Recent Progress in Growth of Single-Crystal Perovskites for Photovoltaic Applications

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1. INTRODUCTION

Since 2009 organic−inorganic lead halide perovskites (LHPs) have been considered as visible-light sensitizers for photovoltaic (PV) devices.1−12 By building on pioneering advances in mesoscopic dye-sensitized solar cells, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has greatly increased from 3.8% to more than 25%, which surpassed the PCEs of the well-known high-efficiency thin-film solar cells based on copper−indium−gallium−arsenide or cadmium telluride.3 These significant improvements are attributed to breakthroughs in perovskite film formation, structural composition, and optimization of both electron and hole transport materials.4−10 Apart from the remarkable achievements of diverse perovskites in the photovoltaic area, LHPs also revealed great potential in many other fields such as field-effect transistors (FETs), light-emitting diodes (LEDs), and photodetectors.11,12 For example, the integration of prototypical MAPbX3 (X = Cl, Br, I) perovskite into ambipolar transistors resulted in room-temperature field-effect mobilities up to 4.7 and 1.5 cm2 V−1 s−1 with 105−106 on−off ratios and low turn-on voltages.13 LHPs are also promising for sensitive X-ray detection, which achieved four times higher sensitivity than α-Se X-ray detectors.14 Such unprecedented achievement in these fields could be ascribed to the intriguing optoelectronic properties of LHPs including high external quantum efficiency (EQE) over a wide absorption spectrum, high absorption coefficient, tunable optical band gap, low trap density, reduced charge carrier recombination rate, and long charge carrier diffusion length and lifetime.15−21 However, the vast majority of reported perovskite optoelectronic devices are based on polycrystalline thin films. It has been reported that the film fabrication method and film quality (surface uniformity, crystallinity, phase purity) play a critical role in device performance.22 Moreover, the polycrystalline perovskite films suffer from severe instabilities arising from morphological disorder at grain boundaries and surface degradation under ambient conditions, which can increase the recombination of the excited carriers.23,24 In turn, perovskite single crystals (SCs) have been demonstrated to surmount these challenges because of exceptional optoelectronic properties such as low trap density, low intrinsic carrier concentration, high mobility, and long diffusion length.15,25,26 Therefore, the utilization of high-quality perovskite SCs hold huge promise for high-performance optoelectronic devices for light harvesting and sensitive photodetection.1,12,27

In this review, we summarize the recent development in the growth of lead halide perovskite SCs focusing solely on PSCs.

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We first describe the structural features and unique properties of lead halide perovskite SCs for solar cell applications. In addition, the synthetic approaches for preparing SCs are discussed that signifies the impact of the growth method on the performance of SCs. Then, the stability of SCs is discussed and we describe how it is better than polycrystalline film counterparts. Finally, we provide the current challenges and future prospects for the further application of SCs in this emerging field.

2. ADVANTAGES OF LEAD-HALIDE PEROVSKITE SINGLE CRYSTALS

The crystal structure of perovskites is similar to that of mineral perovskite CaTiO₃, representing the general formula of cubic ABX₃. The perovskite is consisting of corner-sharing \([BX_6]\) octahedral with the A cation occupying the 12-fold coordination site formed in the middle of the cube of eight such octahedra, as shown in Figure 1.²⁸ In other words, A is a monovalent cation, B is a divalent metal cation (most commonly Pb²⁺, Sn²⁺), and X is a halide. The ideal perovskite structure is rarely possible because minerals also exist in distorted forms. The crystal structure evaluation is simplified by the Goldschmidt tolerance factor (\(T\)), which helps to determine the geometric stability and distortion of crystal structures in terms of the constituent ionic packing. It is the ratio of ionic radii of A, B, and X that the formula of \(T\) is as follows: \(T = (R_A + R_X)/\sqrt{2(R_B + R_X)}\), where \(R_A\), \(R_B\), and \(R_X\) are the ionic radii of A, B, and X, respectively. \(T = 1\) indicates the ideal perovskite structure with a cubic close-packed structure (Figure 1).

If the value of \(T\) deviates from 1, geometric strain and crystal distortions arise in the structure.²⁹ The symmetry of a perovskite also depends on the ionic radii of A, B, and X elements in the structure. The variable chemical composition and tuneable crystal structure impart various prominent properties for photovoltaic applications such as carrier lifetime, diffusion length, trap density, etc. The carrier lifetime and diffusion length are very important parameters to determine the recombination and transport kinetics in solar cells.³⁰ The carrier lifetime of SCs is calculated by eq 1

\[
\frac{1}{\tau} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}}
\]

where \(\tau\) is the carrier lifetime and \(\tau_r\) is the radiative lifetime that depends on the intrinsic property of the absorber layer.³¹ The \(\tau_{nr}\) is the nonradiative lifetime, which is most likely related to the trap density and can be controlled by the quality of the material. The carrier lifetime in perovskite SCs was determined using photoluminescence decay,¹⁷ transient absorption,³² transient photovoltaic (TPV) decay,¹⁷,³² and impedance spectroscopy (IS)¹⁷ methods. The SC perovskites provides the longer carrier lifetime as compared to the corresponding thin films due to lower trap density.³³ For example, the MAPbI₃ SCs gives eight times longer carrier life as compared to the MAPbI₃ film synthesized by the spin coating method.¹⁷,³⁴

