Perovskite Single-Crystal Solar Cells: Advances and Challenges

Luisa De Marco,* Giuseppe Nasti, Antonio Abate,* and Aurora Rizzo

In just over a decade, the power conversion efficiency of metal-halide perovskite solar cells has increased from 3.9% to 25.5%, suggesting this technology might be ready for large-scale exploitation in industrial applications. Photovoltaic devices based on perovskite single crystals are emerging as a viable alternative to polycrystalline materials. Perovskite single crystals indeed possess lower trap state densities, higher carrier mobilities, and longer diffusion lengths, and potentially can achieve higher performance with respect to those fabricated with polycrystalline films, although their integration in a complete device needs particular attention and the use of specifically tailored growth techniques.

In this review, recent advances on single-crystal halide perovskites are reported. First, crystalline structure and fundamental properties of 3D perovskites are discussed, including the emerging mixed-anion cation perovskites, and then the most popular growth methods with a focus on techniques that enable the implementation in photovoltaic devices are presented. Architectures and materials used to produce lateral and vertical solar cells are further introduced and recent improvements in device design and fabrication are summarized. Finally, the strategies used to solve the still open challenge on these materials regarding stability under environmental conditions are critically discussed and the view on the opportunities offered by halide perovskites is reflected.

1. Introduction

Hybrid organic–inorganic perovskites (PVKs) are among the most promising semiconducting materials which have emerged in the last decade thanks to their outstanding optical and charge transport properties combined with mild processing and easily tunable physicochemical and structural properties.\(^{[1,2]}\) They have outperformed many rival materials in a wide variety of optoelectronic applications such as solar cells,\(^{[3]}\) light-emitting diodes (LEDs),\(^{[4]}\) field-effect transistors (FETs),\(^{[5]}\) lasers,\(^{[6]}\) and detectors (e.g., photodetectors, X-ray and γ-ray detectors).\(^{[7,8]}\)

Although these materials have been investigated since the 1970s,\(^{[9]}\) crystalline hybrid organic–inorganic perovskite thin films were first synthesized and used as optoelectronic materials by Mitzi and co-workers in 1995.\(^{[10]}\) Then, in 2009, the pioneering work of Miyasaka\(^{[11]}\) reported the use of CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)NH\(_3\)PbBr\(_3\) as absorbers in sensitized solar cells; MAPbX\(_3\) adsorbed onto a mesoporous TiO\(_2\) scaffold gave solar cells with a light-to-electricity conversion efficiency of approximately 3.8%.\(^{[12]}\) In these first photovoltaic devices, charge transport was assumed to take place through TiO\(_2\) after charge transfer from the sensitizer. A few years later, perovskite solar cells with approximately 9% efficiency were fabricated\(^{[13]}\) and a clear demonstration of efficient transport in PVK itself was provided when Snaith and co-workers\(^{[13]}\) replaced the TiO\(_2\) scaffold with insulating Al\(_2\)O\(_3\) and still produced a high-efficiency photovoltaic device. Later, the same group produced a planar device with only MAPbI\(_3\) as the light absorber and active layer, which achieved a conversion efficiency of 15%.\(^{[14]}\) This study confirmed the function of the PVKs as both light harvester and charge-generating layer and led to a simplification of the device design.

The latest progress has pushed the potential conversion efficiency and, a PCE > 25% was achieved using a mixed-cation and/or mixed-anion composition,\(^{[15–17]}\) which approaches the efficiency of the best single-junction GaAs cells (≈29%).\(^{[18]}\)

Here, in Section 1–3, we introduce crystal structures and synthetic methods of PVKs commonly used in photovoltaic devices. Then in Section 4 we present the most significant examples of implementation of single crystals in lateral and vertical photovoltaic devices. In Section 5, we address the stability issue of these materials, which is a very important challenge to overcome. Finally, we provide an overview on open issues and opportunities for future developments.
2. Crystal Structure

The name “perovskite” refers to the class of materials that possess the same type of crystal structure as calcium titanate (CaTiO$_3$). This mineral was first discovered by German mineralogist Gustav Rose in the Russian Urals mountains in 1839$^{[19]}$, and was named after the Russian mineral collector, Lev Alekseyevich von Perovski.

PVKs have a generic ABX$_3$ structure, where A is a monovalent cation, B is a divalent cation, and X is an anion (mainly a halogen). The crystal structure consists of a 3D corner-sharing (BX$_6$) building blocks where the sixfold-coordinated B cation has an octahedral geometry and A cation is located between these octahedra and is coordinated to 12 X anions, forming a cuboctahedron (Figure 1a)$^{[20]}$.

Replacing the A, B, and X sites with different elements results in a number of compositions, as long as the ionic radii of the elements satisfy the Goldschmidt tolerance factor ($t$) given by the following equation

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

where $R_A$, $R_B$, and $R_X$ are the ionic radii of A, B, and X, respectively.

Although the ideal perovskite with a cubic (Figure 1a) close-packed structure has a tolerance factor 0.9 $< t < 1$, the range of $t$ which leads to the formation of stable 3D structures is between 0.76 and 1.13$^{[21]}$.

In particular, the A cation must be small enough to fit into the voids of the octahedral units to maintain the structural integrity of the 3D lattice. Therefore, the maximum size of A cations, empirically determined by Goldschmidt’s tolerance factor, is equal to a radius of 2.6 Å. Thus, even some organic cations, larger than inorganic cations, can be inserted into the structure, leading to the formation of organic–inorganic hybrid PVK.

When the A cation is too small or the B cation is too large, the structure of the perovskite becomes distorted (0.7 $< t < 0.9$) and the crystal lattice changes from the high-symmetry cubic phase to a low-symmetry tetragonal or orthorhombic phase (Figure 1b, c)$^{[22]}$.

On the contrary, when an oversized A cation is included ($t > 1$), this turns the 3D structure into layered 2D$^{[23,24]}$ or linear 1D structures such as Ruddlesden–Popper PVKs$^{[25,26]}$ Dion–Jacobson PVKs, and the alternating-cation PVKs$^{[1,27]}$.

2.1. Single-Cation Halide Perovskite SCs

The most popular 3D hybrid PVKs consist of a methylammonium cation (MA; CH$_3$NH$_3^+$) at the A site, lead (Pb$^{2+}$) at the B site, and halides (Cl$^-$, Br$^-$, I$^-$) at the X site. Other common PVKs are obtained by using the organic formamidinium cation (FA; H$_2$NCHNH$_2^+$) or cesium (Cs$^+$) cation at the A site. Moreover, there are mixed cations/anions PVKs where the A is a combination of cations and/or X a combination of anions, as reported in Section 2.$^{[28,29]}$ Recently, mixed B-site perovskites are attracting attention due to their increased stability$^{[30]}$ and lead-free PVKs which include Sn$^{2+}$$^{[31]}$ or Ge$^{2+}$ instead of Pb$^{2+}$ at the B-site have been developed in order to reduce the toxicity of these semiconductors$^{[32]}$.

MAPb$_3$ has a cubic Pm$3m$ lattice with the highest symmetry crystal structure which undergoes sequential phase transitions by lowering the temperature: it goes from cubic to tetragonal phase (Figure 2a) below 42–57 °C and from tetragonal to orthorhombic phase at −113 °C.$^{[3]}$ These transitions may change the electronic band structure and, as a result, can affect the functionality of optoelectronic devices based on these materials.

The MA cations reorient inside the octahedral cage very quickly with a residence time of ~14 ps at room temperature.$^{[35]}$ It has been hypothesized that the dynamic reorientation of MA may stabilize the energetic charge carriers through the formation of a large polaron, which, in turn, enhances the lifetime of the hot carriers as well as the band-edge carriers.$^{[36]}$ On the other hand, this dynamic disorder highlights the labile nature of the weak bonds underlying the hybrid organic–inorganic PVKs that leads

![Figure 1. Sketch of the a) cubic, b) tetragonal, and c) orthorhombic CH$_3$NH$_3$PbI$_3$ perovskite crystal structures.](image-url)
to the degradation of MAPbI₃ under illumination or at high temperatures, likely related to the volatilization of the MA cations.

In 2014, FA-based perovskite was proposed as an alternative to overcome the drawbacks of the MAPbI₃ perovskite. FAPbI₃ in its black cubic phase has a relatively lower bandgap (see Figure 2d) of 1.48 eV compared to that of the MAPbI₃ (1.57 eV) and has advantageous photovoltaic properties, as its bandgap is closer to the Shockley–Queisser limit of 1.34 eV.

