

Recent Advances in Perovskite Single-Crystal Thin Film Optoelectronic Devices

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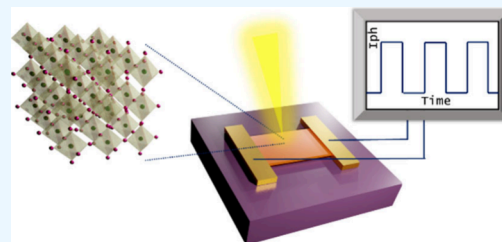
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ABSTRACT: Among novel semiconductors, perovskites have gained significant attention due to their versatility, combining tunable optoelectronic properties with relatively easy fabrication processes. However, certain issues still hinder their widespread use, often related to the presence of defects and traps within the material. Beyond defect passivation in polycrystalline thin films, an alternative approach to enhancing material quality lies in the fabrication of single crystals. This review aims to provide an overview of the promising approaches explored to address specific challenges of perovskites that benefit from the single crystal nature, restricting our analysis to perovskite single crystal thin films (PSC-TF).

We will discuss novel fabrication techniques and highlight recent achievements in devices, such as photodetectors, solar cells, and transistors. By examining the fundamental properties already discovered and showcasing the latest advancements, we aim to provide an overview of the perspectives and open challenges for PSC-TF in next-generation optoelectronic devices.



1. INTRODUCTION

Halide perovskites have emerged as promising candidates for next-generation optoelectronic devices due to their outstanding properties, including tunable bandgaps, high absorption coefficients, excellent photophysical properties, intense luminescence, and low-cost solution-based processability.^{1,2} These attributes have enabled polycrystalline halide perovskites to revolutionize research in photovoltaics, driving an unprecedented increase in solar cell conversion efficiencies from a few percent to over 25% in just 15 years.^{3,4} Significant achievements have also been made in other optoelectronic applications, such as photodetectors and light emitting diodes. Despite these remarkable advancements, polycrystalline perovskites face significant challenges due to structural disorder and vulnerability to environmental conditions, which have limited their large-scale application. These materials in fact display a high density of defects such as grain boundaries, pinholes, vacancies, and various interstitial and substitutional defects, that critically compromise both performance reliability and long-term stability of the devices.²

Alternatively, single-crystal perovskites, thanks to their long-range spatial order and low structural defect density,⁵ inherit the advantages of their polycrystalline counterparts while exhibiting additional exceptional properties such as high charge carrier mobility, extended carrier diffusion lengths and lifetimes, and superior environmental stability. These properties place perovskite single crystals (PSC) among the most promising next-generation semiconductors for optoelectronic applications and among the most interesting novel playgrounds for fundamental physical studies. The exploration and utilization of PSCs in electronic and photonic applications

have recently led to groundbreaking advancements in device performance and functionality. However, synthesizing PSCs from the liquid phase in the form of thin films, which is the suitable form for easy device fabrication and integration, remains a challenging task, with most of the exceptional results so far presented coming from bulk (~mm thick) samples.⁶

Precise control of the size of PSCs, while keeping a high crystal quality, is needed to fully exploit their advantages and facilitate their integration into devices. Particularly, thickness control is crucial to retaining the beneficial effects of single crystals while optimizing the performances of different kinds of devices. In this mini-review, we focus on perovskite single crystal thin films (PSC-TF) for application where optimization needs a thickness comprised between hundreds of nanometers and few microns. Given the attractiveness of the topic, several high-quality reviews have already been published both on synthesis methods and device performances.^{7,8} Here we provide a concise overview of the most recent progresses and key developments in PSC-TF devices, restricting to works published in the last couple of years. After going through synthesis techniques, we explore several applications in a diverse range of devices, including photodetectors, field effect transistors, and solar cells. For every mentioned application,

