interacted with different perovskite components **6**. Calculated possible molecular configurations between (a) FAI and TU, **b**) HAI and TU, **c**) PbI₂

and HAI, **d)** FAI and PbI_2 , respectively, the binding energy E_b was also calculated based on DFT.

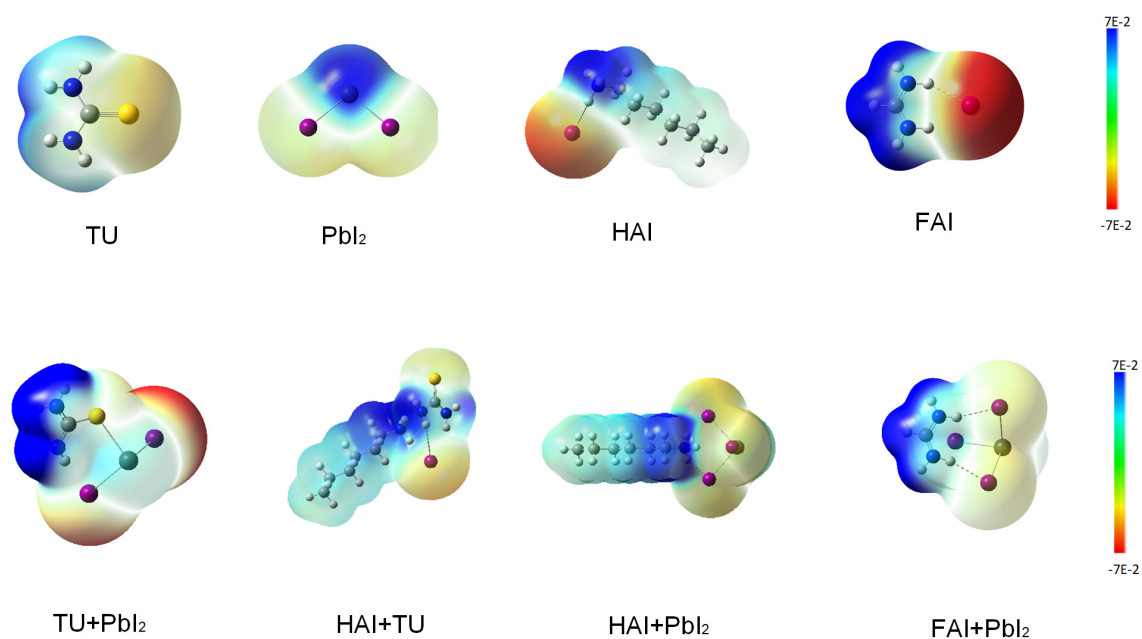


Figure 6-S7. Molecular structures and calculated electrostatic potential (ESP) mapping profiles of TU, PbI_2 , HAI, and FAI, respectively, and the interacted complexes between these components. The ESP color bar ranges from -0.07 to 0.07 for a clear comparison.

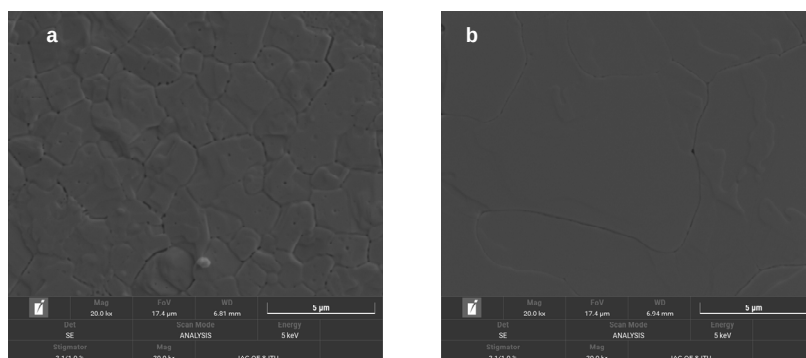


Figure 6-S8. **a)** Top-view scanning electron microscopy (SEM) images of the TTSD sample and **b)** target (SATD) 2D perovskite film, respectively.

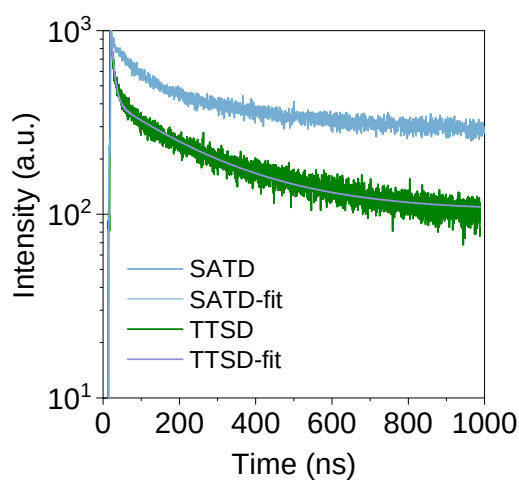


Figure 6-S9. TRPL of the TTSD and the SATD perovskite films and carrier lifetime is summarized in **Supplementary Table 1**.