The carrier lifetime also assists in determining the value of the carrier diffusion length (\(L_d\)). The carrier diffusion length can be determined by eq 2

\[
L_d = \sqrt{\frac{2D \tau}{\pi}}
\]

where \(D\) is the diffusion coefficient.
where $k$, $q$, and $T$ are the Boltzmann constant, element charge, and absolute temperature, respectively. From the above equation, it is stated that a longer carrier lifetime and higher mobility will lead to a longer carrier diffusion length, which is vital for high-efficiency solar cells applications. For example, MAPbI$_3$ SC exhibits a long diffusion length of 175 $\mu$m under 1 sun illumination, which is 10 times longer than the surface of passivated thin films. The composition of the SCs also has a significant impact on the carrier diffusion length. Huang et al. reported a diffusion length of 254 $\mu$m and a carrier lifetime of more than 100 $\mu$s for MA$_{0.45}$FA$_{0.55}$PbI$_3$ SCs at 1 sun illumination, which is found to be significantly higher than MAPbI$_3$ (Figure 2a). Moreover, the absence of grain boundaries in SCs can lead to a higher absorption coefficient and a longer diffusion length as compared to polycrystalline films. Thus, low charge recombination and superior carrier transport could be expected in SC-based PSCs.

The optical properties of the absorber layer play a critical role in defining the photocurrent in solar cells. The perovskite SCs shows extended light absorption and strong below-bandgap absorption than the polycrystalline counterparts. It was observed that MAPbX$_3$ (where X = I, Br, or Cl) SCs consist of outstanding optoelectronic properties such as ultralow defect density (below 10$^{11}$ cm$^{-3}$) and extremely long carrier lifetime (up to 15 $\mu$s) and diffusion length (above 175 $\mu$m) as compared to polycrystalline films. Liu et al. studied the optical properties of CH$_3$NH$_3$PbX$_3$ (X = Cl, Br, I) SCs prepared by a solution growth strategy. The authors observed that the substitution from Cl to Br or to I in the perovskite structure leads to dramatic changes in absorbance from 431 nm for Cl to 574 nm for Br and to 836 nm for I (Figure 2b). Wenger et al. studied the optoelectronic properties of CH$_3$NH$_3$PbBr$_3$ SCs prepared by the rapid growth route at high temperatures. In the SCs, the long-wavelength emission was observed due to reabsorption of the emitted light within the crystal, which is not possible in the case of thin films. The sharp red-shifted absorption edge was often observed due to the large optical thickness of the crystals. A sharp increase in the absorption at 560 nm was also observed, as shown in Figure 2c. Moreover, the optical properties of MAPbBr$_3$ SCs are found almost identical to those of polycrystalline perovskite, but in homogeneity in grain size and presence of grains boundaries limit device performance when measured under solar excitation intensities.

From the above-discussed literature on perovskite SCs, there are no doubts on their superior optoelectronic as than that of polycrystalline thin films. However, the PCE of SC-based PSCs is still lower than that found in thin-film PSCs. Further improvement in the PCE of PSCs is possible by thoroughly understanding the resistive and capacitive nature of perovskite SCs. Very recently, Kalam et al. have interpreted the resistance, capacitance, defect density, and activation energy levels in single crystal MAPbI$_3$ using impedance spectroscopy (IS). The activation energy and electronic trap density in MAPbI$_3$ SC were calculated as 0.53–0.54 eV and 0.96 × 10$^{10}$ cm$^{-3}$, respectively. Moreover, the authors found that the IS spectra of MAPbI$_3$ thin film-based PSCs and MAPbI$_3$ SCs differ from each other in the following ways:

(a) In film-based PSCs, the high-frequency resonance peak (10$^3$–10$^6$ Hz), which is mainly assigned to the recombination resistance and geometrical capacitance, is absent in the case of SC-based PSCs.

(b) In film-based PSCs, the temperature-controlled IS studies showed a high-frequency peak, which is independent of changes in temperature. However, a shift of low- and mid-frequency (10$^2$–10$^3$ Hz) spectra is observed with increasing the temperature. Consistent with the finding of mid-frequency (10$^2$–10$^3$ Hz) spectra of PSCs, MAPbI$_3$ SCs also showed similar temperature-dependent behavior.