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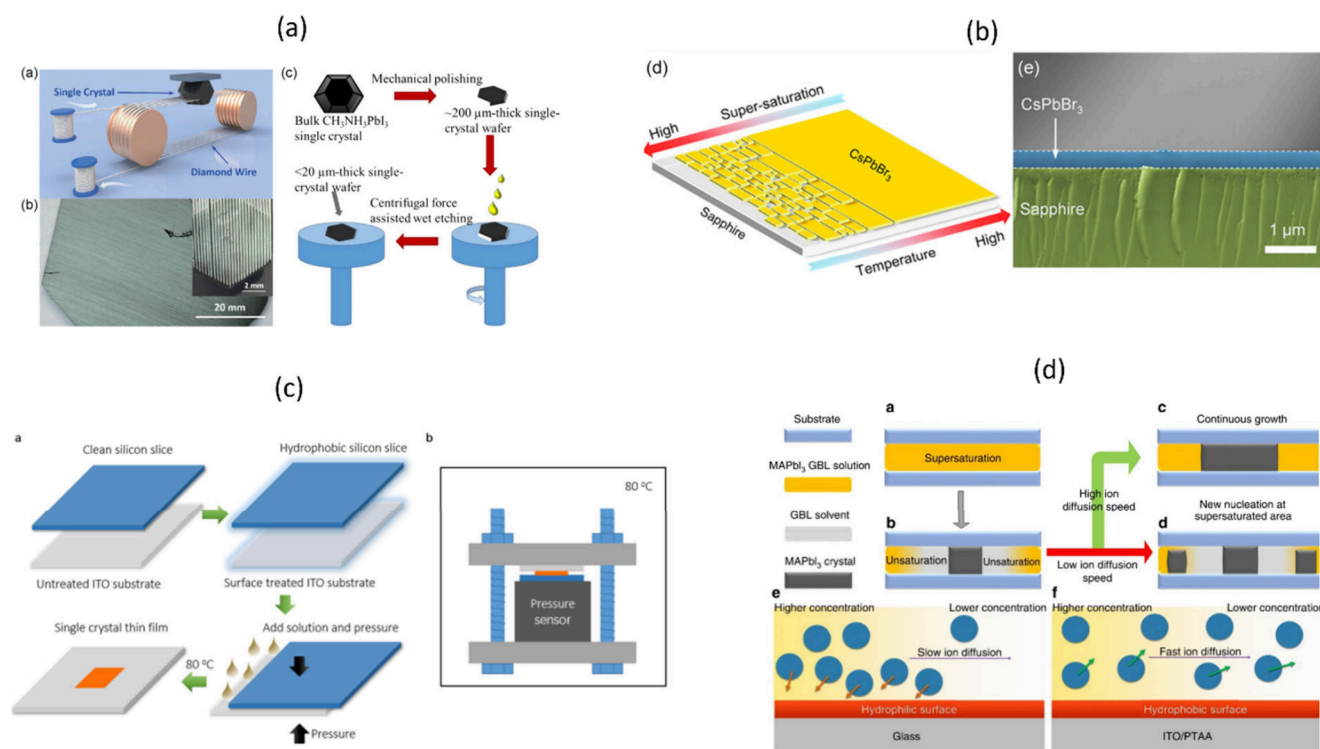


Figure 1. (a) Top-down approaches for the preparation of PSC-TFs: large crystal slicing and thickness reduction via wet etching. Adapted with permission from ref 9, Copyright 2023 Wiley-VCH GmbH. (b) Schematics of the CVD epitaxial growth of PSC-TFs. Adapted with permission from ref 2, Copyright 2023 Springer Nature. (c) Space confined and pressure assisted space confined growth of PSC-TFs. Adapted with permission from ref 10, Copyright 2018 Wiley-VCH GmbH. (d) Effect of the substrate pretreatment on the mechanisms of ion diffusions on the surface and impact on the space confined growth PSC-TFs. Adapted with permission from ref 2, Copyright 2023 Springer Nature.

very recent advances will be analyzed, explaining the specific challenges and proposes solutions.

2. SYNTHESIS OF SINGLE-CRYSTAL PEROVSKITES AND DEVICE FABRICATION

The synthesis of high-quality perovskite single crystal thin films (PSC-TFs) is a complex process that is still lacking full maturity and control. At present, the main approaches used for the growth of PSC-TFs are essentially three: top-down methods, vapor phase epitaxy, and space-confined growth. Top-down techniques, involving slicing large crystals and wet etching to reduce thickness, have demonstrated reliability in producing high quality crystals, but their large-scale application is limited by challenges in subsequent transfer phases for device fabrication and the frequent occurrence of surface defects and cracks.^{9,11} Exfoliation is a viable approach for producing molecularly thin two-dimensional perovskite SCs, with lateral sizes ranging from a few tens to 100 μm .⁹ Vapor phase epitaxy (Figure 1 a), such as molecular beam epitaxy (MBE) and chemical vapor deposition (CVD), is largely employed for the growth of high quality inorganic semiconductors such as III–V materials. Recently, it has also been demonstrated as a valid alternative for producing very thin and high quality PSCs.¹² Space confined growth is a solution-based process, which consists in limiting the material's crystallization to the confined space between two glass slides or between two other type of substrates, creating an anisotropic growth volume that promotes horizontal growth while restricting vertical growth.¹¹ This approach has enabled the synthesis of centimeter-scale single crystals, but the reported thicknesses rarely go below a few tens of μm .^{9,13} Reducing the crystal

thickness to below a few micrometers or into the submicron regime, while maintaining a large area, remains a significant challenge, primarily due to an incomplete understanding of the growth mechanisms involved.⁹