FAPbI₃ crystallizes into a nonperovskite hexagonal phase at room temperature that is converted to a pure cubic phase (Figure 2b) upon annealing at temperature above 150 °C. The cubic phase is maintained after cooling to room temperature. Spontaneous crystallization of the nonperovskite hexagonal phase is probably related to the larger ionic radius of the FA cation compared to that of the MA cation resulting in intrinsic lattice strain (tolerance factor ≈ 0.99), which induces the distortion of the (PbI₃)ₓ⁻ octahedra. The cubic phase is stable at room temperature thanks to the relatively high activation energy (approximately 0.6 eV) for reverse phase conversion to the hexagonal phase.[38] However, ambient humidity significantly enhances the transition to nonperovskite phase because water vapor can attack the FAPbI₃ surface, inducing the formation of defects that reduce the energy barrier for nucleation of the hexagonal nonperovskite phase.[39]

The charge-carrier lifetime and diffusion length in the FAPbI₃ thin film were found to be much longer than those in the MAPbI₃ film. Through solid-state NMR measurements, the reorientation rate of the FA cation in the lattice was found to be higher than that of the MA cation, enabling a superior charge-carrier stabilization capability mediated by polarons formation.[40]

Full inorganic CsPbI₃ perovskite has also been proposed with the purpose of replacing the volatile organic cations MA and FA.[41] Cs cation forms a strong chemical bond with the octahedral lattice (different from the weak hydrogen bonding of organic cations) exhibiting considerably high activation energy for the initiation of the thermal degradation (650 ± 90 kJ mol⁻¹) of CsPbI₃.[3] On the other hand, the small ionic radius of the Cs cation (Goldschmidt tolerance factor of 0.81) leads to the formation of a nonperovskite orthorhombic phase at room temperature. CsPbI₃ PVK cubic phase forms at temperatures higher than 300 °C, but is thermodynamically unstable under ambient conditions and tends to revert to the orthorhombic phase within minutes.[41] It has been reported that the cubic phase can be stabilized by reducing the crystal size with the use of additives (HI, zwitterion, or 2D perovskites).[42,43] The surface and strain energies were found to be the origin of the enhanced thermodynamic stability obtained with small grains size. However, the PCE of CsPbI₃ perovskite solar cells (PSCs) is limited (18%) due to its relatively high bandgap of ≈1.7 eV.[44]

The good performance of hybrid PVKs in solar cells stems from their superior optoelectronic properties. They are direct-bandgap semiconductors, with electronic structure mainly determined by the halides, with strong contribution of the halide p orbitals to the optical transition. The variation of the B cation can also slightly influence the band energies. In contrast, bandgaps are weakly dependent on the A organic cations because the 2p orbitals of carbon and nitrogen and the 1s orbitals of hydrogen do not contribute significantly to the density of states near to the Fermi level. Nevertheless, the A ammonium cations can affect the bandgap by distorting the (BX₆)²⁻ framework through hydrogen bonding and van der Waals interactions.

Iodide-based perovskites, with their bandgaps of ≈1.4–1.6 eV, are best suited for photovoltaic applications because they are close to the optimal value required for single-junction solar cells under the standard solar spectrum, according to the Shockley–Queisser model.

Moreover, they show broad optical absorption covering the visible range from 300 to 800 nm and high light absorption coefficient. These properties enable efficient light collection even
when the thickness of the active layer is reduced to a few hundreds of nanometers, ensuring the achievement of high photoconversion efficiency.

In addition, PVKs exhibit excellent transport properties.\(^\text{45}\) The main figures of merit for evaluating the electrical properties of a material are charge-carrier mobility (\(\mu\)) and diffusion length (\(L_D\)). The carrier mobility (\(\mu\)) defines how rapidly the carriers (electrons and holes) can move through a semiconductor under the presence of an applied electric field while the diffusion length (\(L_D\)) is the average distance traveled by a charge carrier between generation and recombination or trapping. Many investigations have been carried out and published until now, but there is no agreement on \(\mu\) and \(L_D\) values reported by different studies even on the same perovskite. The discrepancies are probably related to differences in the purity, morphology, or synthetic methods of hybrid perovskite polycrystalline films and single crystals (SCs) as well as different measurement techniques.\(^\text{46}\) However, it is generally accepted that perovskite single crystals have carrier diffusion length \(\approx 100\) times longer than polycrystalline thin films.\(^\text{21}\) This is related to the fact that trap densities are much higher in polycrystalline perovskite: grain boundary-free bulk single-crystal perovskites exhibit an extremely low trap density \((10^2–10^{12}\ \text{cm}^{-3})\), which is several orders of magnitude lower than that of polycrystalline films \((10^{15}–10^{19}\ \text{cm}^{-3})\).\(^\text{47,48}\)

In the latter, grain boundaries severely restrict charge-carrier mobilities because they scatter the carriers when transporting from grain to grain, and surface defects may lead to deep trap states. On the contrary, the long-range ordered pattern in perovskite single-crystal lattices considerably decreases charge carrier trapping, leading to minimal charge recombination loss in devices.\(^\text{49}\)

2.2. Mixed-Halide Perovskite SCs

The substitution or mixing of the halogen ions on the X sites impacts the perovskite electronic structure allowing for a convenient bandgap modulation over the entire vis to NIR spectrum.\(^\text{50,51}\)

One of the first approaches for synthesizing mixed-halide perovskite \((\text{CH}_3\text{NH}_3\text{PbBr}_{1–x}\text{Cl}_x)\) single crystals devised the solvothermal growth of stoichiometric PbBr\(_2\) and \([1–y] \text{CH}_3\text{NH}_3\text{Br} + y\text{CH}_3\text{NH}_3\text{Cl}]\) precursor in DMF. Thanks to the higher solubility of Cl in CH\(_3\)NH\(_3\)PbBr\(_3\) with respect to CH\(_3\)NH\(_3\)PbI\(_3\), the Cl could be included in the perovskite structure inducing a gradual contraction of the unit cell dimensions with increasing Cl content that induced a continuous widening of the SC bandgap.\(^\text{52}\)

The halogen doping of CH\(_3\)NH\(_3\)PbI\(_3\) with Br and CH\(_3\)NH\(_3\)PbBr\(_3\) with Cl was lately demonstrated via the inverse temperature crystallization method (ITC, see Section 3.2). The X-ray diffraction characterization evidenced a linear variation of the lattice constant of the CH\(_3\)NH\(_3\)PbI\(_{3–x}\)Br\(_x\) and CH\(_3\)NH\(_3\)PbBr\(_{3–x}\)Cl\(_x\) SC change linearly with the \(x, y\) values, which also reflected a variation in the bandgaps (Figure 3). Cubic to tetragonal phase transition occurred upon increasing the iodine content in CH\(_3\)NH\(_3\)PbI\(_{3–x}\)Br\(_x\).\(^\text{53}\)

A laser trapping crystallization approach was demonstrated to growth mixed of mixed chloride–bromide perovskites \((\text{MAPbBr}_{3–x}\text{Cl}_x)\) with a higher chloride content. To the scope unsaturated precursors solutions were irradiated with a NIR laser, which increased the local concentration of precursor complexes due to the generation of an optical potential; subsequently, the nucleation of SC is activated by the high concentration. By this method, brilliant mixed-halide SCs with emission spanning from blue to green could be obtained.\(^\text{54}\)

Mixed-halide composition was also exploited to modulate the hole density and to increase the resistivity of perovskite SCs. The Cl– alloying was developed to the scope, and CH\(_3\)NH\(_3\)PbBr\(_{3–x}\)Cl\(_x\) single crystals with different Cl\(_x\) percentages were grown by the ITC approach and used for gamma-ray spectroscopy.\(^\text{55}\)

Bidimensional mixed-halide Cu-based perovskite \((\text{CH}_3\text{NH}_3)_2\text{CuCl}_x\text{Br}_{2–x}\) SC were recently synthesized. These crystals are characterized by a strong orientation along the c-axis direction with preferable (00l) diffraction peaks and no grain boundaries. By increasing the Br content, the bandgaps can vary in the range 2.24–1.43 eV. The Cl-rich perovskites showed also reversible thermochromic behavior originating from structural changes.\(^\text{56}\)

It is worth underlining that the convenient bandgap tuning in accompanied with a detrimental halide segregation that occurs upon illumination, causing bandgap instability. It was recently discovered that such light-induced segregation is composition and strain dependent, and two regimes can be identified: strain-activated and intrinsic light-induced segregation regimes. In free-standing MAPb(I\(_{1–x}\)Br\(_x\)) light-induced halide segregation is strain-activated below 50% of Br and is intrinsic above 50%.\(^\text{57}\)

Finding a way to stabilize mixed-halide perovskite SCs is a highly desirable prospect to expedite the actual optoelectronic device implementation. Therefore, recent research focused on multiple-cation mixed-halide perovskite SCs, which are relatively more stable featuring suppressed ionic migration. In the following subsections, we provide an overview of the recent progresses on dual-cation and triple-cation perovskite SCs.

2.3. Dual-Cation Perovskite SCs

In general, in perovskite polycrystalline films, stabilization of the black \(O\)-phase of FAPbI\(_3\) was obtained by a partial replacement of FA with smaller cations, i.e., MA, Rb, Cs, and of I with Br, conceiving a plethora of mixed cation and halide compositions.\(^\text{17,58}\)

Accordingly, the inclusion of different cations or halogen in a single-crystal perovskite was mainly exploited to stabilize the black \(O\)-phase of FA-based perovskite.

Mixed cation and halide perovskite, \((\text{FAPbI})_{1–x}(\text{MAPbBr})_x\) growth by the ITC method were first used as a bench test to understand the thermodynamic and kinetic effects of MA\(^+\) and Br\(^–\) inclusion on the black FAPbI\(^{11}\) \(O\)-phase stabilization.

It was found that the incorporation of smaller MA\(^+\), with respect to the FA\(^+\), induces a contraction of the volume of the unit cell adjusting the effective Goldschmidt tolerance factor approaching 1, which corresponds to a perfect cubic perovskite structure. Moreover, the strong dipole and the fast rotation of MA\(^+\) were found to generate a higher degree of cation disorder that might enhance the contribution of entropy, thermodynamically stabilizing the \(O\)-phase. From the kinetic point of view, it was found that the Br\(^–\) incorporation induces an anticipated
nucleation, as corroborated by a faster perovskite growth reached upon increasing bromine content. As MAPbBr$_3$ adopts a cubic structure and has a lower surface energy, Br inclusion might favor the formation of the black phase of mixed cation/halide SC with high crystallinity and low defects. The best range to avoid MAPbBr$_3$/FAPbI$_3$ phase separation was also defined to be between $x = 0.10$ and 0.15. Centimeter scale (FAPbI$_3$)$_{1-x}$(MAPbBr$_3$)$_x$ SC with long carrier lifetime, 11.0 $\mu$s, were finally growth.