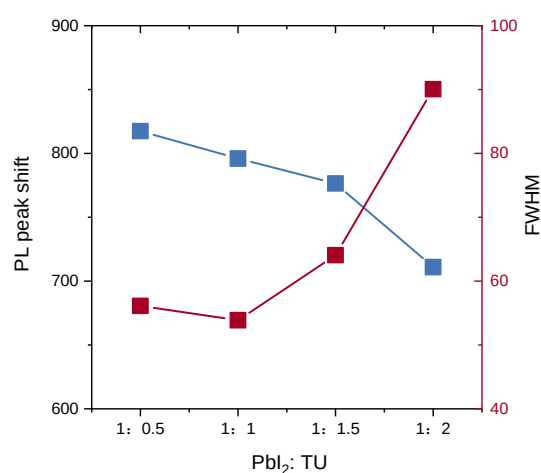


Figure 6-S10. Corresponding PL peak shift (excited from the front side) and FWHM variation of 2D FA perovskite films with different TU incorporated ratios, from PbI₂: TU: =1:0.5 to PbI₂: TU: =1:2, respectively.

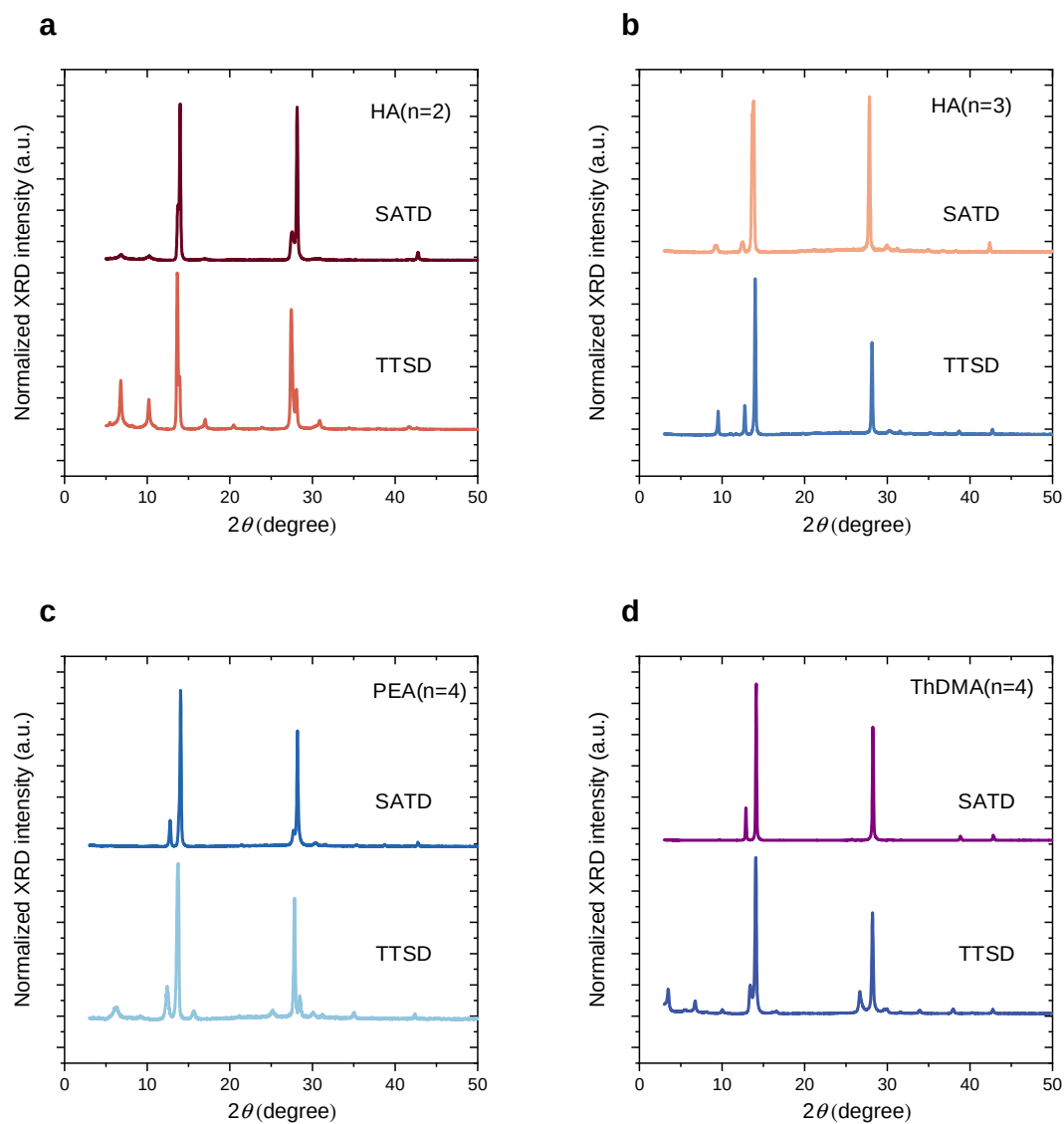


Figure 6-S11. XRD patterns of 2D FA perovskite films treated by TTSD and SATD strategy, respectively. **a)** HA ($n = 2$), **b)** HA ($n = 3$), **c)** PEA ($n = 4$), and **d)** ThDMA ($n = 4$).