A recent approach to grow relatively large-area PSCs with thickness control ranging from 100 μm down to 600 nm involves the use of bulk SCs as substrates for the solution-based epitaxial growth of PSC-TFs.¹⁴ This process uses lithographically prepatterned thin polymers as growth masks. A simpler approach for obtaining SCs with thicknesses from tens of nanometers to a few micrometers is a modified space-confined growth method. This method combines space confinement with the application of pressure to the sandwich structure, using weights, clamps, or press tools, and sometimes using substrates with prepatterned thickness defined spacers (Figure 1 c).^{9,11} Specifically, the thickness of the film can be adjusted by regulating the pressure, which determines the distance among the substrates. The drawback of this approach is that the lateral size of the obtained crystals, at present limited to the hundreds of μm range, hinders its validity for device applications requiring large areas, such as solar cells. The use of very narrow space-confined gaps is believed to pose limitations to the transport of fresh precursors along the substrate surface, resulting in multiple nucleation sites instead of facilitating the growth of a single large crystal.⁹

Considerable research effort is currently dedicated to understanding the various mechanisms affecting SCs growth dynamics in a space-confined environment and finding strategies to overcome these limitations.¹¹ According to current literature, the mechanisms predominantly affecting crystal nucleation and growth dynamics include the surface wett-

Table 1. Comparison between the Most Used Methods for the Growth of PSC-TFs

| growth method | advantage | disadvantage | ref. |
|------------------------------------------------|---------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------|---------|
| <i>space-confined</i> | low T, solution based process, large lateral size (>1 cm) | low thickness control usual range few μm to tens of μm | 9,11,13 |
| <i>vapor phase epitaxy</i> | high crystal quality, sub- μm thickness, lateral crystal size tens μm to mm | complex-high temperature process (>500 °C) need for suitable epitaxial substrates | 9,11,12 |
| <i>top-down</i> | high crystal quality | challenges to get thickness below tens of μm difficult postgrowth sample handling and transfer | 9,11 |
| <i>modified space-confined</i> | low T, solution based process, thickness control in sub- μm range | lateral sizes limited to few hundreds of μm | 2,11 |
| <i>mechanical exfoliation of bulk crystals</i> | molecularly thin crystals, high crystal quality | small lateral sizes (1 μm to few tens of μm) need of sample transferring for device fabrication | 9 |

ability, the diffusion rate of precursor solutes, which can be adjusted by modifying the surface properties (e.g., hydrophobicity, surface tension, etc.), the evolution of the supersaturation conditions of the precursor solution in the confined volume, which is affected by temperature, solvent evaporation dynamics, and concentration.⁹ According to present studies, the hydrophobicity of the substrates, obtained by surface functionalization via superhydrophobic chemical treatment or by deposition of hydrophobic thin layers, appears to be a key parameter for enhancing the ion diffusion in the space confined volume and ensuring the supply of fresh solution to the growing crystal.² The achievement of a full comprehension of these dynamics, which is still a matter of investigation, would represent a significant technological advancement for the development of next-generation perovskite-based optoelectronics. In Table 1, the advantages and disadvantages of the most commonly used approaches for the synthesis of PSC-TFs are presented.

Another key challenge for the integration of halide perovskite single-crystals in practical optoelectronic devices and circuits is advancing in high-precision device fabrication and downscaling. Similarly to standard silicon-based technology, this necessitates the development of suitable micro- and nanopatterning processing techniques, which requires dedicated research effort, since standard top-down microelectronic processing techniques cannot be directly applied to perovskites. These materials are in fact sensitive to most solvents routinely used in the semiconductor industry, and suitable alternatives needs to be found.¹⁵ So far, most of the reported studies were based on the mechanical exfoliation of perovskite single-crystals onto prepatterned substrates. However, the gap in the precise control of on-chip fabrication of perovskite micro- and nanostructures is starting to be filled. Studies reporting the successful bottom-up growth of large areas of well-ordered arrays of single-crystal halide perovskites pixels, with size down to 2 μm , combining photolithography with solution-based growth, have been reported.¹⁶ Recently Mastria et al., thanks to an accurate solvent engineering study, demonstrated a perovskite-compatible electron beam lithography patterning process,¹⁷ opening the way to the fabrication of advanced device architectures for integrating perovskite device into practical circuits and exploring new physics phenomena.