Meanwhile, the ITC method was used to growth perovskite SC with dual-cation and mixed iodide–bromide compositions: Cs$_x$FA$_{1-x}$PbI$_3$,Br$_y$ ($x = 0–0.1$, $y = 0–0.6$). The motivation was to prevent the transition from black phase to the yellow phase, by partially substituting the FA$^+$ cations with Cs$^+$ (up to 10%) and I$^-$ halide with Br$^-$ ions (up to 30%). The use of smaller cation and/or anions was found once again to decrease the Goldschmidt tolerance factor, eventually stabilizing the $\alpha$-phase. All the explored compositions, indeed, were found to generate phase-pure perovskite SC with cubic lattice and tunable bandgap with composition. The as-obtained SC featured enhanced phase stability upon shelf-life aging tests, excellent electronic quality (high-carrier mobility $\times$ lifetime product ($\mu\tau$) of up to $10^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$) and sensitive gamma detectivity.$^{[66]}$

Very recently, double-cation perovskite SCs were successfully integrated in an actual inverted solar cell device with a record power conversion efficiency of 22%.$^{[61]}$ The mixed-cation composition FA$_{0.6}$MA$_{0.4}$PbI$_3$ was found to further redshift the band-edge absorption with respect to FAPbI$_3$ polycrystalline perovskite of about 50 meV, and this allowed to reach very good performances, as discussed in Section 4.1.

A generalized approach was recently developed to stabilize the perovskite precursor’s solution and to intervene in the perovskite nucleation process, demonstrating the possibility to realize a facile compositional tuning of the perovskite SC.

Different polymer macromolecules with oxygen groups were tested: polyethylene glycol (PEG), polypropylene glycol (PPG), polyacrylic acid (PAA), and polyvinyl alcohol (PVA). The as-developed method relies on the coordination between the oxygen groups of the polymer and the lead polyhalide complex in the mother solutions, as schematized in Figure 4a. In the conventional ITC method, the solvents used to coordinate with Pb–solvent complexes at room temperature. Heating the system above the nucleation temperature, the perovskite nucleation occurs upon the dissociation of the precursor–solvent complexes, resulting in a rather fast nucleation and numerous nuclei with small size, i.e., $\approx 10$ nm. According to
the proposed mechanism, the oxygen groups of the polymer coordinate the Pb$^{2+}$ ions, partially replacing solvent molecule and iodide ions (see Figure 4a). Upon heating the system, the monomers formed by the iodoplumbates complexes with the polymer dissociates, decreasing the number of nuclei. Then the fewer nuclei formed by Pb–I$_6$ complexes can reach sizes in the range of 100–300 nm, then further growing to reach centimeter-sized perovskite SC.

Perovskite SC with different compositions, spanning from FAPbX$_3$ ($X = I, Br$), CsPbBr$_3$, and MAPbX$_3$ ($X = I, Br, Cl$) to mixed-halide MAPb$_{1-x}$Cl$_x$/MAPbBr$_{1-x}$Cl$_x$ ($0 \leq x \leq 3$) and mixed-organic cation MA$_y$FA$_{1-y}$PbX$_3$ ($X = I, Br$) ($0 \leq y \leq 1$) single crystals. Reproduced with permission. Copyright 2021, Nature Publishing Group.

A polydimethylsiloxane (PDMS)-assisted crystallization method was developed to growth double-cation and halide perovskite SC with composition (FAPbI$_{3-x}$MAPbBr$_x$)$_{0.85}$MAPbBr$_{0.15}$, which can be readily integrated in the actual solar cell devices. In this method, the precursors solution is injected in the channel formed by the PDMS stamp and the desired substrate. The high porosity of the PDMS stamp allows the solvent to slowly evaporate. The evaporation rate determines the dimensions of the single crystals, which could be tuned from 500 µm to 2 mm in lateral size and 10–50 µm in thickness.

As reported in Section 2.1, SCs with mixed metal compositional gradient from MAPbI$_3$ to MAPb$_{0.5}$Sn$_{0.5}$I$_3$ were efficiently growth via a solution-based lithography-assisted epitaxial-growth-
and-transfer method and readily integrated in an actual solar cell device architecture. Importantly, such a controlled vertical lead–tin gradient alloying induced the formation of a graded electronic bandgap, which resulted in higher carrier mobility and inhibits detrimental carrier recombination.\[64]\n
It is worth mentioning that recently alternative lead-free double halide perovskite SCs, such as Cs$_2$AgBiBr$_6$, Cs$_2$AgBiCl$_6$, Cs$_4$CdBi$_2$Cl$_{12}$, and Cs$_3$InBiCl$_6$ were proposed. These materials are stable and nontoxic; nonetheless, most of them are characterized by an indirect or direct forbidden bandgaps, whose values are also not optimal for photovoltaic applications.

2.4. Triple-Cation Perovskite SCs

It is only recently that triple-cation mixed-halide perovskite single crystals were successfully developed through the ITC approach. In the first approach, a series of single-crystal alloys of cesium containing mixed-cation/halide perovskites with different composition, i.e., (FAPbI$_3$)$_{1-x}$MAPbBr$_3$$_x$(CsPbBr$_3$)$_y$, were synthesized by partially replacing the MAPbBr$_3$ precursor with CsPbBr$_3$.\[69]\n
The authors found that the stability of the perovskite SC is dependent on the Br and Cs content, which needs to be accurately adjusted. A content of Cs $\geq$ 10% and/or Br15% introduced a relevant lattice stress or defects caused by the ionic size mismatch, which results in deleterious phase separation of the alloys. The optimized composition was found to be (FAPbI$_3$)$_{0.9}$(MAPbBr$_3$)$_{0.05}$(CsPbBr$_3$)$_{0.05}$, featuring a long carrier lifetime (16 $\mu$s), and excellent stability under ambient condition, light and thermal stresses.

Triple-cation mixed-halide SCs with inch size suppressing phase segregation were lately demonstrated. The method relies upon addition of the chemically reducing formic acid in the mother solution of precursors. This reducing reactant hinders the unwanted iodide oxidation and inhibits the deprotonation process that occurs upon heating the perovskite precursor’s solution, as schematized in Figure 5a.\[70]\n
The oxidation and deprotonation indeed were found to be responsible of a reduced supersaturation of ionic species, eventually lowering the crystallization rate. Moreover, the iodide oxidation into I$^-$ and I$_2$, which in turn reacts with I$^-$ to form I$_3^-$ (see Equation (2) in Figure 5a), results in a disproportion of the ionic precursor’s ratio likely resulting in the formation impure SCs, i.e., including $\delta$-phase domains of CsPbI$_3$ and FAPbI$_3$ (see Figure 5a,b,c). The presence of bigger I$^-$ ions in the solution can also favor the formation of hole-trapping sites in the forming SCs, which eventually degrade the optoelectronic quality of the material. In this frame, the inclusion of tiny amount (2%) of FAH was found to have a great impact on the quality of the resulting phase-pure perovskite SCs, with composition FA$_{0.9}$Cs$_{0.05}$MA$_{0.05}$PbI$_{2.7}$Br$_{0.3}$ (Figure 5b,c).

The quality of the as-obtained SC was corroborated by the excellent stability in ambient conditions and by the state-of-the-art charge transport properties (carrier lifetime of 8.74 $\pm$ 0.62 $\mu$s, mobility of 219 $\pm$ 18 cm$^2$ V$^{-1}$ s$^{-1}$, carrier diffusion distance of 71 $\pm$ 5 $\mu$m) and the possibility to build an actual integrated circuit photodetector with large responsivity (598.6 A W$^{-1}$), high photoconductive gain (1613.8), detectivity of $6.7 \times 10^{11}$ cm Hz$^{1/2}$ W$^{-1}$, and a fast response of 0.88 $\mu$s.

Figure 5. a) Mechanism of Iodide oxidation, reduction reaction, and deprotonation/protonation occurring in the growth of perovskite SC from FAMACs solution. b) Powder XRD patterns of ground powder from perovskite SC grown with and without the aid of formic acid. c) Photographs of the FAMACs SCs grown without formic acid for about 10 days and with 2% formic acid for about 27 days, respectively, evidencing suppressed phase segregation in SCs grown with formic acid. Reproduced with permission.\[70]\n
Copyright 2021, American Association for the Advancement of Science.
The same material was also exploited to fabricate high-performance X-ray detectors with a sensitivity as high as $(3.5 \pm 0.2) \times 10^6 \text{μC Gy}^{-1} \text{cm}^{-2}$ and very low detection limit of $42 \text{nGy s}^{-1}$, stable photocurrent, and dark current output.\[^{[71]}\]

### 3. Single-Crystal Synthesis Techniques Suitable for PV Applications

The optoelectronic properties of single-crystal perovskite can be affected by the growth technique. Several synthetic approaches have been developed in recent years and all of them rely on crystallization in a well-controlled precursor environment. Crystallization in solution is the most widely adopted strategy because of the strong temperature- and solvent-dependent solubility of perovskite that allows a fine control of supersaturation levels and crystal growth. In particular, when the solubility is reduced by altering the temperature or the concentration, nucleation of crystals seeds occurs in the supersaturated solution. The nucleation rate is usually governed by the degree of supersaturation, which must be carefully controlled to avoid an excess of nuclei that would result in small-size crystals.