In another study, Mahapatra et al. reported an IS study on the role of guanidinium (GUA) cation in ion transport in single-crystal GUA-MA$_{1-x}$PbI$_3$ perovskite compositions. The authors found that the incorporation of GUA into the MAPbI$_3$ structure decreases the activation energy for iodide ion migration as compared to pristine MAPbI$_3$ SC. This is due to the presence of a large-ionic-size GUA cation in the three-dimensional (3D) perovskite structure that induces a lattice enlargement, which perturbs the atomic interactions within the perovskite lattice (Figure 3). Consequently, a decrease in the activation energy and lattice enlargement in GUA-MA$_{1-x}$PbI$_3$ crystal causes a higher degree of hysteresis during current–voltage ($J–V$) measurements as compared to their single-crystal MAPbI$_3$ counterparts.

Mahapatra et al. also studied the effect of surface passivation of MAPbBr$_3$ SC by IS. Lead sulfate (PbSO$_4$) was used to passivate the surface of SCs. The IS as a function of temperature for control and PbSO$_4$-passivated SCs is studied. The direct signature of passivation on the resistance and capacitance of SCs is difficult to detect via other electrical techniques.
characterizations such as current−voltage or space-charge-limited current (SCLC) measurements. It was found that coordination between surface Pb$^{2+}$ and SO$_4^{2−}$ leads to an increase in the activation energy of surface mobile ions. The IS studies of SCs are helpful to understand the fundamental electrical properties of SCs, which will be crucial for designing the SC-based perovskite devices.

3. SINGLE-CRYSTAL GROWTH METHODS

The optoelectronic properties of SCs for photovoltaic applications are found to be depending on the growth methods. Thus, the adoption of a synthesis approach for the design of high-PCE PSCs is crucial. In this section, we summarize the recent advancement in the various growth and nucleation mechanisms adopted in the literature for perovskite SCs. The various methods such as antisolvent vapor-assisted crystallization (AVC),$^{17}$ inverse-temperature crystallization (ITC),$^{32}$ top-seeded solution growth (TSSG) method,$^{47}$ etc. are commonly reported in the literature. Although the bulk crystals obtained using these methods possess superior properties as compared to the polycrystalline thin films, these crystals were not found to be suitable for solar cell applications. As the thickness of these grown crystals is uncontrollable against the need for thickness in a few micrometers, i.e., in the range of carrier diffusion length for efficient PSCs.

3.1. Cavitation-Triggered Asymmetric Crystallization (CTAC). The method of cavitation-triggered asymmetric crystallization (CTAC) was first reported to prepare MAPbBr$_3$ monocrystalline thin films by Peng et al.$^{48}$ The focus of this method is to overcome the energy barrier required for heterogeneous nucleation by the use of ultrasound. The ultrasound promotes nucleation by forming continuous cycles of compression and rarefaction sound waves, which create and collapse cavities. These events render ultrahigh energy sufficient to overcome the nucleation barrier. Furthermore, film thinning, reduction in particle size, and ultimately asymmetric crystal growth are realized through the process of microjetting. This process is observed because the collapse of cavities is asymmetric near the surface, generating high-speed jets of the fluid. The schematic illustration of the complete process is given in Figure 4a. By carefully controlling the rate and time of crystal nucleation and growth, the moment of introduction of sonication and postsonication time, the crystals of thickness ranging from $\mu$m to 60 $\mu$m were obtained. It was shown that the PCE of the PSCs decreases with the increase in thickness. The reason for this was found that part of the perovskite crystals located away from the indium tin oxide (ITO) surface acts as a carrier transporter and not a light absorber. Moreover, higher thickness also leads to an increase in series resistance that eventually decreases the fill factor (FF) of PSCs. However, the advantages of this method are as follows: (i) it does not depend on the properties of the substrate and (ii) it does not affect the crystallinity of the film, although an external disturbance is provided. The maximum efficiency obtained for a solar cell is 6.53% having configuration FTO/TiO$_2$/MAPbBr$_3$/Au with a thickness of 1 $\mu$m.

3.2. Vapor Phase Epitaxial (VPE) Growth. Wang et al. utilized the method of vapor phase epitaxial (VPE) growth for synthesizing the monocrystalline thin films of CsPbBr$_3$, which has proven to be a powerful technique for III−V semiconductor fields.$^{49}$ In the case of halide perovskites, the chemical wetting of the surface becomes equally important along with lattice constants and symmetry, which are traditionally believed to be the prerequisites for this technique. Therefore, an alkali halide substrate, typically NaCl, was chosen for preparing CsPbBr$_3$. The as-prepared thin film showed excellent crystallinity and optoelectronic properties.