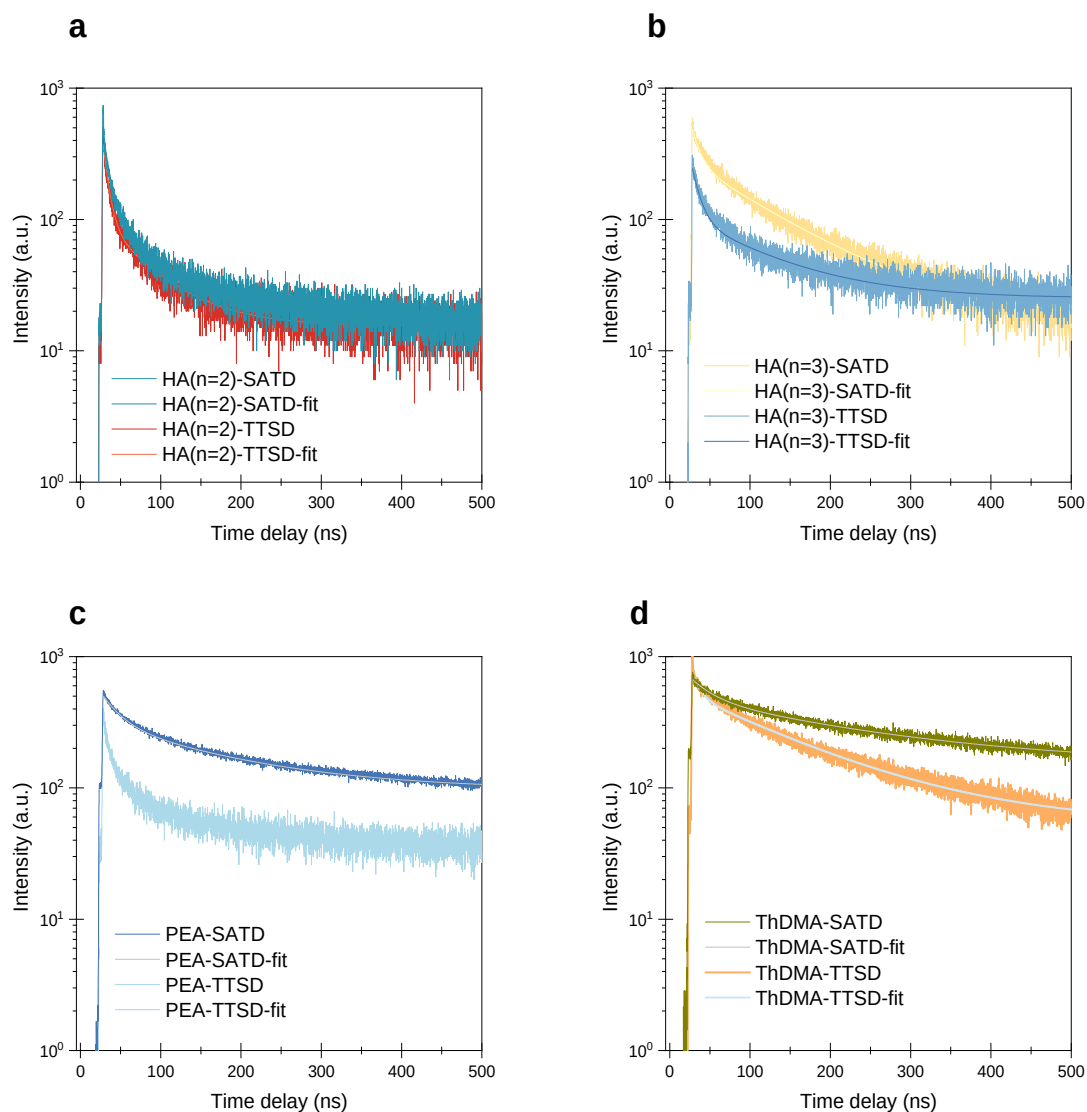


Figure 6-12. Comparison of TRPL of 2D FA perovskite films treated by TTSD and SATD strategy, respectively. **a)** HA ($n = 2$), and **b)** HA ($n = 3$), **c)** PEA ($n = 4$), **d)** ThDMA ($n = 4$). The charge carrier lifetime is summarized in **Table 6-S1**.