3. PEROVSKITE SINGLE-CRYSTAL DEVICES

3.1. Photodetectors. One of the most appealing fields of applications for single-crystal perovskites are photodetectors, thanks to the high absorption coefficient and charge carrier

mobility, combined with the low defectivity of crystals, enabling the realization of devices with low dark currents, high sensitivity, and fast response times. In this section, after introducing basic concepts of photodetectors, we are going to focus on latest advances on different PSC-TF devices for photodetection, imaging, and sensing in diverse wavelength ranges and with different configurations.

Semiconductor-based photodetectors absorb photons to generate electron–hole pairs, which can be found in different forms: either free electron and holes or bound excitons. Excitons can form when the Coulombic interaction between electron and holes in the material is allowing the formation of a hydrogen-like bound system, with exciton binding energy (E_b) determined by dielectric constants and confinement conditions. The ratio between bound excitons and unbound electron–hole pair populations is dictated by Saha's equation. If E_b is small enough, the thermal energy is sufficient to dissociate them resulting in an abundance of free carriers in the material. The presence of excitons with high E_b could be detrimental since they are charge-neutral, and a higher voltage would be required to dissociate them in unbound electron and holes and direct them toward the electrodes. In the case of 2D perovskites single crystals, however, despite their E_b exceeding hundreds of meV, this could be avoided owing to polaron-assisted exciton dissociation.¹⁸

Performances of photodetectors depend on experimental parameters such as the incident power P_0 , voltage bias, active area, and frequency bandwidth Δf . A key parameter for photodetectors is the external quantum efficiency (EQE), which is derived as the ratio between photocurrent and incident photon flux φ , according to equation $\text{EQE} = I_{\text{ph}}/e\varphi$. The development of ultrasensitive sensors needs to push the EQE to its upper limit by minimizing nonradiative decay channels for photocarriers, which could be achieved through defect passivation. Other commonly evaluated figures of merit include the dark current vs photocurrent ratio and linear dynamic range (LDR) which depends on the minimum and maximum power P_{min} and P_{max} within the linear photoresponse range, as from the definition:

$$\text{LDR} = 20 \times \log(P_{\text{max}}/P_{\text{min}})$$

which is particularly relevant for imaging applications. Most important figures of merit include also photoresponsivity R , defined as

$$R = \frac{I_{\text{light}} - I_{\text{dark}}}{P_0 \times \text{area}}$$

Table 2. Performances of PSC-TF-Based Photodetectors Mentioned in This Review

| PSC-TF | wavelength [nm] | $I_{\text{dark}}/I_{\text{light}}$ | I_{dark} [pA] | resp. time | R [A/W] | max D^* [Jones] | LDR [dB] | ref. |
|---------------------------------------------------------------------------|-----------------|------------------------------------|------------------------|------------|-----------|-----------------------|----------|------|
| MAPbBr ₃ | 532 | 1.5×10^3 | 153 | 0.5 ms | 7 | 4.2×10^{11} | 50.35 | 16 |
| (FASnI ₃) _{0.1} (MAPbI ₃) _{0.9} | 750–860 | n.r. | 2.4 | 0.02 ms | 0.53 | 7.09×10^{10} | 163.5 | 20 |
| (R/S-VPEA) perovskite | 450–550 | 2×10^4 | 0.98 | n.r. | 1.6 | 2.17×10^{13} | 105 | 23 |
| (PA) ₂ PbBr ₄ | 405 | 4.15×10^4 | 0.7 | 1.59 ms | 2.22 | 2.3×10^{13} | 152 | 21 |
| F-PEAI | 375–514 | n.r. | n.r. | 1.5 ns | 1100 | 5×10^{17} | 228 | 17 |
| F-PEAI beeswax | 450–650 | 500 | 1 | n.r. | 2200 | 2.4×10^{18} | n.r. | 15 |