Figure 4. (a) Optical image and cross-sectional scanning electron microscopy (SEM) image of the MAPbBr$_3$ monocrystalline thin film along with the complete schematic illustration of the growth process. Reprinted with permission from ref 48. Copyright 2016 Wiley-VCH. (b) Graph illustrating lower nucleation barrier for the surface as compared to the solution volume. Reprinted with permission from ref 51. Copyright 2017 American Chemical Society. (c) Scheme for crystal growth on the aqueous solution surface. Reprinted with permission from ref 52. Copyright 2019 Wiley-VCH.
evidenced by spectral analysis. Additionally, the technique can produce films with thickness varying from micrometers to a few hundred nanometers. In other reports, Chen et al. used SrTiO3 as a substrate to produce CsPbBr3 thin films as it showed excellent lattice match and promoted heteroepitaxial growth. Conclusively, the two important factors of this method are high-temperature processing and epitaxial growth. Additionally, an excellent lattice match between the substrate and perovskite film for growth is needed, which can be considered as a demerit of this method, and to date, only all-inorganic halide perovskites are synthesized using this method.

3.3. Surface Tension-Assisted Growth. The surface tension-assisted growth method was first introduced by Zhumekenov et al., in which the central role of surface tension on nucleation and growth was discussed in detail. Both lead- and tin-based large-area (1 cm²) monocrystalline thin films with high aspect ratio were prepared using this method. The method is based on the observations that the higher the surface tension and accordingly the cohesion energy on the surface, the lower the nucleation barrier, and so, the nucleation rate on the surface is higher than that at the solution volume. A higher aspect ratio of ∼10³ was observed for these films due to the fact that the edge sides of the floating crystal on the surface grow faster than the bottom side. Moreover, the authors also proposed that high solution density (ρ) and surface tension coefficient (σ) helps in prolonging the crystal growth on the surface. Liu et al. prepared wafer-scale MAPbI3 SCs on the aqueous solution surface and fabricated a solar cell with a PCE of 5.9%. Owing to the use of an aqueous solution, the reaction time is reduced to 30 min, which is considerably lower than that of the methods that use organic solvents and take days or several hours for growth. The typical growth speed reported for this method is 3.0 cm·h⁻¹. As per the report, the crystal thickness is governed by the exposure area between cover glasses, solution height, and bottom temperature (Figure 4c).

3.4. Top-Down Method. The other approach to obtain SCs with controllable thickness for solar cell application is the top-down method. In this method, the bulk single crystal is initially prepared and then it is sliced down or etched to the desired thickness. Using this method, Liu et al. have prepared for the first time FAPbI3 monocrystalline wafers with thicknesses up to ∼100 μm. First, the seed crystal was prepared using an inverse-temperature crystallization method, and then, it was sliced down using a diamond wire slicing process to form thin wafers (Figure 5a). As the extension of this report, MAPbCl3, MAPbBr3, MAPbI3, MAPb(ClₓBr₁−ₓ)₃, and MAPb(BrᵧI₁−ᵧ)₃ thin wafers were reported using the same procedure. However, the thickness reduction obtained after this process was 100 μm and to go beyond this thickness is difficult. So, this method is not suitable for fabricating solar cells with high PCEs and rather they reported an array of photodetectors on a single piece of wafer. To overcome this issue, Lv et al. combined this slicing process with the dipping of the crystals in an etching solution, which is the mother liquor with excess solvent (Figure 5b). The thickness obtained in this way was reduced to ∼15 μm. The thinning mechanism is based on the dissolution–precipitation equilibrium. The control over the thickness is achieved by...
optimizing the immersion time, temperature, and concentration of the etching solution. Although this method enables large-area fabrication and there are no physical constraints for growth, the method is not much suitable for solar cell applications as the integration of these crystals with the transport layers is only through physical contact. So, this makes the device fabrication complex.

3.5. Space-Confin ed Method. The space-confined method is one of the most used methods for fabricating high-efficiency PSCs to date. Liu et al. used this method for preparing crystals with different thicknesses. The setup used to grow the SCs is shown in Figure 5c. Briefly, the crystal is grown between the two glass slides separated by a spacer, which eventually defines the resulting crystal thickness. The setup is called a geometry-defined dynamic-flow reaction system. Single crystals of MAPbI3 with thicknesses ranging from ~150 to ~1440 μm were obtained. Subsequently, Rao et al. used this method for growing a MAPbBr3 monocrystalline film with a thickness of 16 μm and fabricated a solar cell with a PCE of ~7% (FTO/TiO2/MAFPbBr3/Spiro-OMeTAD/Au). They also reported a 120 cm2 monocrystalline thin film with a thickness of 0.1–0.8 mm on an FTO substrate. Chen et al. extended this method for preparing MAPbCl3 SCs as well. Unlike the previous reports, they placed the two substrates vertically in a hot perovskite precursor solution and clipped them together to obtain the desired thickness. The capillary pressure drove the solution to the top side and also the temperature gradient generated at the top and bottom sides of the substrate provided a continuous flow of the solution for crystallization.