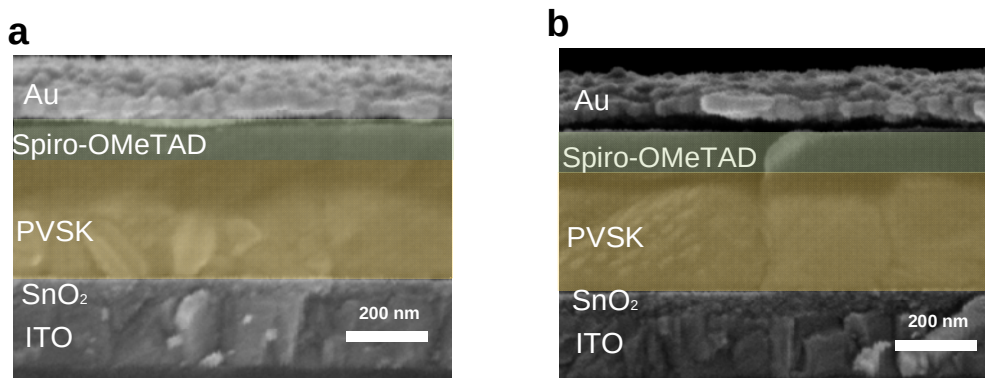


Figure 6-S13. Cross-section scanning electron microscopy (SEM) image of PSC fabricated based on **a)** the TTSD method and **b)** the target (SATD) method, respectively.

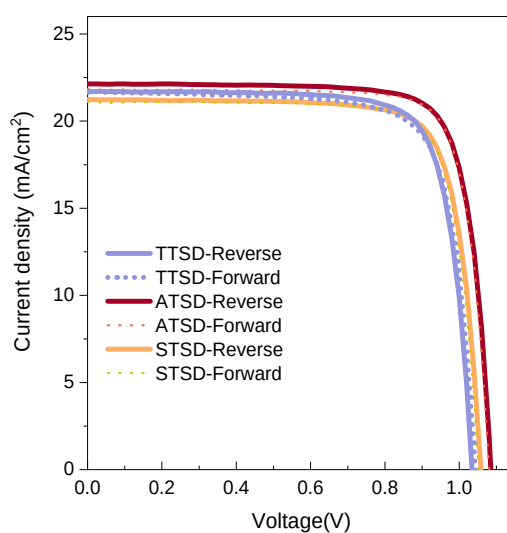


Figure 6-S14. J – V curves (under forward and reverse scanning direction) of the optimized FA-based 2D PSCs based on TTSD, ATSD, and STSD methods, respectively. The main parameters of the best devices are summarized in **Table 6-S2**.

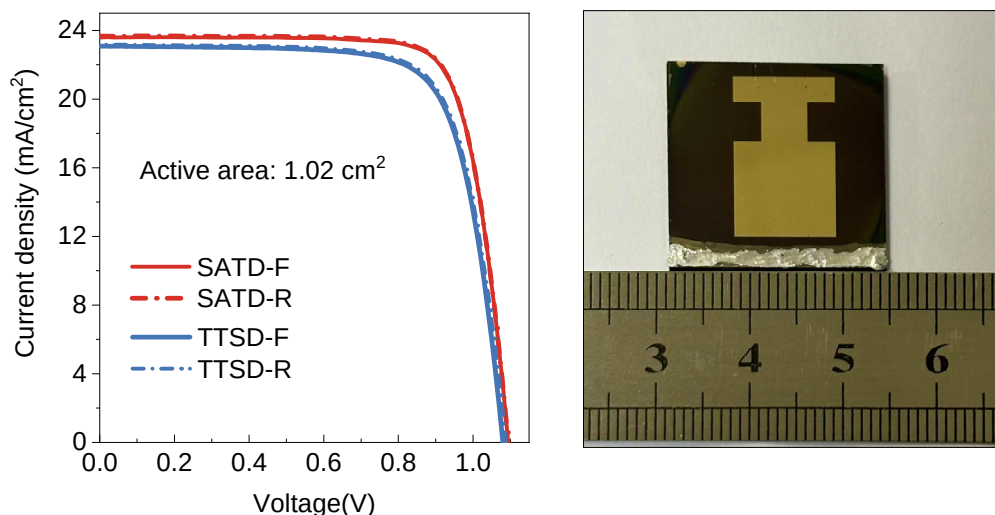
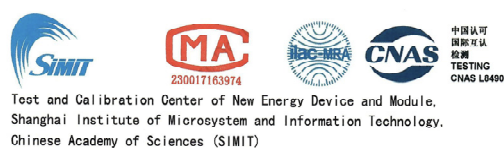


Figure 6-S15. (a) J – V curves (under forward and reverse scanning direction) of 2D FA-based PSCs with the active area of 1.02cm^2 , based on TTSD and SATD strategy, respectively. (b) and corresponding device image. The main parameters of the best devices are summarized in **Table 6-S3**.



Measurement Report

Report No. **24TR082701**

Client Name Shanghai Jiao Tong University
Client Address 800 Dongchuan Road, Minhang, Shanghai, China
Sample Perovskite solar cell
Manufacturer Shanghai Jiao Tong University
Measurement Date 27th August, 2024

Performed by: Qiang Shi *Qiang Shi* **Date:** 27/08/2024
Reviewed by: Wenjie Zhao *Wenjie Zhao* **Date:** 27/08/2024
Approved by: Yucheng Liu *Yucheng Liu* **Date:** 27/08/2024

Address: No.235 Chengbei Road, Jiading, Shanghai **Post Code:** 201800
E-mail: solarcell@mail.sim.ac.cn **Tel:** +86-021-69976905

The measurement report without signature and seal are not valid.
 This report shall not be reproduced, except in full, without the approval of SIMIT.