In this section, we summarize the most significant growth methods adopted for single-crystal perovskite: 1) solution temperature slow cooling method, 2) ITC, and 3) antisolvent method.

#### 3.1. Solution Temperature Slow Cooling Method

The solubility of perovskite in a hydrohalic acid aqueous solution decreases with decreasing solution temperature. This basic principle was first exploited by Poglitsch and Weber more than 20 years ago to produce single-crystal perovskites.\[^{[72]}\] Briefly, cooling a concentrated aqueous solution of HX acid, Pb\(^2+\) and CH\(_3\)NH\(_3\)\(^+\) from \(\approx 100 \text{ °C}\) to room temperature, allows the formation of MAPbX\(_3\) (\(X = \text{Cl, Br, I}\)) crystals. Nevertheless, in the case of MAPbI\(_3\) at temperature below 40 °C, yellow needle-like crystals of (CH\(_3\)NH\(_3\))\(_4\)PbI\(_6\)·2H\(_2\)O appear, as by-product contamination.

To avoid this problem, Tao and co-workers introduced the so-called bottom-seeded solution growth (BSSG) method. They fixed a seed crystal at the bottom of the vessel on a rotating holder immersed in a saturated solution of MAPbI\(_3\) in HI (see Figure 6a) whose temperature was adjusted from 65 to 40 °C.\[^{[73]}\] After approximately 1 month, centimeter-sized single

![Figure 6](https://www.solar-rrl.com/)  
Figure 6. a,c) Schematic illustration of BSSG method and b,d) photographs of the single crystals obtained by this method. e) Schematic illustration of BSSG method and f) photographs of the single crystal obtained by this method. Reproduced with permission.\[^{[22]}\] Copyright 2016, The Royal Society of Chemistry.
crystals were obtained as shown in Figure 6b. In a similar way, Lian et al. fixed a small crystal at the end of a platinum wire as shown in Figure 6c, and, by carefully controlling the temperature from 100 to 57 °C, obtained a 12 mm × 12 mm × 7 mm-sized crystal (see Figure 6d) of MAPbI\(_3\) in 15 days.\(^{[74]}\)

Top-seeded solution growth (TSSG) method reported by Huang and co-workers exploits the same crystallization principle with the only difference that the seed crystal is placed on top of the solution.\(^{[75]}\) In this technique, a silicon (Si) substrate was immersed in the precursor solution to provide a low-energy barrier zone for nucleation and many small-sized MAPbI\(_3\) crystals were added to the solution in order to maintain supersaturation (see Figure 6e). A vertical temperature gradient between the bottom of the container heated at 75 °C and the lower temperature at the top of the vessel induced the nucleation of small crystals on Si substrate. Then, only one crystal was selected and left on the substrate. This crystal grew at a crystallization rate of 2 mm day\(^{-1}\) and reached a final size of 10 × 3.3 mm, as shown in Figure 6f. The advantage of TSSG method over BSSG is the shortened synthesis time.

### 3.2. ITC

The ITC method is based on an unusual retrograde solubility regime where the solubility decreases in specific organic solvents as the temperature increases. The molecules of the solvent establish stable complexes with perovskite precursors at low temperature, but at high temperature the bonding energy decreases and free perovskite building blocks get concentrated in the solution. Once the solution reaches supersaturation, nucleation appears at some point, followed by crystal growth. The growth process in this method is a balance of dissolution and precipitation, and the formation of high-quality halide perovskite single crystals strongly depends on temperature and type of solvent. This method was first developed by Bakr and co-workers.\(^{[76]}\) Briefly, 1 M precursors PbX\(_2\) and MAX (X = Br or I) were stirred in DMF at room temperature or GBL at 60 °C, respectively, and then filtered, transferred into a vial, and kept undisturbed in oil bath at 80 or 110 °C for Br or I, respectively. After few hours, 5 mm-sized MAPbBr\(_3\) and MAPbI\(_3\) crystals were obtained (Figure 7c,b, respectively).

Gamma-butyrolactone (GBL), dimethylformamide (DMF), and dimethylsulfoxide (DMSO) were found to be the most favorable solvent for MAPbI\(_3\), MAPbBr\(_3\), and MAPbCl\(_3\), respectively. In addition, full inorganic CsPbBr\(_3\) perovskite single crystals (Figure 7d) were grown at 90–110 °C from a mixture of DMSO, DMF, and cyclohexanol\(^{[77]}\) and FAPbI\(_3\) single crystals (Figure 7e) were obtained from GBL at 100 °C.\(^{[78]}\)

The most important advantage of this method, which makes it very popular and widely used, is that the crystallization shows an order of magnitude faster growth rate than other solution phase methods.

### 3.3. Antisolvent Vapor-Assisted Crystallization Method

Antisolvent vapor diffusion crystallization (AVC) is based on the different solubility of perovskite materials in different solvent
Generally, MAPbX$_3$ (X = Cl, Br, I) PVKs show high solubility in DMSO, DMF, and GBL, and very low solubility in chlorobenzene, benzene, diethyl ether, etc. The latter are called antisolvents. In this technique, the supersaturation condition is reached by mixing the perovskite precursors solution: as antisolvent vapors slowly diffuse into perovskite solution, its solubility is reduced, with the consequent formation of single crystals. The growth of perovskite in this approach is affected by several parameters, including the solvent and antisolvent volume ratio and the antisolvent diffusion rate.

The AVC method was first reported by Bakr and co-workers.$^{[47]}$ They synthesized high-quality, millimeter-sized MAPbBr$_3$ and MAPbI$_3$ single crystals using dichloromethane (DCM) as antisolvent. Briefly, precursors of MAPbBr$_3$ and MAPbI$_3$ were dissolved in DMF and GBL, respectively; the vessel containing the solution was placed into a larger container with DCM and the system was sealed and left undisturbed. As volatile antisolvent vapors reached the solution and mixed with perovskite solvents, crystals started to form and grew at room temperature.

Although bulk crystals synthesized by means of these techniques show superior properties compared to polycrystalline films, they are not always suitable for photovoltaic applications. In fact, their thickness reaches a few millimeters, which is beyond the carrier’s diffusion length. This leads to charge recombination within the devices and severely limits their performances.

To overcome this problem, several synthetic methods have been developed to obtain high aspect ratio perovskite single crystals with a thickness of few micrometers and a lateral dimension up to a few millimeters.

Two are the most common approaches: 1) slicing bulk crystals or 2) combining well-known solution synthesis strategies with a geometrically confined space tool.

### 3.3.1. Slicing Bulk Crystals (Top-Down Method)

A universal method to obtain thin perovskite single crystals consists in reducing the dimensions of bulk crystals by slicing or etching. The fabrication of inch-sized FAPbI$_3$ SC with a thickness of 100 μm was first reported by Liu et al.$^{[78]}$ They sliced a bulk single crystal into thin wafers using a diamond wire slicing machine (shown in Figure 8a–c) and observed that thin crystals had the same optical and electrical properties of the bulk, including carrier mobility and trap density. Subsequently, the same group applied this technique to different perovskites.

![Figure 8. a) The schematic illustration of the single-crystalline wafer slicing process. b) FAPbI$_3$ wafers sliced at the parallelogram natural crystallographic facets of a single-crystalline FAPbI$_3$, cross-sectional view. c) Single-crystalline FAPbI$_3$ wafers, top view. d) A schematic illustration for the preparation of a CH$_3$NH$_3$PbI$_3$ single-crystalline film by combined slicing and etching method. e) Cross-sectional view of a (100)-oriented CH$_3$NH$_3$PbI$_3$ single crystal after thickness reduction carried out by etching. (a–c) Reproduced with permission.$^{[78]}$ Copyright 2016, Wiley-VCH. (d,e) Reproduced with permission.$^{[80]}$ Copyright 2018, The Royal Society of Chemistry.](image-url)
and obtained thin wafers of MAPbI₃, MAPbBr₃, and MAPbCl₃ and of dual-halide perovskites, MAPb(BrₓI₁₋ₓ)₃ and MAPb(BrₓCl₁₋ₓ)₃.⁷⁹

However, the minimum thickness of the resulting crystals was around 100 μm. To further reduce the thickness, Lv et al. proposed a combined method using wire cutting, mechanical polishing, and wet etching. As shown in Figure 8d,e, wet etching was performed by dipping the sliced wafers crystals in the unsaturated precursors solution. The thinning mechanism was based on the dissolution–precipitation equilibrium and was controlled by optimizing the immersion time, temperature, and concentration of the etching solution. The thickness of the crystals obtained in this way was reduced to ≈15 μm.⁸⁰

This method is suitable for obtaining large-area SC perovskite, although they are not ideal for integration into a complete photovoltaic device. In fact, as they are not grown directly on the cell electrode, it is difficult to integrate them and create an optimal interface with electron and hole transport layers and transparent conductive substrates. In addition, their high thickness (a few microns) does not support very good performance due to saturation and less efficient charge transport.