Apart from this, Huang et al. grew mixed-cation and mixed-halide perovskites (FAPbI3)0.85(MAPbBr3)0.15 on an ITO/NiO2 substrate. The crystallization was assisted by PDMS using a solvent evaporation crystallization method. The high porosity of PDMS facilitates the slow evaporation of the solvent during crystallization, which in turn governs the dimension of the crystal. On the other hand, Li et al. showed conversion of MAPbBr3 to MAPbBr3−xIx using a gas–solid exchange reaction. Another approach to this method is the seeded space-limited crystallization and printing approach. Gu et al. prepared CsPbBr3, MAPbCl3, MAPbI3, (BA)2PbBr4, and (BA)2(MA)2PbBr4 SCs using the general printing approach, as shown in Figure 5d. Yue et al. confined the seed crystal of MAPbI3 between two glass substrates to induce crystallization and produced SCs with thicknesses ~50 μm and fabricated a solar cell with the architecture of ITO/PEDOT:PSS/MAPbI3/PCBM/Ag. The layer of PCBM in chlorobenzene (2.3%) was incorporated at the perovskite/Ag interface, which increased significantly the photocurrent and PCE. The reason for the higher photocurrent can be attributed to improved exciton separation at the perovskite/PCBM interface and a lower level of exciton quenching at the Ag electrode. Therefore, interfacial engineering using PCBM buffer layers is critical in enhancing the performance of solar cells.

The best results were obtained by the hydrophobic interface-confined lateral crystal growth method. The hydrophobic nature of the substrate becomes important as the ion diffusion rate is governed by the interaction of the solvent and substrate when the gap is limited to a few tens of micrometers. Chen et al. proposed the use of ITO coated with hydrophobic PTAA as the substrate, and unlike the previous reports, no spacer was used in this method. Instead, they allowed the crystal to grow directly between the two hydrophobic substrates prefilled by the γ-butyrolactone (GBL) solvent. The entire mechanism and optical images of the crystal growth process are shown in Figure 6a. Using this approach, a remarkable PCE of ~17% for the best performing device was obtained. Notably, they passivated the crystal surface with an excess of MAI. To overcome the issue of MA loss at high temperatures, Alsalloum et al. engineered the solvent mixture and achieved the highest efficiency of 21.9% for SC-based PSCs. By mixing propylene carbonate with GBL, the temperature required for crystallization dropped significantly, and as a result, the MA loss is controlled (Figure 6b).

This method offers the advantage of integration of the PCs with the transport layers, and thus, it is widely used. However, the drawback of this method is that only limited crystallization methods such as inverse-temperature crystallization (ITC) are suitable. Moreover, as discussed above, the nature of the substrate becomes critically important to have lateral growth of crystals; otherwise, island growth with many small crystals is observed. Conclusively, as described above, each of the methods has its own advantages and disadvantages. However, the maximum efficiency of SC-PSC is realized using the space-confined method recently.
attributed to the synergy between the advantages of this method and solvent engineering.

4. SINGLE-CRYSTAL-BASED PSCS

The efficiency of SC-based PSCs depends on the optical properties, carrier dynamics, and recombination loss of SCs, which are directly correlated to the growth method of the crystals. In this chapter, we discuss the different types of SC-based PSCs and the effect of the growth method on the performance of PSCs. Table 1 lists a detailed summary of the SC-based PSCs prepared by different methods.

4.1. MAPbBr3 SC-Based PSCs. The MAPbBr3 SCs could be synthesized via various preparation routes such as antisolvent vapor-assisted crystallization, a classical cooling method, a top-seeded solution growth method, and inverse-temperature crystallization (ITC). In 2016, Peng et al. reported PSC devices based on MAPbBr3 SCs with controlled thickness by a cavitation-triggered asymmetric crystallization (CTAC) method and achieved a maximum PCE of 6.5%. Furthermore, the space-limited inverse-temperature crystallization growth method was used to prepare a laminar MAPbBr3 SC with a controllable thickness of 16 μm. The efficiency of MAPbBr3 SC-based PSCs increased to 7.11% from 6.5% with excellent stability due to having high mobility (23.7 cm² s⁻¹ V⁻¹) and low trap density (2.5 × 10¹⁰ cm⁻³). Still, the charge recombination loss remains a challenge in this type of SC-based PSCs. In another work, Peng et al. fabricated two different hole-transport-free types of devices with architectures of ITO/MAPbBr3/Au and FTO/TiO₂/MAPbBr3/Au via the cavitation-triggered asymmetric crystallization method. The main advantage of this method is to overcome the energy barrier required for heterogeneous nucleation by ultrasound that promotes nucleation by forming continuous cycles of compression and rarefaction sound waves, which create and collapse cavities. They reported ITO/MAPbBr3/Au and FTO/TiO₂/MAPbBr3/Au devices with efficiencies of 5.49 and 6.53%, respectively. Until now, the PCE of the MAPbBr3 SC-based PSCs is limited to 7.11%.