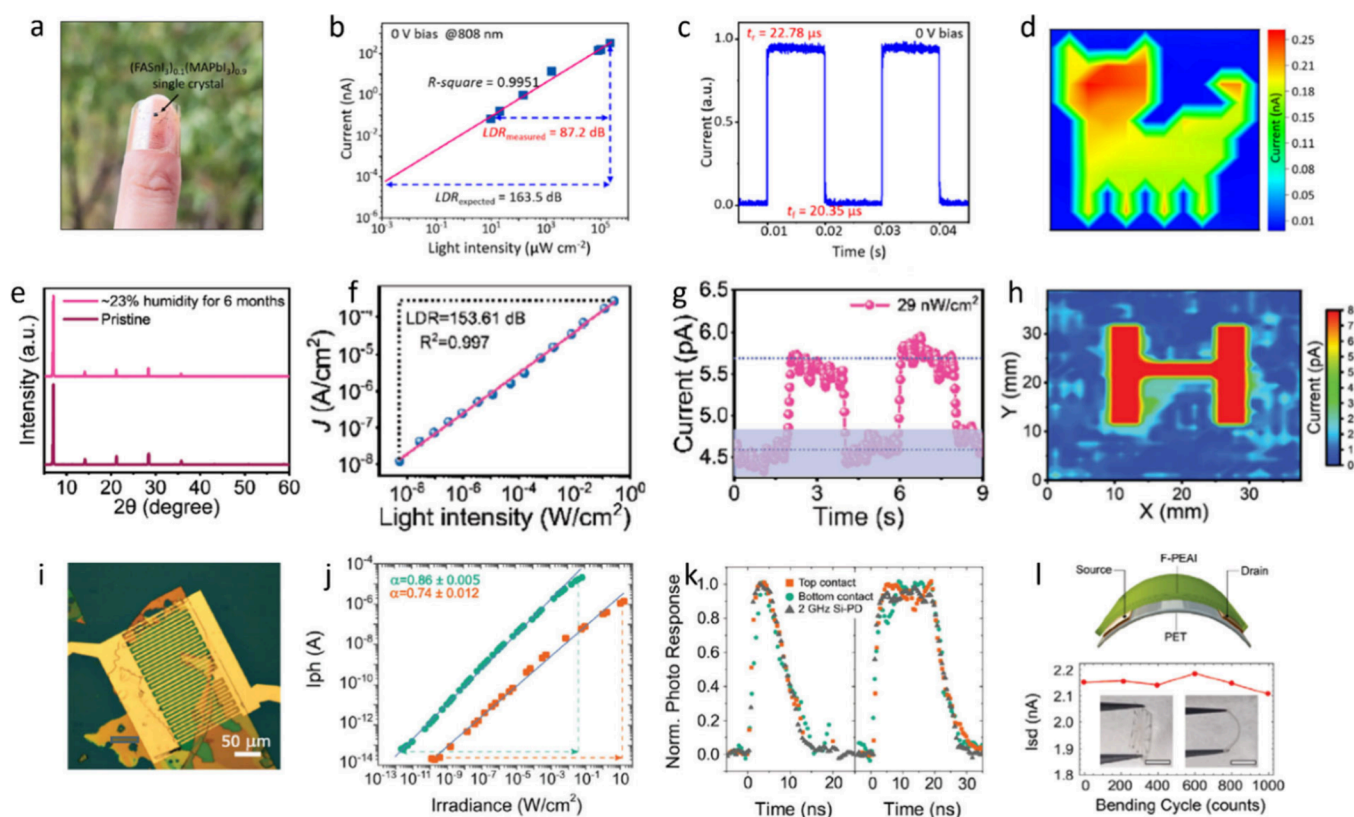


Figure 2. Results of recent PSC-TF imaging: (a–d) mixed Sn–Pb perovskite photodetectors on flexible substrate for health monitoring and NIR imaging, Adapted with permission from ref 20. Copyright 2023 Royal Society of Chemistry; (e–f) 2D perovskites for weak UV light imaging with major environmental stability. Adapted with permission from ref 21. Copyright 2023 Wiley-VCH GmbH; (i–l) 2D perovskites with nanoscale integration for high-resolution real-time imaging in the visible range. Adapted with permission from ref 17. Copyright 2024 Wiley-VCH GmbH.

which is linked through noise equivalent power ($NEP = I_{\text{noise}}/R$) to specific detectivity D^* :

$$D^* = \frac{\sqrt{\text{area} \times \Delta f}}{NEP}$$

It should be noted that detectivity also depends on the applied voltage bias, which can cause irreversible degradation in polycrystalline perovskite materials due to ion migration at interfaces and grain boundaries.¹² This effect happens to be faster in the case of light exposure and depends on the detailed composition and defect density. Responsivity may strongly be affected by internal gain mechanisms that can bring low-power signals above the noise level. A viable strategy to improve internal gain can be based on selective trapping of photo-carriers achievable by defect engineering in the absorbing medium and at interfaces, eventually searching for a compromise between good responsivity and LDR. Response time is another crucial parameter, especially for ultrafast sensors, and it is defined in terms of both rise- and fall-time (in response to a rectangular waveform), respectively, the time for

the signal to go from 10% to 90% of the final output, or vice versa. Factors affecting the response time include the absorbing medium-electrode interface, which can require contact engineering to avoid charge accumulation, and displacement currents, which can become more relevant in the case of excess charge carriers.