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Report No. 24TR082701

====Measurement Results====

	Forward Scan (Isc to Voc)	Reverse Scan (Voc to Isc)
Area	101.91 mm ²	
Isc	23.951 mA	23.955 mA
Voc	1.116 V	1.119 V
Pmax	19.869 mW	19.430 mW
Ipm	21.669 mA	21.341 mA
Vpm	0.917 V	0.910 V
FF	74.34 %	72.47 %
Eff	19.50 %	19.07 %

- Spectral Mismatch Factor SMM=0.9980.
- Designated illumination area defined by a thin mask was measured by measuring microscope.
- Test results listed in this measurement report refer exclusively to the mentioned measured sample.
- The results apply only at the time of the test, and do not imply future performance.

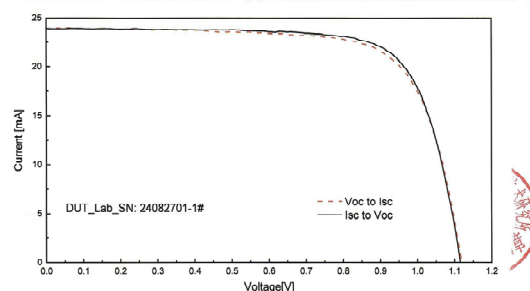


Fig.1 J-V curves of the measured sample

-----End of Report-----

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Figure 6-S16 (a) The PCE of the champion FA-based 2D PSCs certificated from Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Science (SIMIT).

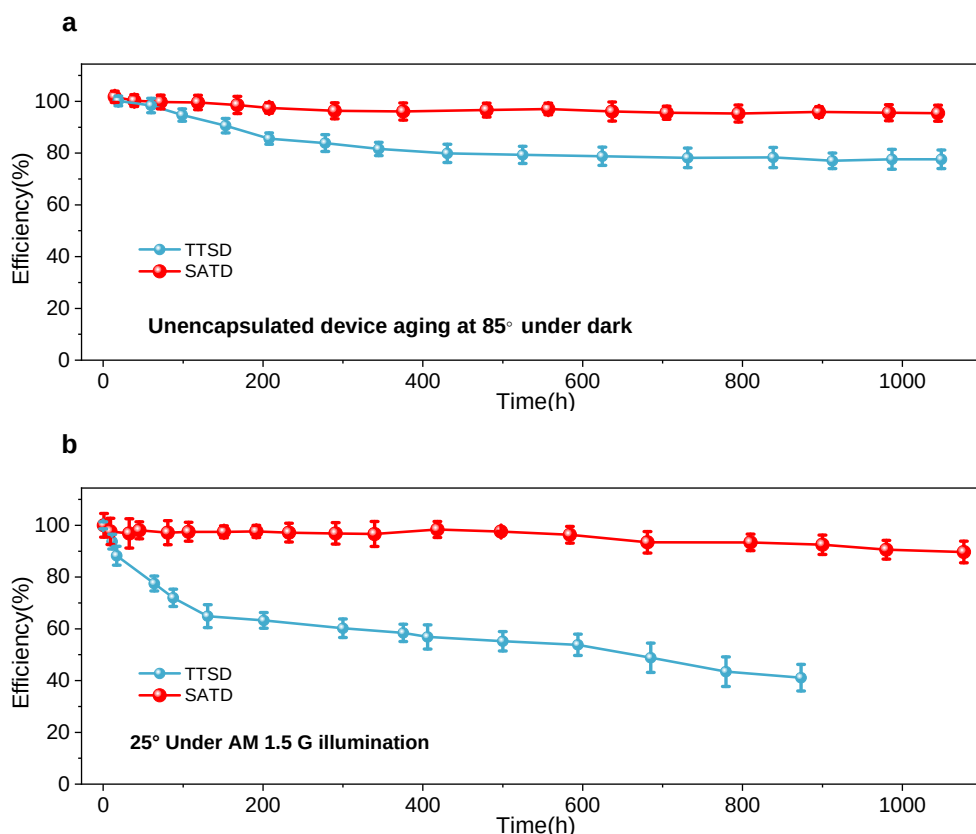


Figure 6-S17. The comparative stability of unencapsulated 2D PSCs employing TTSD and SATD strategy. **a)** Thermal endurance tested at a sustained temperature of 85 °C (dark condition, RH~30±5%), and **b)** photo-stability of the devices exposed under AM 1.5 G illumination at 25°C.

Table 6-S1. The charge carrier lifetime of the 2D perovskite film based on different spacer cations, such as ThDMA, PEAI, and HAI (n = 4) 2D perovskite films, and HA-based 2D perovskite films with different thicknesses of QWs prepared by the TTSD and SATD strategy.