4.2. MAPbI₃ SC-Based PSCs. In 2017, Chen et al. reported the use of MAPbI₃ SC-based thin films for solar cell applications and narrowed down the band gap from the optimum value to meet the Shockley–Queisser efficiency limit. They adopted a hydrophobic interface-confinned lateral crystal growth method for SC growth directly on the hole-transport-layer covered substrates to extend the spectral response up to 820 nm without surrendering the device photovoltage and fill factor, which resulted in a PCE value of 17.8% with increased values of Jsc and FF (Figure 7a). In another work of the same group, a MAPbI₃ thin film of 20 μm was grown on a charge-selective contact using a solution space-limited inverse-temperature crystal growth method and reported a very high PCE value of 21% with an enhanced FF value of 84.3% (Figure 7b). In this method, postspin coating was beneficial for the proper attachment of SC with the

| crystal | preparation method | Jsc (mA cm⁻²) | Voc (V) | FF (%) | PCE (%) | ref |
|--------|-------------------|--------------|--------|--------|---------|-----|
| MAPbBr3 | space-confined method | 8.77 | 1.31 | 62 | 7.11 | 56 |
| ITO/MAPbBr3/Au | cavitation-triggered asymmetric crystallization method | 7.39 | 1.25 | 59 | 5.49 | 48 |
| FTO/TiO₂/perovskite/Au | cavitation-triggered asymmetric crystallization method | 6.96 | 1.36 | 69 | 6.53 | 48 |
| MAPbI₃ | space-confined method | 23.46 | 1.076 | 83.5 | 21.09 | 63 |
| MAPbI₃ | surface tension-assisted growth | 5.06 | 0.66 | 44 | 5.9 | 52 |
| MAPbI₃ | space-confined method | 21.9 | 1.08 | 78.6 | 17 | 25 |
| MAPbI₃ | space-confined method | 22.49 | 0.93 | 55.1 | 11.52 | 66 |
| MAPbI₃, inverted perovskite | space-confined method | 23.99 | 1.15 | 81.3 | 21.0 | 64 |
| (MA₀.₂FA₀.₈PbI₃)₁₀(CsPbBr₃)₉₀ | facile method | 21.7 | 0.71 | 70 | 17.17% | 66 |
| MAPbI₃ | top-down method | ~13.5 | ~1 | ~0.296 | ~4 | 54 |
| MAPbI₃ | space-confined method | 22.15 | 0.75 | 0.27 | 4.4 | 61 |

Figure 7. PCE and Jsc values of MAPbI₃ SCs produced by (a) hydrophobic interface-confinned lateral crystal growth method. Reprinted with permission from ref 25. Copyright 2017 Nature Publishing Group. (b) Solution space-limited inverse-temperature crystal growth method. Reprinted with permission from ref 63. Copyright 2019 American Chemical Society.
active layer for the improvement of cell efficiency. The authors set a new benchmark after reporting the high PCE value and reach the characteristics of polycrystalline PSCs. It is also observed that MAPbI3 SCs produced by the hydrophobic method is highly stable as compared to the SCs produced by the inverse-temperature crystal growth method. So, the growth method is not only affecting the PCE value of the solar cell, while its stability is also dependent on the crystal growth method. MAPbI3 SC-based PSCs not only result in high efficiency but also suffer from the charge collection problem on the surface due to the presence of defects created during the passivation process. To avoid this issue, prolong synthesis and high temperature are required for high-quality thin-film crystal growth.

In 2019, Liu et al. developed wafer-scale MAPbI3 SC thin films by the low-temperature solution method. The crystals prepared via this method have distinguished characteristics such as high crystallinity, broader light absorption, and a long carrier recombination lifetime. All of these properties help to maintain stability but not have much impact on the performance of MAPbI3 single crystals, which was 5.9%. Recently, the Alsalloum group devised a solvent engineering approach for surface passivation of single crystals to improve the crystalline quality on the surface. The MAPbI3 SC film was prepared by the space-confined method using an optimized solvent mixture for crystal growth at low temperatures (<90 °C). The fabricated MAPbI3 SC-based PSC shows an efficiency of 21.9% with a $V_{oc}$ value of 1.15 V, which represents the current highest reported values among the other MAPbI3-based devices (Figure 8).

In another work, Song et al. designed the lateral structure of the MAPbI3 SC film by a simple methylammonium iodide treatment procedure. Surface treatment using MAI at the crystal/Au anode interface not only renders better band alignment but also effectively passivates the surface. The PSC efficiency was reported to be 11.52% with a $J_{sc}$ of 22.49 mA cm$^{-2}$, $V_{oc}$ of 0.93 V, and FF of 55.1%. The efficiency of the SC-based PSC is not much high as compared to available reports in the literature; however, the stability is very high and no

Figure 8. Effect of low-temperature preparation method on PCE and $V_{oc}$ of SCs. Reprinted with permission from ref 64. Copyright 2020 American Chemical Society.