Defect migration in polycrystalline thin films have also been recently demonstrated to be responsible of inconsistencies in the characterization of the device's performances.¹⁹ Transient phenomena such as photocurrent drifting on the time scale of seconds were in fact shown to affect the estimated detectivity of up to 2 orders of magnitude on the same device. Proposed solutions are based on defect passivation techniques, which can, however, alter the properties and sometimes reduce controllability. From this perspective, the intrinsic reduction of defects and grain boundaries in PSC-TF can be a preferential route to solve the issue of instabilities and unreliability in perovskite photodetectors under operating conditions.

The most popular application for perovskites is probably that of solar cells, where, to reduce intrinsic defect density,

single crystals with large surface area would be required. This is not, however, necessary in the case of photodetectors, as they can be implemented in the form of pixel arrays, especially for imaging applications. Recently, controlled growth of MAPbBr₃ perovskite microplates was reported,¹⁶ based on a combination of conventional photolithography method with space-confinement and antisolvent-assisted crystallization (SC-ASC). Visible-range sensitive photodetectors were realized with a vertical architecture, where 20 individually patterned layers were merged to maximize photocurrent. Performances of a device with a 5 × 5 pixel matrix are reported in Table 2 in comparison with other PSC-TF-based photodetectors.

A more specific range of application for PSC-TF is that of NIR photodetectors relying on Sn-based perovskite owing to their narrow band gap, with an absorption edge falling in the near-infrared. As well-known, the instability due to the tendency of tin to oxidize from Sn²⁺ to Sn⁴⁺ is a major problem to be faced, which seems to find a viable answer in compositions with mixed Pb–Sn cations. When trying to realize single crystals of these compounds, however, the different crystallization temperatures of Pb and Sn lead to phase separation.²⁰ This issue could be solved with the low-temperature space confinement method, as reported by Chang et al. in ref 20 where phase-pure (FASnI₃)_{0.1}(MAPbI₃)_{0.9} single crystals were successfully used in the implementation of flexible sensors in the VIS–NIR range. The high absorption in the NIR region was matched with good charge mobility and low surface trap density, superior to those of Sn/Pb polycrystalline thin films. Among the figures of merit, the high estimated LDR of 163.5 dB and the short response time, on the order of 22 μs, are particularly noteworthy. Devices have been tested both as real-time and self-powered health monitoring sensors, as shown in Figure 2, as well as for imaging applications, achieving an operating time of 1000 s in atmospheric environment without detrimental effects thanks to the improved stability of SCs. Shifting toward higher energies, a viable route to improve the stability and performances of perovskite-based photodetectors is relying on 2D layered materials, where large cations, such as butylammonium BA, or phenethylammonium PEA, are introduced in the chemical composition. Organic cations are assembling as organic spacers between octahedra layers, either in the form of Ruddlesden–Popper (RP) or Djon–Jacobson (DJ) depending on the layer orientation with respect to the substrate, affecting the material conductivity. 2D perovskites can be realized with different ratios of octahedra layers and organic spacers, as identified by number *n* (*n* = 1 for one layer of octahedra between organic spacers, *n* = 2 for two layers of octahedra, etc.).

Phase-pure forms can be obtained when only the large cation is present, leading to an *n* = 1 structure, while, to get *n* > 1, a composition with mixed small and large sized cations is needed, leading to polycrystalline thin films constituted by grains with different phases and high trap density at grain boundaries. To improve the performances of 2D perovskite-based devices, possible options include phase-pure materials or single crystals. In fact, it has been shown that phase-pure 2D RP SC-like, thanks to their large-sized grains (>10microns), have a much lower defect density than standard polycrystalline films. Ref 22 reports on phase-pure BA₂MA_{*n*-1}Pb_{*n*}I_{3*n*+1} with *n* = 1, 2, 3, 4, 5 with BAAc, an ionic liquid, as organic spacer source, fabricated by spin coating on a patterned ITO substrate at high temperature (100–110 °C). Transient absorption spectroscopy and photoluminescence measurements were

employed to verify the phase-purity. Despite not being strictly single-crystals, they have a single-crystal-like behavior, outperforming analogous polycrystalline devices.