2D PVS	TTSD		SATD	
	τ_1 [ns]	τ_2 [ns]	τ_1 [ns]	τ_2 [ns]
HA(n=3)	9.78	89.03	18.37	109.71
HA(n=2)	5.73	47.20	8.45	60.77
ThDMA(n=4)	18.65	144.83	26.35	212.01

PEA(n=4)	9.79	91.58	23.06	153.12
HA(n=4)	6.38	221.41	88.59	932.42

Table 6-S2. Main parameters of the best devices of various FA-based 2D perovskites films based on different methods, respectively.

	Direction	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Efficiency (%)
TTSD	Forward	1.043	21.67	76.60	17.32
	Reverse	1.034	21.69	78.40	17.59
ATSD	Forward	1.081	21.82	79.83	19.06
	Reverse	1.085	21.47	79.55	19.11
STSD	Forward	1.052	21.10	79.77	17.70
	Reverse	1.058	21.23	78.91	17.72
SATD	Forward	1.126	23.71	79.25	21.16
	Reverse	1.122	23.65	79.05	20.98

Table 6-S3. Summary of the representative low-n 2D PSCs with small areas (< 0.1 cm²).

Perovskites	n	PCE (%)	J_{sc} (mA/cm ²)	Method	Ref
RP type PSCs					
BA ₂ MA ₃ Pb ₄ I ₁₃	4	11.10	14.20	Co-solvents	[273]
BA ₂ MA ₃ Pb ₄ I ₁₃	4	12.52	16.76	Hot casting	[274]
BA ₂ MA ₃ Pb ₄ I ₁₃	4	13.68	19.94	Cesium doping	[275]
BA ₂ MA ₃ Pb ₄ I ₁₃	4	17.26	19.86	Annealing	[276]
BA ₂ MA ₃ Pb ₄ I ₁₃	4	16.25	16.75	Additives	[277]
BA ₂ MA ₃ Pb ₄ I ₁₃	4	16.48	18.67	Additives	[278]
BA ₂ MA ₃ Pb ₄ I ₁₃	4	17.10	17.56	Memory seeds	[279]
(BA) _{1.6} (MA) _{3.4} Pb ₄ I ₁₃	4	16.29	20.44	Nonpreheating	[280]
BEA ₂ MA ₃ Pb ₄ I ₁₃	4	16.10	20.63	Spacer cations	[281]
(3BBA) _{1.8} MA _{2.5} Pb ₃ I ₁₀	3	18.20	18.22	Hot casting	[282]

(ThMA) ₂ MA ₂ Pb ₃ I ₁₀	3	15.42	18.89	Additives	[283]
PEA ₂ FA ₃ Pb ₄ I ₁₃	4	11.30	14.70	Additives	[284]
PEA ₂ MA ₃ Pb ₄ I ₁₃	4	18.48	18.52	Additives	[285]
PEA ₂ MA ₃ Pb ₄ I ₁₃	4	17.03	18.47	Additives	[286]
FPEA ₂ MA ₃ Pb ₄ I ₁₃	4	15.20	13.70	Hydrothermal	[287]
PEA _{0.2} BA _{1.8} MA ₃ Pb ₄ I ₁₃	4	15.81	16.51	Post-treatment	[288]
(NpMA) ₂ MA ₃ Pb ₄ I ₁₃	4	17.25	20.89	Anti-solvents	[295]
ThFA ₂ MA ₂ Pb ₃ I ₁₀	3	16.72	20.17	Anti-solvents	[292]
F-PEA ₂ MA ₃ Pb ₄ I ₁₃	4	18.10	19.04	Additives	[296]
BA ₂ FA ₃ Pb ₄ I ₁₃	4	18.14	21.62	Additives	[305]
HA ₂ FA ₃ Pb ₄ I ₁₃	4	20.03	23.60	Additives	[387]
(BM)(BA)MA ₃ Pb ₄ I ₁₃	4	17.30	19.80	Ionic Liquid	[289]
AA ₂ MA ₃ Pb ₄ I ₁₃	4	18.42	18.57	Post annealing	[291]
BA ₂ FA ₂ Pb ₃ I ₁₀	3	15.4	15.12	Solvent vapor	[361]
(DFAz) ₂ (MA _{0.95} FA _{0.05}) ₃ Pb ₄ I ₁₃	4	19.85	22.28	Spacer cations	[357]
HA ₂ FA ₃ Pb ₄ I ₁₃	4	21.16	23.71	SATD	This work
DJ and ACI-type PSCs					
GAMA ₄ Pb ₄ I ₁₃	4	15.27	20.14	Additives	[293]
(GA)(MA) ₃ Pb ₃ I ₁₀	3	18.48	22.26	Additives	[294]
GA(MA) _n Pb _n I _{3n+1}	4	18.90	23.10	Interfacial	[388]
BDA ₂ MA ₃ Pb ₄ I ₁₃	4	14.38	19.90	Additives	[290]
(PDMA)(MA) ₃ Pb ₄ I ₁₃	4	15.81	21.10	Hot casting	[297]
(MAMP)MA ₃ Pb ₄ I ₁₃	4	16.53	17.97	Additives	[298]
(3AMP)(MA _{0.75} FA _{0.25}) ₃ Pb ₄ I ₁₃	4	18.67	19.51	Annealing	[301]
(3AMP)(MA _{0.75} FA _{0.25}) ₃ Pb ₄ I ₁	4	16.25	17.91	Additives	[302]
PDMA ₂ FA ₃ Pb ₄ I ₁₃	4	7.11	11.48	Space cations	[303]
PDAFA ₃ Pb ₄ I ₁₃	4	13.80	17.30	Additives	[251]
PDA _{0.9} PA _{0.2} FA ₃ Pb ₄ I ₁₃	4	16.00	17.60	Additives	[304]