3.3.2. Geometric Space-Constrained Strategies

Combining the ITC method and the space-confined crystallization in 2016, Liu’s group⁸¹ developed an ultrathin geometry-

![Figure 9](https://example.com/figure9.png)

Figure 9. A schematic illustration of the microreactor for the space-confined synthesis of SC wafer. a) Photograph of a single-crystal wafer. c) Scheme for growth of perovskite SC by clipped substrates method. d) Schematic illustrations of diffusion rate in the confined gaps using hydrophilic and hydrophobic substrates. e) Photographs of the diffusion process of MAPbI₃ precursor solution in the confined gaps using hydrophilic glass and hydrophobic PTAA-covered ITO substrates. f) Photographs of MAPbI₃ thin single crystal and g) MAPbBr₃ thin single crystal using the hydrophobic interface confined lateral growth method. (a,b) Reproduced with permission.⁸¹ Copyright 2016, Wiley-VCH. (c) Reproduced with permission.⁸² Copyright 2016, American Chemical Society. (d–g) Reproduced with permission.⁸³ Copyright 2017, Nature Publishing Group.
defined dynamic flow microreactor system in which two glass slides were separated by two spacers, thus confining crystal growth within the slit channel (as schematically shown Figure 9a). The microreactor was equipped with a peristaltic pump that improved mass transport and constantly provided fresh solution for crystal growth. The resulting single crystal of MAPbI\(_3\) possessed large lateral dimensions up to 1 cm and the thickness, determined by the gap between the two glass slides, as thin as 150 μm (Figure 9b).

The crystal thickness was further reduced by using two flat substrates clipped together and vertically immersed into the perovskite precursors solution as reported by Chen et al. (shown in Figure 9c).\(^{[82]}\) The gap size of the two substrates was tuned by changing the clamping force, and hence, the thickness of the resulting MAPbBr\(_3\) crystal was adjusted from 13 to 4.5 mm.\(^{[82]}\) Using this method, different types of perovskites have been successfully grown on various substrates, including quartz, ITO, Si, and PET, although the small lateral sizes (hundreds of micrometers) limited their application in devices.

An improvement of this method was reported by Huang’s group in 2017.\(^{[83]}\) They introduced a hydrophobic interface using the hole-transport material poly[bis(4-phenyl)(2,4,6-trimethyl-phenyl)amine] (PTAA). The ITO substrates were coated with PTAA, which effectively reduced the wettability of the growth substrates and lead to favorable diffusion of the precursors solution (see Figure 9d) resulting in the formation of millimeter-sized MAPbI\(_3\) and MAPbBr\(_3\) single crystals with the thickness of tens of micrometers.

Kong et al. combined an antisolvent vapor-assisted technique and a space-confinement strategy to crystallize MAPbI\(_3\) single crystals with millimeter size and thickness from tens of nanometers to micrometers. The best PCE achieved was 20.1% thanks to large grain size, uniform surface morphology, and high hole mobility.\(^{[84]}\)

Another method to achieve preferential growth in the lateral direction was reported by Zhumekenov et al.\(^{[85]}\) They demonstrated a surface tension-controlled ITC technique that exploits surface tension to direct the growth of monocrystalline perovskites on the solution surface, resulting in cm-sized crystals with thicknesses on the order of ~5–10 μm.

These different techniques have been profitably employed to produce crystals with appropriate sizes for implementation in photovoltaic devices, as we discuss in Section 4.

4. Single-Crystal Perovskite Solar Cells Architectures and Performances

The structural configuration of the solar cell has a profound impact on the overall performances of the devices. A proper choice of the cell geometry should be done in order to mitigate the defects of the perovskite absorber and optimize the transport and collection of the charges to the selective contacts. The two main categories of devices can be divided into vertical (Figure 10a) and lateral (Figure 10b) structures. The vertical structure is the most adopted in the literature and is obtained by sequentially stacking the different layers of the device. In this configuration, a transparent electrode is needed in order to ensure the access of the light toward the perovskite absorber.

The most used transparent electrodes are the well-known ITO and FTO oxides that have the huge disadvantage of representing a big portion of the PSC cost.\(^{[86,87]}\) Moreover, the transparent oxides limit the theoretical external quantum efficiency (EQE) of the device to a value of about 90% caused by intrinsic losses due to partial light absorption.\(^{[87]}\) In the lateral configuration, both the positive and negative electrodes are placed on the same side of the perovskite crystal and, therefore, one side of the devices is free from obstructions and can be used to collect the sun light. The main advantage of this structure is the absence of the expensive transparent electrodes reducing the overall cost and increasing, theoretically, the maximum achievable efficiencies.\(^{[88,89]}\) Another advantage is that the thickness of the perovskite does not need to be strictly controlled as the charges separation and transport happen along the plane of the device and is only controlled by the geometry of the electrodes. The drawback of this configuration is that, after the absorption of a photon close to the surface of the device, the photogenerated charges need to travel longer distances, in the order of few tens of μm, and therefore the charge carriers diffusion lengths must be long enough to ensure their collection by the electrodes avoiding recombination.\(^{[89]}\) In the following sections we will describe separately the state-of-art for both the vertical and the lateral device configurations, describing the overall effect of the photovoltaic parameters of the perovskite SC on the device performances.

4.1. Vertical Devices

One of the first attempts to make a working device using a SC perovskite is reported in the study of Peng et al. and was published only few years ago in 2016.\(^{[92]}\) In their work they used a technique called cavitation-triggered asymmetrical crystallization (CTAC) in order to induce the crystallization of a MAPbBr\(_3\) perovskite SC on the surface of an ITO-coated substrate. As suggested by the name, this technique uses short ultrasonic pulses in order to trigger a heterogeneous crystallization providing, mechanically, the energy needed to overcome the nucleation barrier. By means of antisolvent vapor diffusion, a mild supersaturation level was reached in the solution and the formation of cavitating bubbles in the precursor solution acted as a seed for the growth of the monocrystal. The advantage of this
technique is the formation of a SC perovskite directly on the surface of the substrate while the most common technique used for the growth of SC, at that time, usually led to the formation of self-standing crystals. The best device prepared using this technique showed an efficiency of 6.53% and a remarkable high $V_{OC}$ of 1.36 V for a 1.0 mm-thick crystal in an HTL-free configuration (i.e., FTO/TiO$_2$/MAPbBr$_3$/Au). The very high value for the $V_{OC}$ is related to the p–n junction formed between the MAPbBr$_3$ and the TiO$_2$.

In 2017, Rao et al. developed a method to produce 16 μm-thick perovskite SC with a size of 6 × 8 mm. The technique was named SLITC, standing for space-limited inverse temperature crystallization, which is the method used to fabricate the most efficient SC PSC up to date.[93,94] Using two glass slides to spatially confine the solution, and consequently space available for the crystal, they induced the seeding and growth of the perovskite by locally heating one of the substrates. The so-grown SC showed excellent optoelectronic properties as a low trap density ($2.5 \times 10^{10}$ cm$^{-3}$) and high mobility (23.7 cm$^2$/V·s). The best efficiency achieved using this method, for a vertical device with an FTO/TiO$_2$/PVK/HTM/Au stacking, was 7.11% with a 93% efficiency maintenance after 1000 h of aging. They measured, using TRPL, the photocarrier dynamics of the absorber in three different configurations of the cell: 1) FTO/PVK, 2) FTO/TiO$_2$/PVK, and 3) FTO/TiO$_2$/PVK/HTM. Interestingly, the charge extraction by illumination from the FTO side resulted highly accelerated compared to the charge extraction from the PVK side. This is related to the built-in potential formed on the FTO/PVK interface. As expected the addition of the extracting layers improved the decay time constants going from 122 ns for case (1), to 24 ns for case (2) to a remarkable 0.42 ns for case (3). This behavior was clearly reflected on the photovoltaic performances of the three devices. Using TPV and TPC the authors also calculated the charge diffusion length, $L_d$, going from 27 μm for case (1), to 56 μm for case (2) and 60 μm for case (3) (see Figure 11).

A similar approach to grow the SC perovskite for a vertical device was used by Zhao et al. that used a PTFE spacer to grow the crystal exploiting capillary forces to drag the precursor solution between the two surfaces. The overall performances of the cell, using an n–i–p configuration FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$/Spiro-OMeTAD/Ag, were remarkable with a $V_{OC}$ of 0.649 V, 22 mA cm$^{-2}$, 57% FF, and 8.22% efficiency. In their work they measured and compared the average carrier lifetime for both SC and polycrystalline perovskite. They found out that the SC had 25.5 times longer lifetime compared to the PC, going from 8.1 to 206 ns, confirming that the grain boundaries strongly deteriorate the excitons lifetime and increase the transport resistance and the bimolecular recombination.[95]

A big leap forward in the performance of SC PSC occurred in 2017 with the work of Chen et al. They grew MAPbI$_3$ single crystal through the SLITC method directly between two PTAA-covered substrates, finding that the hydrophobicity of PTAA plays a crucial role to achieve a lateral and continuous growth of the single crystal, which results in a larger area up to 10 × 10 mm$^2$.