A peculiarity of pure 2D perovskites is their high absorption coefficient, with sharp excitonic spectral features and large bandgap with respect to 3D counterparts. This makes them appealing to cover the field of UV imaging, currently suffering a lack of good alternatives to silicon, whose efficiency and spatial resolution are currently limited by the large mismatch between its absorption edge and the UV photon energy. By combining the wide bandgap achievable with 2D perovskites with the blue-shifting effect of bromine, Dong et al. reported UV photodetectors made of (PA)₂PbBr₄ single crystals. In their work, nanometer-thick microplatelet SCs were realized on various substrates by means of a modified space-confined antisolvent-assisted crystallization (SC-AAS) method.²¹ The reported performances are very promising, especially considering the high LDR and low dark current, as reported in Table 2. Thanks to the stabilizing effect of PSC-TF, thermal, humidity, and durability tests have proven their extremely good stability, without noticeable decomposition after 6 months of exposure to ambient air or 2 months with high humidity, as shown in Figure 2e. Thanks to the high responsivity, it was possible to perform imaging in conditions of weak illumination, with an intensity as low as 0.89 μW/cm² as shown in Figure 2h.

In the subfield of integrated nanoscale photodetectors, outstanding performances were reported in a recent work by R. Mastria et al., where nanoscale planar photodetectors of 2D-fluorinated phenethylammonium lead iodide perovskite (F-PEA)₂PbI₄ (F-PEAI) were fabricated.¹⁷ The 2D perovskite flakes were grown at room temperature by antisolvent vapor-assisted crystallization, followed by exfoliation on different substrates with a top-down fabrication of metal contacts achieved by perovskite-compatible electron beam lithography. The characterization of the realized devices, based on perovskite flakes with very low thickness (around 150 nm) showed that they are outperforming by orders of magnitude other perovskite photodetectors, as reported in Table 2. Noticeable figures of merit include low-intensity light detection and the extremely extended LDR, with a linear regime covering 11 orders of magnitude. Out of the same material, the same group recently reported on single crystal photodetectors with a beeswax coverage to protect it in high humidity environment, keeping high detectivity and responsivity.¹⁵ They tested the beeswax-encapsulated FPEAI integrated photodetectors kept in a liquid environment over a period of 12 months, showing their exceptional overall stability, making this material an interesting candidate for sustainable optoelectronic devices for environmental and healthcare monitoring.

Within the framework of photodetection, PSC-TF could also play a key role in the field of circular-polarization selective detectors. In fact, 2D perovskites with chiral large-sized organic molecules are broadly explored, because of their strong anisotropic absorption for circularly polarized light. In these materials an efficient transfer of chirality from the R- and S-organic cations to the octahedral structure results in a relevant circular dichroism (CD). The main criticalities of chiral 2D perovskite polycrystalline thin films are sensitivity to UV light, humidity, and high temperature, with PSC-TF representing a possible solution to these issues. In a recent work by Zhao et al.,²³ perovskite single crystals with R/S-1-(4-vinylphenyl)-ethanamine (R/S-VPEA) with major stability were obtained by

combining an in situ cross-linking polymerization with a space-confined crystallization. The cross-link of organic molecules acts on modifying the spacing of the interlayer, which can be confirmed by XRD patterns, which were also measured after long exposure to ambient conditions to determine the improvement in environmental stability with respect to a control sample. This composition was found to be particularly suitable for its resistance to bending cycles when deposited onto a flexible substrate, revealing that crossed-linked S-VPEA single crystals preserve a smooth surface after mechanical stress rather than cracking as typically happens with polycrystalline films. Perovskite single crystals are also known as excellent X-ray detectors, offering potential applications in medical imaging and security screening. For this kind of application, however, higher thickness, on the order of several tens of micrometers, is necessary, thus going beyond the range that is subject of this work.

3.2. Field-Effect Transistors (FETs). Field effect transistors (FETs) are fundamental device architectures for both the development of modern electronic components and the investigation of fundamental material transport properties. FETs are extensively employed as platforms for studying the intrinsic properties of semiconductors and novel physical phenomena in emerging materials, exploiting electric fields applied through gate electrodes. Hybrid perovskites possess a multitude of physical properties that are very promising for field effect transistor and phototransistor applications, particularly their intrinsic ambipolar characteristics and excellent transport properties.²⁴

Research on hybrid perovskites FETs has been ongoing for more than two decades, however, compared to other types of devices, progress in enhancing their performances has proven challenging and reported applications remain limited.^{12,24} The main parameters characterizing FET performance are the charge carrier mobility (μ), the ratio between the current value in the on-state and the current value in the off-state ($I_{\text{on}}/I_{\text{off}}$), and the subthreshold swing (SS), which describes how quickly and efficiently the transistor can be turned on by the applied gate voltage and is expressed in mV per decade of current. The smaller the SS value, the higher the FET performance and the lower the power consumption.¹²