Table 6-S4. Main parameters (obtained in the forward scanning and reverse scanning) of the best devices of various FA-based 2D perovskite films at the active area of 1.02cm².

	Direction	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	Efficiency (%)
TTSD	Forward	1.080	22.64	74.09	18.11
	Reverse	1.088	22.71	74.17	18.33

SATD	Forward	1.094	23.53	77.67	20.00
	Reverse	1.095	23.47	77.74	19.99

Table 6-S5. Summary of the representative 2D PSCs with large areas ($\geq 1\text{cm}^2$).

Perovskites	n ^a	Types	Areas (cm ²)	PCE (%)	Ref
BA ₂ MA ₃ Pb ₄ I ₁₃	4	RP	1	14.81	[389]
BA ₂ MA ₃ Pb ₄ I ₁₃	4	RP	16	11.13	[389]
HA ₂ FA ₃ Pb ₄ I ₁₃	4	RP	1	18.70	[1]
(4FPEA) ₂ (FA) ₄ Pb ₅ I ₁₆	5	RP	1	18.40	[214]
GAMA ₅ Pb ₅ I ₁₆	5	ACI	1	19.08	[390]
GAMA ₅ Pb ₅ I ₁₆	5	ACI	1.01	19.68	[391]
GAMA ₅ Pb ₅ I ₁₆	5	ACI	65.7	14.70	[391]
HA ₂ FA ₃ Pb ₄ I ₁₃	4	RP	1.02	20.00	This work

^a Designated layer thickness of QWs.

Chapter 7 Summary and Prospective

Solar power is an infinite energy source
provided by the universe.
Humanity needs to learn how to harness it
better to ensure our future survival.
----- Stephen Hawking

7.1 Summary

In this thesis, we briefly explored the origins of solar cells, tracing from the initial discoveries of the photovoltaic and photoelectric effects to the evolution of crystalline silicon and thin-film solar cells. The introduction of halide perovskites as a novel semiconductor material has transformed the landscape of high-performance photovoltaics over the past decade. However, the inherent instability of 3D PSs has impeded their commercialization. In contrast, dimensionally reduced perovskites, particularly two-dimensional (2D) PSCs, have demonstrated superior stability, enhanced tunability, and diverse optoelectronic properties, indicating substantial commercial potential. This thesis reviews the classic theories of solution nucleation and crystal growth, alongside recent advancements in nucleation management and crystal growth regulation strategies. The focus of this thesis is on controlling the crystallization process through spacer cation engineering, additive engineering, and process engineering strategies to optimize crystal orientation and improve film quality, thus enhancing the efficiency of 2D PSCs. Efforts to narrow the performance gap between 2D and 3D PSCs are also discussed, aiming to advance the practical application of 2D perovskite solar cells in renewable energy technology.

In Chapter 4, we developed a high-efficiency and stable FA-based 2D PSCs. Organic spacer cation engineering reduced micro-strain and lattice distortion, while SENA additives optimized crystallization kinetics, promoting vertical crystal growth and reducing non-radiative

recombination. This approach enhances photovoltaic performance and holds promise for advancing perovskite-based energy and optoelectronic technologies [1].

In Chapter 5, we developed a method to drive the orientation of low-n 2D perovskites using NH_4SCN additives. The synergistic effects of NH_4^{4+} and SCN^- retarded crystallization, inhibited heterogeneous nucleation and promoted a controlled templated growth via ionic exchange. Films treated with NH_4SCN showed improved crystallinity, vertical orientation, larger grain size, and fewer defects, which resulted in longer carrier lifetimes and reduced trap density. Such results offer valuable insights into the role of ionic additives to enhance FA-based 2D perovskite solar cells [2].

In Chapter 6, we demonstrated a de-templated crystallization strategy to produce high-quality 2D perovskite films. By establishing a stable intermediate state, this approach suppressed in-plane nucleation and controlled the crystallization process. The strategic deposition of FAI at high surface concentrations further enabled preferred out-of-plane crystallization. Additionally, this versatile method was effectively applied to create 2D perovskite with various organic spacer cations and layer numbers, offering a promising pathway for developing highly efficient and stable 2D PSCs.