Figure 9. SCs grown separately followed by spin coating for the production of high-efficiency PSC. Reproduced with permission from ref 67. Copyright 2020 Springer Nature.
4.3. Mixed-Cation SC-Based PSCs. Compared with single-cation PSCs, the mixed-cation SC-based PSCs have numerous advantages, such as adjustable band gap, high efficiency, high crystallinity, large grain, low trap density, and good stability. However, the mixed-cation SC-based PSCs are very sensitive to air/moisture and have a significant impact on the PCE of PSCs. Thus, the problem of air instability has been solved by adopting a different approach to single-crystal growth and device fabrication. For example, perovskite SCs with the formula of (MA0.2FA0.8PbI3)1.0(CsPbBr3)0.05 were fabricated by a new engineered method in the presence of ambient air, as shown in Figure 9. In this method, two SCs (MAxFAyPbI3 and CsPbBr3) grown separately rather than solution mixing in the conventional method. Further, both the crystals were dissolved in a solution of N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) to form a precursor of SC perovskites that is used for film preparation by the spin coating process. The antisolvent method was used to prepare the perovskite film under 25 °C temperature in air with humidity <25%. The PSC with the optimum composition of (MA0.2FA0.8PbI3)1.0(CsPbBr3)0.05 resulted in 17.17% PCE with an enhanced grain size of ∼75% and a reduced trap density of ∼28% compared to the conventional method. It is proved that the growth and
fabrication method have also a significant impact on the PCE value of mixed-cation SC-based PSCs and also on the $J_{sc}$ (21.7 mA cm$^{-2}$), $V_{oc}$ (0.71 V), and FF (70) (Figure 9).

5. STABILITY OF PEROVSKITE SCs AND SC-BASED PSCs

PSC technology still suffers from low stability. The current research is focused on the improvement of device stability using additive engineering, different fabrication methods, and device structures. Generally, nanostructures and thin-film-based PSCs have high defect density and grain boundaries, which are responsible for low stability toward humidity and temperature. Moreover, grain boundaries in the perovskite film may act as recombination centers that accelerate the degradation of PSCs. Several studies have shown that the stability of perovskite SCs is much better than their thin-film counterparts due to fewer amounts of defects and the absence of grain boundaries.

For example, Chen et al. synthesized the (FAPbI$_3$)$_{0.9}$(MAPbBr$_3$)$_{0.05}$(CsPbBr$_3$)$_{0.05}$ SCs, which depicted the excellent light, thermal, and water–oxygen stability. These SCs exhibited 1000 and 10 000 h stability measured under light and water–oxygen, respectively. Intriguingly, the polycrystalline MAPbI$_3$(I$_{0.5}$Br$_{0.5}$) thin-film-based PSCs showed stability for almost 20 days when exposed to 55% humidity. On the other hand, MAPbI$_3$ SC-based PSCs are found to be stable with almost no significant reduction of their photovoltaic parameters when measured in open ambient conditions (at 23 °C and 30% humidity). Recently, Shin et al. studied the stability of the precursor solution for PSC: mixture (FAI + Pb$^+$) versus the synthetic FAPbI$_3$ crystal. Their results revealed that the synthetic FAPbI$_3$ crystal has better stability than the laboratory prepared precursor solution of PSC. They also reported the study on the comparison of fresh and aged samples. The resulting PSCs for fresh and aged perovskite samples were 18.86 and 18.94%, respectively (Figure 10a). However, the aged sample lost their stability in 4 weeks and efficiency due to change in the pH from basic to acidic by ageing, which prevents the formation of α-phase of FAPbI$_3$. Thus, the fresh SC-based PSCs show excellent stability and almost no degradation in the ambient air. Recently, Li et al. crystallized the thermodynamically stable MA$_{0.05}$FA$_{0.95}$PbI$_3$ SCs, which have maintained remarkable stability over 14 months in ambient air.

It was also found that the performance of PSCs is affected by the operating temperature. The electrical, charge transport, and optical properties of perovskites were found to be phase-dependent. The temperature-dependent phase transitions are usually observed in perovskites. Hence, the performance of the PSCs is largely depending on the device operating temperature. Generally, segregation occurs at higher temperatures and grain boundaries. It is reported that perovskite SCs have higher thermal stability than their polycrystalline counterparts due to the absence of grain boundaries. Kalam et al. reported that MAPbI$_3$ SCs can sustain up to 90 °C and the temperature-dependent powder X-ray diffraction (pXRD) analysis confirms the structural stability (Figure 10b). Therefore, SC-based PSCs are expected to show better thermostable optoelectronic performance.