Tuning the single crystal thickness, they also proved how it was possible to benefit of the much higher charge diffusion length in combination with the higher thickness of perovskite SC to exploit below-bandgap indirect transition and so increase the absorption spectrum in comparison to their polycrystalline analogous (Figure 12a). Because indirect bandgap photon absorption has several order of magnitude smaller probability to occur, it is necessary to increase of the same order of magnitude the thickness of the absorbing layer in order to make it a significative phenomenon. As shown in Figure 12b, theoretical calculations suggest that going from 0.5 to 200 μm-thick perovskites, the theoretical cutoff of the absorption spectrum shows a clear red shift toward lower bandgaps. The lower bandgap has also as a direct consequence the increase in the theoretical maximum photocurrent ($J_{SC}$) that the device can generate but, on the other side, a decrease in the maximum $V_{OC}$ that it can produce (see the plots in Figure 12c). Using a ITO/PTAA/PVK/PCBM/C60/BCP/Cu configuration they prepared working devices showing an optimal thickness for the perovskite layer of about 10 μm. The best working devices showed a PCE of 17.8%, $J_{SC}$ of 21 mA cm$^{-2}$, $V_{OC}$ of 1.08 V, and FF of 79%.[83]

In 2019, Chen et al. obtained even better performances for the same device architecture of ITO/PTAA/PVK/C60/BCP/Cu with a perovskite absorbing layer 20 μm thick, with the best device reaching 21.09% with an ultra-high FF of 83.5%, 1.076 $V_{OC}$, and 23.45 $J_{SC}$. The dramatic improvement of the FF was obtained changing the atmosphere during SC processing from air to N$_2$. This, suppressed the formation of I$_3^-$ hole traps on the crystal.

Figure 11. TRPL with illumination from a) PVK side and b) FTO side, c,d) band configuration and TPV/TPC (plot on the right) for SLITC vertical device. Reproduced with permission.[93] Copyright 2017, The Royal Society of Chemistry.
surface, increasing the crystal quality and carrier diffusion length reducing non-radiative recombination loss.\(^{[96]}\)

The same group, with the work of Allsalloum et al., also optimized the precursor solution solvents, in order to reduce the temperature needed to activate the process of ITC, which normally stays around 120 °C. The scope of lowering of the process temperature is to avoid the escape of the MA\(^+\) cation that occurs at the high temperature normally employed for the ITC. The optimization of the propylene carbonate (PC) and \(\gamma\)-butyrolactone (GBL) volume ratio, allowed the activation of the ITC nucleation at a temperature of only 60 °C and a growth of the crystal at only 90 °C. Thanks to XRD analysis they showed that in this condition a lower fraction of MA\(^+\) can escape the crystal reducing the number of crystal defects. The average carrier lifetime improved from 42 ns, for high temperature crystals, to 164 ns (Figure 13). Comparing low-temperature and high-temperature devices, the \(J_{SC}\) and FF were very similar (respectively \(\approx 23\, \text{mA cm}^{-2}\) and 82\%) with the main difference being the \(V_{OC}\) that improved from 1.067 to 1.144 V, corresponding to an increase of the PCE from \(\approx 20\%\) to \(\approx 21.5\%\).\(^{[97]}\)

All the considerations discussed before are confirmed by the work of Lei et al. published in 2019. They used a "solution-base lithography-assisted epitaxial-growth-and-transfer" method to fabricate SC perovskite. Their method also allowed the formation of a compositional gradient along the thickness of the perovskite SC that they used to prepare a graded electronic bandgap, going from a lead perovskite to a mixed lead-tin perovskite. The function of this peculiar structure should be the increasing of the carrier mobility and the reduction of their recombination. Using TRPL they measured an increase in the carrier diffusion length with the increase of the SC thickness. This value appeared to saturate at about 5–7 μm thickness. Interestingly, the EQE spectra showed an optimal value for the SC thickness at around 2 μm (Figure 13a), indicating that the extraction efficient plays an important role in the device. Their best device showed a PCE of 20%.\(^{[64]}\)

Recently, in 2021, a further improvement in the efficiency of SC perovskite solar cells was obtained again by Alsalloum et al. They focused on the optimization of the perovskite precursor composition in order to push the absorbance toward lower wavelengths. Using a mixed FA\(_{0.6}\)MA\(_{0.4}\) composition they managed to redshift the EQE absorbance cutoff of about 50 nm (Figure 13c), resulting in an increase of the \(J_{SC}\) from about 24 mA cm\(^{-2}\) to about 26 mA cm\(^{-2}\) resulting in a remarkable PCE of 22.8\%, which is the actual record efficiency for perovskite single-crystal solar cells.\(^{[61]}\)

### 4.2. Lateral Devices

One of the first works proposing the preparation of a lateral device using perovskite as absorbing materials goes back to 2016 and was proposed by Dong et al. Before their work the best lateral device involving perovskite had a PCE lower than 0.1%. Their device was based on an Au/PVK/Au symmetrical structure which showed no photovoltaic response when as-prepared cells were tested. In order to break the symmetry of the cell they performed an electrical poling of the crystal in order to induce migration of ions and form a p–i–n junction due to self-doping. The electrical field applied to the material was in order of 1 V μm\(^{-1}\) and induced the formation of a diode-like junction.
in the material. Under illumination the device showed a very small current density of 2.28 mA cm$^{-2}$ and a $V_{OC}$ of 0.82 V leading to a record efficiency of 1.88%. Remarkably the EQE spectra showed an extended cut-off wavelength of 850 nm, in contrast with the 800 nm usually measured for the same MAPbI$_3$ perovskite (see Figure 14). An interesting approach was proposed in 2017 by Lee et al., who developed a roll-printing technique to grow MAPbI$_3$ SC exploiting the fast evaporation of the precursor solution solvent when deposited on a hot substrate. The perovskite formed using their technique showed a remarkable improvement in the mobility of the charges, compared to polycrystalline perovskite, going from 0.25 to 46 cm$^2$V$^{-1}$s$^{-1}$ (Figure 15a,b). Using an Au/PVK/PCBM/Ag structure, deposited using a lateral configuration (Figure 15c,d), they demonstrated that a working device could generate a photocurrent of 18.33 mA cm$^{-2}$, a $V_{OC}$ of 0.801 with the major limiting factor represented by the very low FF of about 25%. The maximum PCE showed by their lateral devices was a remarkable 4.14%.

Liu et al. in 2019 developed a method to grow centimeters large perovskite SC with thickness below 100 μm. Such a technique represents an interesting approach to grow SC perovskite wafers without the need of slicing a thick SC. In order to obtain such structures, they used an aqueous solution that was led to supersaturation by accurately controlling the velocity of evaporation of the solvent at low temperature (Figure 16a). The equilibrium between surface tension and buoyancy induced a planar preferential direction of growth of a seed crystal. Analyzed with TRPL (Figure 16c), the SC perovskite grown on the liquid surface showed a clear improvement in the charge lifetimes ($\tau_1 = 59$ ns and $\tau_2 = 324$ ns) compared to the SC grown on a solid substrate ($\tau_1 = 9.6$ ns, $\tau_2 = 103$ ns). The EQE spectra for these two types of SC showed an extension of the absorption cutoff of more than 50 nm. The lateral device obtained using the SC, with an Au/PVK/C60/BCP/Au configuration, showed, under an illumination of 0.25 Sun, a $J_{SC}$ of 5.06 mA cm$^{-2}$, a $V_{OC}$ of 0.66 V, an FF of 44%, and a PCE of 5.9%.

Figure 13. EQE spectra for different graded perovskite SC. Reproduced with permission. Copyright 2020, Macmillan Publishers. Carrier lifetime and photoluminescence for high and low-temperature-processed SC perovskites. Reproduced with permission. Copyright 2020, American Chemical Society. EQE spectra for polycrystalline and SC MAFA perovskites. Reproduced with permission. Copyright 2021, The Royal Society of Chemistry.

Figure 14. EQE for a lateral SC-PSC. Reproduced with permission. Copyright 2016, Wiley-VCH.

Figure 15. (a) EQE spectra for different film thicknesses. (b) PL intensity as a function of time. (c) PL intensity as a function of wavelength. (d) Normalized EQE spectra.
Figure 15. Charges mobility for a) single crystalline and b) polycrystalline perovskites; c,d) lateral device configuration. Reproduced with permission.\cite{98} Copyright 2017, Nature Publishing Group.

Figure 16. a) Schematic representation of the SC growth on the liquid surface; b) EQE and c) TRPL characterization of the perovskite SC grown on the liquid surface and on a solid substrate. Reproduced with permission.\cite{99} Copyright 2019, Wiley-VCH.
A huge improvement of the efficiency of SC lateral device was obtained by Song et al. in 2020 adopting a MAI surface treatment, in order to passivate the surface of the SC. In fact, this passivation showed a clear 11 nm blue shift in the PL spectra, suggesting the suppression of the surface traps. The charge recombination lifetime also improved doubling from 263 to 468 ns for the passivated SC. They characterized the device for many different illumination conditions going from 0.05 to 1.5 Sun. The nonpassivated devices showed a $J_{SC}$ ranging from 1 to 23 mA cm$^{-2}$, with an almost constant $V_{OC}$ of 800 mV and the efficiency going from 3.67% to 4.00% (Figure 17b). All the photovoltaic parameters improved for the passivated devices and showed a $J_{SC}$ ranging from 2 to 32 mA cm$^{-2}$, with an almost constant $V_{OC}$ of 900 mV and the efficiency going from 9.53% to 11.20% (Figure 17a). Remarkably, the devices remained stable under MPP tracking at 1 Sun illumination for at least 200 h (Figure 17d).\[89\]

It is worth noting that the growth technique most often determines the type of HTL or ETL used, especially in the case of crystals directly grown on the substrates, due to the compatibility between the different materials. Therefore, although the type of HTL or ETL can have a great impact on the performance of a photovoltaic device, a correlation between type of ETL (or HTL) and efficiency of single-crystal perovskite solar cells has to be established, given the limited number of HTL or ETL investigated so far for these kinds of devices. Indeed, it would be very useful to investigate in the near future how the different wettability of the ETL (or HTL) can affect the growth of perovskite crystals and their quality and therefore how this influences the performance of the devices.