In conclusion, we underscore the critical importance of a profound understanding of the structure and properties of 2D perovskite. Our comprehensive review summarized the latest advancements in 2D perovskites, including their fundamental structures, crystallization dynamics, optoelectronic characteristics, stability, and applications in solar cells. We particularly highlight the crystallization control techniques and orientation adjustment, which are vital for fabricating large-area 2D perovskite films and highly efficient solar cell assemblies.

7.2 Prospective

Although the exceptional performance and potential applications of 2D halide perovskites have been extensively recognized in the last decade, the rapidly expanding field of optoelectronic device research needs a more systematic comprehension of the material's structure, properties,

and its impact on device performance. Additionally, several key scientific and technological challenges merit further investigation to advance the development of 2D perovskite technology.

7.2.1 Tuning quantum wells in 2D perovskite for tandem solar cells

2D perovskite materials, due to their inherent quantum well structures, display greater design flexibility and performance advantages compared to their 3D perovskite. By modifying the thickness n and chemical composition of the organic interlayer, the 2D perovskites bandgap can be precisely tuned, which is crucial for optimizing the light absorption spectrum and adjusting the emission wavelengths. Strategic selection and design of components allow for the adjustment of bond angles and orbital overlap between metal and halide elements, thereby facilitating exact control over the bandgap. The tunability of the bandgap is not only critical for the efficiency of single junction 2D PSCs but also opens new possibilities for the design and performance of 2D/3D heterostructure PSCs and other composite structures such as 2D perovskite/silicon and all-perovskite tandem solar cells. By modulating the bandgap across these layered and multi-structured systems, it is possible to optimize their response to the solar spectrum, achieving broader spectral absorption and higher energy conversion efficiency.

7.2.2 Leveraging theory and simulation to explore new 2D perovskite

When selecting new spacer cations, theoretical simulations, and theoretic simulations, including size of cations, charge properties, and shapes, are very critical in the parameters of new spacer cations. Further, machine learning was proved to have high potential toward the discovery of novel 3D halide perovskites; it is meaningful to expand in the realm of 2D perovskite research.

However, relevant research into the diverse structures of 2D perovskites is still in its nascent stages, it is necessary to establish a comprehensive database of 2D halide perovskites to support future research and development. 2D metal halide perovskites exhibit a variety of unique physical properties, for example, nonlinear optics, anisotropic charge transport, spin-orbit coupling effects, and ferroelectricity, opening new possibilities for various applications. Using physical simulation software like COMSOL Multiphysics and Computer Simulation Technology (CST) allows us to investigate these characteristics, providing theoretical guidance

for experimental design to optimize material performance and reduce trial and error in experiments. This approach could effectively accelerate the translation of 2D perovskite from laboratory to industrial applications.

7.2.3 Fundamental photo physics research by in-situ characterization

The 2D perovskite films offer an interesting variety of complex compositions and unique physical properties, such as exciton-exciton annihilation, exciton-phonon coupling, carrier dynamics, and energy loss. Very little is known about the charge and energy transfer mechanisms between different layers. These properties pose challenges for spectroscopic characterization techniques, yet a deep understanding of exciton formation, charge separation, and their dynamic recombination in 2D perovskites is crucial for elucidating the fundamental mechanisms of their optoelectronic centers. Consequently, more extensive in situ and real-time spectroscopic studies are essential. These studies ensure precise, real-time monitoring of these rapidly occurring physical processes, enhancing material design and significantly improving photovoltaic performance. This knowledge is also pivotal for expanding applications to photodetectors, LEDs, FETs, and other photoelectric devices.

7.2.4 Advancing scalability of 2D perovskite for industrial applications

Most high-efficiency 2D PSCs reported in the literature are fabricated on small areas (<100 cm²) using spin-coating or other processing methods within inert environments. To enable large-scale applications, 2D perovskites should meet critical criteria, including homogeneous crystallization on large areas, high reproducibility, and air-processability. Recent advances in large-scale manufacturing processes, like blade coating, slot-die, and roll-to-roll fabrication methods, bring significant potential for the scaling of 2D perovskites and solar cells. However, precise control of the alignment and orientation of quantum wells, along with the distribution of mixed-n phases, remains a unique challenge in such dynamic, high-speed processes. To achieve uniformity over larger substrates requires rigorous control of the crystallization

kinetics. In-situ characterization techniques, such as in-situ UV-Vis absorption, XRD, and GIWAXS can provide immediate feedback on film quality, thus enabling immediate adjustments on key parameters like substrate temperature, solvent ratios, and deposition rates. Moreover, for large-scale integration of 2D PSCs into modules, appropriate encapsulation strategies should be considered to avoid encapsulation damage and prevent moisture and oxygen ingress. Thus, developing high-speed, precise manufacturing processes, in-situ characterizations, and appropriate encapsulation methods is crucial for scaling and commercialization of next-generation 2D PSCs and optoelectronic devices.

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