On the other hand, it is well established that the migration of ionic defects (such as interstitials or vacancies) in a perovskite leads to the instability of PSCs and has also been proposed as a possible cause for the switchable photovoltaic or hysteresis effect. There are several primary ion migration paths between neighboring positions and several candidates to act as the migrating ions in the MAPbI$_3$ perovskite, i.e., (i) methylammonium (MA), (ii) iodide, and (iii) hydrogen (H+) ions. The H$^+$ ions play a considerably minor role in comparison with other ions due to their low concentration in PSCs. Moreover, Pb$^{2+}$ migration within the perovskite structure is hindered due to its high activation energy ($E_a$). Thus, MA and iodide ions are primary migrating ions that affect the stability and hysteresis of PSC devices due to their low activation energy to move through the perovskite structure (0.5–0.8 eV for MA and 0.2–0.7 eV for iodide ions). Generally, ion migration accelerates under illumination and it fastens the degradation of the cells. Yang et al. observed that $E_a$ of ion migration under illumination was declined to 0.104 eV from 0.228 eV in the dark conditions for Cs$_{0.05}$FA$_{0.81}$MA$_{0.14}$PbI$_2$$_{0.53}$Br$_{0.45}$ thin film-based solar cells (Figure 10c).

A similar trend was observed for perovskite SCs, and $E_a$ of ion migration under illumination was declined to 0.33 eV from 0.83 eV in the dark for MAPbI$_3$ SCs. Therefore, both single and polycrystalline perovskite have light-induced degradation. However, perovskite SCs show better stability under illumination due to slower ion migration (higher activation energy and lower vacancy defects) than their polycrystalline counterparts, which lead to highly stable PSCs. In addition, the ambient-fabrication of PSCs is also required for future commercialization. Wang et al. developed anti-solvent-free FAMA-perovskite-Cu:NIo composites crystals under full ambient air to boost the nucleation of homogeneous perovskite by improving the perovskite film quality with fewer grain boundaries and more orientated crystalline domains.

The addition of a small amount of Cu:NIo nanoparticles (size 10–15 nm) resulted in 20.7% PCE with better thermal and long-term air stability (97% of the initial PCE over 240 days) without any encapsulation, as shown in Figure 10d.e. The strong chemical bonding and interactions between Cu:NIo and perovskite molecules decreased the trap density and suppressed charge recombination. The MAPbI$_3$-Cl$_x$-Cu:NIo composite-based PSCs were also fabricated by Wang et al. The 3D crystal structure of MAPbI$_3$-Cl$_x$-Cu:NIo and its associated strong chemical bonding are shown in Figure 10f. The FTO/SnO$_2$/Al$_2$O$_3$/Cu:NIo/MAPbI$_3$-Cl$_x$-Cu:NIo/Spiro-OMeTAD/Au architecture was used in PSCs to achieve long-term stability (~94% of PCE and FF and 100% of the initial values of $J_{sc}$ and $V_{oc}$ over 280 days) with negligible hysteresis.

6. CHALLENGES AND FUTURE OUTLOOK

Over the decades, the improvement of solar cell efficiency is receiving great attention. For this, an ideal material should satisfy the functional requirement such as high efficiency, long-term stability, and low cost. While the applications of various perovskites in the field of solar cells have been widely explored, the use of SC perovskites for solar cells has remained in its infancy. In this review, we summarized the recent advancement of SC perovskites paying special attention to the growth method, properties, and stability of SCs and exemplified their application in solar cells. Although SC perovskite emerged as a new class of material owing their outstanding optoelectronic properties and low cost solution processing. The photovoltaic properties of the PSCs are correlated to the growth of crystals and the film fabrication methods. The highest efficiency and stability of the SC-based PSCs are realized with MAPbI$_3$ SCs prepared by the space-limited
inverse-temperature crystal growth method that can maintain their stability for 20 days when exposed to air. The MAPbI$_3$ SCs-based PSC is still suffering from charge collection problem. Additionally, the growth of SC thin films of MAPbI$_3$ is also a challenging task due to the intrinsic tetragonal shape of the crystal, which may not prefer the growth direction along the substrate owing to the difference in the solubilities of MAI and PbI$_2$. The geometry of the crystals can be controlled by controlling the concentration of MAI, by varying the concentration of the ligand, by alloying the cations, etc. Compared to single-cation PSCs, the mixed-cation SC-based PSCs have not attained very high efficiency but consist of several better properties such as adjustable band gap, high efficiency, high crystallinity, large grains, and low trap density. Still, the space-limited inverse-temperature crystal growth is one of the best methods for the growth of single-cation SC perovskites and a new engineered approach is suitable for mixed-cation SC-based PSCs, where crystals were grown separately and then mixed in solution followed by spin coating. However, the problem of charge collection in single-cation and air instability in the mixed-cation SC-based PSCs are still some critical challenges that need to be addressed to facilitate high efficiency with good stability for their practical applications. For that, the interface modification can be considered a way to improve the charge extraction. Moreover, this kind of interfacial engineering not only will help in energy level alignment but can also passivate the surface charge traps, which is considered a major limiting factor for affecting the optoelectronic properties. Apart from this, the issue of thickness and quality of single crystals should be solved simultaneously, and for that, some new additive materials need to be developed. Undoubtedly, it is still required to develop the SC-based PSCs with high moisture and thermal stability for photovoltaic applications.

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### Notes

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