5. Stability

Degradation upon exposure to humid environment, poor thermal, and photostability along with the ion diffusion-induced decomposition are urgent issues to be solved before perovskite-based devices can enter the market. In this scenario, the low density of defects and the absence of grain boundaries make perovskite devices inherently more stable than the polycrystalline films, which is very attractive for device applications. The chemical structure and photophysical properties of SC indeed have shown to be preserved upon ambient air exposure and thermal stress for a longer time if compared to polycrystalline films.\[49,104\]

The stability of MAPbI$_3$ SC-PSCs was recently improved by performing a surface treatment on MAPbI$_3$ SCs with methylammonium iodide (MAI). The passivating effect of such treatment results in doubled power conversion efficiency and in a long-term stability of the solar cell under continuous output at maximum power point and 1 Sun illumination. The best performing SC-PSC retained 99.77% of its efficiency after 200 h.\[89\] Polystyrene (PS) polymer was exploited to control the nucleation and growth of MAPbI$_3$ SCs, which results in more crystalline. The as-prepared SCs featured an enhanced photostability in ambient environment, that up to 50 days RH of 40–45% and under a continuous illumination of 0.1 sun, along with higher stability to thermal stress.\[105\]

The benchmark MAPbI$_3$ composition in polycrystalline films is generally regarded to be less stable than mixed cation, consequently mixed-cation compositions were recently proposed as a promising strategy to improve the stability of perovskite SCs as well. Perovskite SC with MA$_{0.45}$FA$_{0.55}$PbI$_3$ formulation was first reported, featuring a stability of 14 months of storage in air with 45–55% relative humidity (RH) combined with excellent transport properties.\[106\] The mixed-cation composition was found to also produce SCs with higher decomposition temperature. Thereafter, alternative mixed-cation compositions such as MA(EA)PbI$_3$, where EA stands for ethylammonium (EA), were also demonstrated with the precise scope of improving the

Figure 17. a–c) $J$–$V$ curves under different illumination conditions and d) stability test under MPP tracking at 1 Sun illumination. Reproduced with permission.\[89\] Copyright 2016, Nature Publishing Group.
ambient stability of the perovskite SC. Mixing cations with different sizes, being the MA\(^+\) (2.03 Å) and EA\(^-\) (2.42 Å), can induce a lattice dilation, eventually increasing the crystal symmetry.\(^{[107]}\) Importantly, the presence of EA cation imparts a higher thermal stability as well.\(^{[108]}\)

An original approach devised the incorporation of PbS QDs in MAPbBr\(_3\) single crystals.\(^{[109]}\) This approach exploits the small lattice mismatch between PbS QDs and perovskite forming a heteroepitaxial interface which can impact the transport property and ambient stability of the resulting perovskite SCs, which can be stored for 2 months without sings of degradation.

It was found that in mixed-halide perovskite SC, the control over the composition is mandatory to enhance the stability. In (FAPbI\(_3\))\(_{1-x}\)(MAPbBr\(_3\))\(_x\) perovskite single-crystal alloys, the excess of Cs and Br induced a relevant lattice stress that eventually results in detrimental phase separation. The selection of the proper composition, namely, (FAPbI\(_3\))\(_{0.9}(\text{MAPbBr}_{0.05}\text{CsPbBr}_{0.95})\), improved moisture, light, and thermal stability of perovskite SC.\(^{[109]}\)

The use of 2D cations also imparts an improved tolerance to moisture and heating stress.\(^{[110]}\) Stability to light exposure of mechanically exfoliated flakes of (PEA)\(_2\)PbI\(_4\) (PEA, 2-phenylethylammonium) was taken as a model to investigate the inherent photostability of 2D perovskites, revealing that organic cations volatized starting from the SC edges and surface. An encapsulation strategy with 2D hexagonal boron nitride (hBN) and/or polycarbonates has been proposed to mitigate the light induced degradation. To intrinsically reinforce the 2D perovskite flakes, the hydrophobic nature of fluorinated carbon, 4-fluorophenethylammonium lead iodide (PEAI-F), was exploited. The PEAI-F formed indeed a robust barrier that hinders photo-oxidation and decomposition induced by moisture, eventually leading to enhanced material stability.\(^{[111]}\)

Thermally stable 2D perovskite (PEA)\(_2\)PbI\(_4\) single-crystalline perovskite membrane was also demonstrated by the so-called peripheral crystallization method, which allowed to fabricate large-area flexible devices. Thermogravimetric analysis (TGA) and exposure to a relative humidity of 65% at 25 °C evidenced that as-grown perovskite did not show any observable degradation until 230 °C and until 32 days of storage, respectively.\(^{[112]}\)

Another source of accelerated degradation in 3D perovskite-based devices is the ion migration. It was recently proven that such unwanted ion migration can be suppressed in quasi-2D Ruddlesden–Popper-type BA\(_2\)MA\(_2\)PbI\(_{10}\) (n = 3) SCs synthesized by space-confined method.\(^{[113]}\)

Replacing organic cation with the inorganic Cs\(^+\) is regarded as one of the most straightforward ways to improve the stability of the perovskite material.\(^{[114]}\) Although cesium lead iodide (CsPbI\(_3\)) is characterized by a higher decomposition temperature than the organic counterparts, the inclusion of the small Cs\(^+\) cation makes the optically and electrically active α-CsPbI\(_3\) not stable at room temperature. In addition, the moisture speeds up the conversion from active α-CsPbI\(_3\) to the yellow δ-CsPbI\(_3\).\(^{[114]}\)

Stable γ-CsPbI\(_3\) SCs at room temperature were demonstrated which, however, rapidly converted to δ-CsPbI\(_3\) in humid environment.\(^{[115]}\)

An interfacial modification of the HTL/perovskite interface has been proved effective in order to reduce defect density, suppress nonradiative recombination, improve charge transport, and extraction, leading to MAPbI\(_3\) single-crystal devices with 22.1% efficiency and long-term stability under air condition, maintaining 90% of the initial PCE after 1000 h.\(^{[116]}\)

Recently, stable CsPbBr\(_3\) SCs where synthesized via a low-temperature crystallization strategy in water. If compared to the CsPbBr\(_3\) SCs grown with the inverse-temperature approach in DMSO, the newly developed material is characterized by a higher stability in ambient conditions and inhibited ion migration.\(^{[117]}\)

### 6. Perspectives and Challenges

The concept of building solar cells starting from perovskite single crystals has recently emerged as a means to improve the device performance and stability. If compared with polycrystalline perovskite films that can suffer from chemical defects, mostly linked to grain boundaries’ unavoidable presence, perovskite SCs are characterized by the intrinsic absence of grain boundaries, the high crystallinity, and phase purity. Those features can beneficially result in lower defect density orders and higher carrier diffusion lengths.

Although the great potential, the maximum power conversion efficiencies of SC-PSCs thus far are still below the values reported for the state-of-the-art polycrystalline counterparts. Record efficiency of SC-PSCs approached 22.8% in the conventional vertical geometry, and 11.2% in the planar configuration.

The challenge of making SC-PSCs in the vertical device architectures is obvious to include a submicrometer-thick and millimeter-large perovskite crystal between a bottom and a top contact. To date, no optimal growth method has been demonstrated to achieve high aspect ratio (lateral dimension/thickness) crystals by effectively and simultaneously controlling both lateral size and thickness of a single crystal. This poses several limitation concerning the possible scale-up of the devices, which indeed was not yet demonstrated and appears not to be feasible especially for perovskite SC be grown from solution in conditions that can hardly be precisely controlled.

A viable solution to this problem could be to exploit the confined space growth approach in combination with tailored polymeric templates (e.g., PDMS) to be removed at the end of crystal synthesis. This would allow for optimal control of seeds nucleation and crystal growth and enable predetermination of crystal size, thickness, and position. In addition, a device design can be established, where the patterning of ITO, the crystal geometry, and the top contacts are drawn and the device can be fabricated semiautomatically using predefined masks. This can ensure reproducibility and fast fabrication of the complete device because the process does not need to be readjusted from time to time as it happens for transferred or randomly grown crystals.

Moreover, we envision that there are many rooms for improvements in the development of SC-PSC in the lateral configuration, which can also benefit from the technological background on Si-based solar cells.

These are necessary steps toward high throughput and affordable manufacturing.

Concerning the perovskite stability, although the introduction of single crystals helps to mitigate the problem, efficient long-term device operation remains to be achieved. One possible
way to address this issue is to use mixed perovskites or additives in order to engineer the composition and improve the tolerance of perovskite SCs upon ambient air exposure and thermal stress.

In addition, postcrystallization treatments and interface engineering are suitable strategies that should be evaluated to optimize energy-level alignment, passivate the surface charge traps, and improve the charge extraction, establishing effective electronic contacts between the interfaces, in order to minimize defects and maintain a good structural stability.

Finally, the stability of the device can be improved by the introduction of more stable 2D/3D mixed perovskites that include engineered organic cations to reduce the bandgap of the organic part and align it with that of the inorganic part. This should ensure high performance and device durability.

Acknowledgements
This research was funded by Apulia Region, project “Progetto Tecnopolo per la Medicina di precisione,” grant number: Deliberazione della Giunta Regionale n. 2117 del 21/11/2018 and by the project BestU—“Tecnologia per celle solari bifacciali ad alta Efficienza a 4 terminali per utility scale” founded by the Italian Ministry of University and Scientific Research (MIUR), Bando PON R&I 2014-2020 e FSC “Avviso per la presentazione di Progetti di Ricerca Industriale e Sviluppo Sperimentale nelle 12 aree di Specializzazione individuate dal PNR 2015-2020”—decreto concessione agevolazione protocollo 991 del 21 maggio 2019 MIUR (contract no.: PON ARS01_00519; CUP B88D19000160005). The Italian Ministry of Ecological Transition supported this work in the framework of the Operating Agreement with ENEA for Research on the Electric System. The corresponding authors have been updated on July 11th, 2022 after initial online publication.

Open Access Funding provided by Universita degli Studi di Napoli Federico II within the CRUI-CARE Agreement.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
perovskite stability, photovoltaic devices, single-crystal growth, single-crystal perovskite

Received: December 23, 2021
Revised: April 19, 2022
Published online: May 26, 2022

[1] M. D. Smith, B. A. Connor, H. I. Karunadasa, Chem. Rev. 2019, 119, 3104.
[2] B. Tureddi, V. Yeddu, X. Zheng, D. Y. Kim, O. M. Bakr, M. I. Saimadinov, ACS Energy Lett. 2021, 6, 631.
[3] J. Y. Kim, J.-W. Lee, H. S. Jung, H. Shin, N.-G. Park, Chem. Rev. 2020, 120, 7867.
[4] Y. Cao, N. Wang, H. Tian, J. Guo, Y. Wei, H. Chen, Y. Miao, W. Zou, K. Pan, Y. He, H. Cao, Y. Ke, M. Xu, Y. Wang, M. Yang, K. Du, Z. Fu, D. Kong, D. Dai, Y. Jin, G. Li, H. Li, Q. Peng, J. Wang, W. Huang, Nature 2018, 562, 249.
[5] C. R. Kagan, D. B. Mitzi, C. D. Dimitrakopoulos, Science 1999, 285, 945.
[6] Q. Zhang, Q. Shang, R. Su, T. H. Do, Q. Xiong, Nano Lett. 2021, 21, 1903.
[7] H. Wei, Y. Fang, P. Mulligan, W. Chirurazii, H.-H. Fang, C. Wang, B. R. Ecker, Y. Gao, M. A. Loi, Lei. Cao, J. Huang, Nat. Photonics 2016, 10, 333.
[8] D. E. Mccoy, T. Feo, T. A. Harvey, R. O. Prum, Nat. Commun. 2018, 9, 1.
[9] D. Weber, Z. Naturforsch. B 1978, 33, 1443.
[10] D. B. Mitzi, C. A. Feld, Z. Schlesinger, R. B. Laibowitz, J. Solid State Chem. 1995, 114, 159.
[11] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, J. Am. Chem. Soc. 2009, 131, 6050.
[12] H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphrey-Baker, J.-H. Yum, J. E. Moser, M. Grätzel, N.-G. Park, Sci. Rep. 2012, 2, 591.
[13] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, H. J. Snaith, Science 2012, 338, 643.
[14] M. Liu, M. B. Johnston, H. J. Snaith, Nature 2013, 501, 395.
[15] J. Y. Yoo, G. Geo, M. R. Chua, T. G. Park, Y. Lu, F. Rotermann, Y.-K. Kim, C. S. Moon, N. J. Jeon, J.-P. Correa-Baena, V. Bulović, S. S. Shin, M. G. Bawendi, J. Seo, Nature 2021, 590, 587.
[16] E. H. Jung, N. J. Jeon, E. Y. Park, C. S. Moon, T. J. Shin, T.-Y. Yang, J. H. Noh, J. Seo, Nature 2019, 567, 511.
[17] D. P. McMeeking, G. Sadoughi, W. Rehman, G. E. Eperon, M. Saliba, M. T. Hö rantner, A. Haghhighirad, N. Sakai, L. Korte, B. Rech, M. B. Johnston, L. M. Herz, H. J. Snaith, Science 2016, 351, 151.
[18] W. Li, Z. Wang, F. Deschler, S. Gao, R. H. Friend, A. K. Cheetham, Nat. Rev. Mater. 2017, 2, 1.
[19] G. Rose, Annu. Phys. 1839, 124, 551.
[20] L. She, M. Liu, D. Zhong, ACS Nano 2016, 10, 1126.
[21] C. J. Bartel, C. Sutton, B. R. Goldsmith, R. Ouyang, C. B. Musgrave, L. M. Chirgihelli, M. Scheffler, Sci. Adv. 2019, 5, eaav693.
[22] Y. Dang, D. Ju, L. Wang, X. Tao, CrystEngComm 2016, 18, 4476.
[23] L. Polimeni, G. Lerario, M. Di Giorgi, L. De Marco, L. Dominici, F. Todisco, A. Coriolano, V. Ardizzone, M. Pugliese, C. T. Prontera, V. Maiorano, A. Moliterni, C. Giannini, V. Olieric, G. Gigli, D. Ballarini, Q. Xiong, A. Fieramosca, D. S. Dolynshkov, G. Malpuech, D. Sanvitto, Nat. Nanotechnol. 2021, 16, 1349.
[24] A. Fieramosca, L. Polimeni, V. Ardizzone, L. De Marco, M. Pugliese, V. Maiorano, M. Di Giorgi, L. Dominici, G. Gigli, D. Gerace, D. Ballarini, Sci. Adv. 2021, 5, eaav9967.
[25] M. Cinquino, A. Fieramosca, R. Mastria, L. Polimeni, A. Moliterni, V. Olieric, N. Matsugaki, R. Panico, M. De Giorgi, C. Giannini, A. Rizzo, D. Sanvitto, L. De Marco, Adv. Mater. 2021, 33, 2102326.
[26] C. C. Stoumpos, D. H. Cao, D. J. Clark, J. Young, J. M. Rondinelli, J. I. Jang, J. T. Hupp, M. G. Kanatzidis, Chem. Mater. 2016, 28, 2852.
[27] X. Li, J. M. Hoffman, M. G. Kanatzidis, Chem. Rev. 2021, 121, 2230.
[28] M. Saliba, T. Matsu, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, M. Grätzel, Energy Environ. Sci. 2016, 9, 1899.
[29] M. Karlsson, Z. Yi, S. Reichert, X. Luo, W. Lin, Z. Zhang, C. Bao, R. Zhang, S. Bai, G. Zheng, P. Teng, L. Duan, Y. Lu, K. Zheng, T. Pullerits, C. Deibel, W. Xu, R. Friend, F. Gao, Nat. Commun. 2021, 12, 361.
[30] M.-H. Shang, J. Zhang, P. Zhang, Z. Yang, J. Zheng, M. A. Haque, W. Yang, S.-H. Wei, T. Wu, J. Phys. Chem. Lett. 2019, 10, 59.
[31] F. Hao, C. C. Stoumpos, D. H. Cao, R. P. H. Chang, M. G. Kanatzidis, Nat. Photonics 2014, 8, 489.
[32] W. Ke, M. G. Kanatzidis, Nat. Commun. 2019, 10, 965.
[33] A. Amat, E. Mosconi, E. Ronca, C. Quarti, P. Umari, M. K. Nazeeruddin, M. Grätzel, F. De Angelis, Nano Lett. 2014, 14, 3608.
Luisa De Marco received in 2010 her Ph.D. in nanoscience from National Nanotechnology Laboratory (NNU), Università del Salento (Italy). In the period 2010–2016, she joined the Italian Institute of Technology working on nanostructured semiconductors for photovoltaics. Since 2016 she is researcher at (NNL), Università del Salento (Italy). In the period 2010
Giuseppe Nasti has received a Ph.D. in materials science and engineering in 2016, worked at the National Research Council (CNR) in Pozzuoli between 2016 and 2019, and is currently a postdoc fellow researcher at the University of Naples “Federico II” in the Department of Chemical, Materials and Production Engineering (DICMAPI). His expertise ranges from material processing to finite element simulations, with a focus on the relationship between structure and properties of materials. Since 2019 his research activities have been focused on the development of tin-based perovskite solar cells.

Antonio Abate is the head of the department of “Novel Materials and interfaces for photovoltaic solar cells” at the Helmholtz-Centrum Berlin in Germany, professor at the University of Naples Federico II in Italy. He is researching solar energy conversion with halide perovskites. Before his current position, Antonio led the solar cell research at the University of Fribourg in Switzerland as a team leader. He was a Marie Skłodowska-Curie Fellow at École Polytechnique Fédérale de Lausanne. He worked for 4 years as a postdoctoral researcher at the University of Oxford and the University of Cambridge.

Aurora Rizzo received a Ph.D. degree in innovative materials and technologies from National Nanotechnology Laboratory (NNL), Università del Salento, CNR-INFM, Lecce. In the period 2008–2009, she joined the group of Prof. Olle Inganäs at the University of Linköping (Sweden), working on “Bio-Organic Light Emitting Diodes.” She is currently a researcher at the Nanotechnology Institute of the National Research Council (CNR), Lecce, Italy. Aurora Rizzo research interests include the design and developed of innovative hybrid inorganic–organic and 2D materials, such as metal halide perovskites, colloidal nanocrystals, and transition metal dichalcogenides for third generation solar cells, optic and optoelectronic devices.