Theoretical studies predicted for hybrid perovskites carrier mobilities surpassing $10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, justified by the low estimated electron and hole effective masses,²⁵ and by their balanced values, which also suggest potentially good ambipolar characteristics.^{24,26} However, at present, the experimentally obtained field-effect mobilities are still far from reaching the predicted values, with the best reported mobilities struggling to go beyond a few tens of $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.²⁵ The highest performances were recently reported for triple-cation tin halide perovskite, which displayed a mobility of $70 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, subthreshold swing of 0.9 V/dec, and an impressive $I_{\text{on}}/I_{\text{off}}$ current ratio of over 10^8 .²⁵ As a benchmark for comparing these values with those of other emerging semiconductors, such as 2-dimensional materials, MoS_2 , which is one of the most promising for FET applications, displays field-effect mobilities of the order a few hundred of $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, a $I_{\text{on}}/I_{\text{off}}$ ratio of the order of 10^7 and a SS of approximately 0.5 V/dec.²⁶ Black phosphorus FETs exhibit (p-type) mobilities ranging from a few hundred $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ to $10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and a significant $I_{\text{on}}/I_{\text{off}}$ ratio of 10^5 . However, the reported SS are very large, exceeding several V/dec, and the material suffers from severe instability.²⁶ Organic materials are also emerging

as potential electronic materials. Currently, the field effect mobility is still limited to around $10 \text{ cm}^2/\text{V}\cdot\text{s}$, with interesting $I_{\text{on}}/I_{\text{off}}$ ratios, in some cases approaching 10^7 . Recent studies have also highlighted significant advancements in the switching capabilities of these devices, driven by improvements in material synthesis. These advancements have brought the subthreshold swing closer to the theoretical thermionic limit of 60 mV/decade at 300 K.^{27,28}

In the case of hybrid perovskites, the reduced values of the mobility and subthreshold swing suggest the presence of a high density of defects and trap states in the channel, which still requires further research in material synthesis. One of the major challenges in achieving high-performance devices is ion migration, which significantly affects the device operation by generating screening mechanism of the gate-induced electric fields and by generating detrimental hysteresis behaviors in the transfer characteristics and device instabilities. In this context, single-crystal perovskites with their enhanced structural order should display improved performances. In particular, 2D perovskites attract significant interest due to the substantially suppressed ion migration observed in these compounds.²⁵ However, this field is still in its nascent phase, and an experimental demonstration of remarkably improved performance is still lacking. This is due to both the immature growth process of high-quality thin single-crystals, which are the suitable form for integrating these materials into real devices, and the need to optimize device fabrication and contact engineering.

So far, a mobility of $40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was demonstrated in mechanically exfoliated single-crystals flakes of 2D PEA_2PbI_4 perovskites, a value among the best observed performances in these materials. However, establishing high-quality contacts between exfoliated perovskites and metal electrodes remains challenging, as achieving flat and smooth surfaces is still difficult.²⁵ Contact engineering also requires dedicated studies, as standard Au contacts appear not ideal for perovskites FETs applications due to the occurrence of electrochemical reactions at the Au/perovskites interfaces during device operation.²⁶

3.3. Photovoltaic Cells. Similarly to photodetectors, also in solar cells, photogenerated carriers are collected and transferred to an external circuit, with obviously different requirements and different device architectures. In perovskite solar cells, the separation of charges is provided by interposing the active layer between a hole transport layer (HTL) and an electron transport layer (ETL), whose relative order defines the n-i-p or p-i-n structure of the cell. Performances of the cell are primarily evaluated by the power conversion efficiency (PCE) which can be directly linked with the J - V curve parameters of the cell, namely the open circuit voltage V_{OC} , short circuit current density J_{SC} and fill factor FF of the curve at a given input power P_{in} , as defined by the well-known relation:

$$\text{PCE} = \frac{V_{\text{OC}}J_{\text{SC}}\text{FF}}{P_{\text{in}}}$$

The optimization of the devices depends on a multitude of factors, including not only the absorber but also transport layers and interfaces. Even though it is well established that a high defect concentration is detrimental to their performances, it is indeed questionable whether perovskite solar cells could take advantage of single-crystal features. In fact, until now, the best single-crystal solar cells are still far from the record

achieved by polycrystalline cells, with small area single-junction devices now exceeding 26%.^{4,29,30} According to many reports, the challenge to realize large-area single crystal devices requires an effort that could not be easily paid off by the foreseen performance. However, the motivation for perovskite single crystals solar cells remains of particular interest for some mixed-cation mixed-halide composition such as $(\text{FAPbI}_3)_x(\text{MAPbBr}_3)_{1-x}$ already popular for the realization of semitransparent cells, due to their wide bandgap with respect to pure-iodine compounds. Their optoelectronic properties make them particularly suitable for silicon-perovskite tandem solar cells, as well as for building integrated photovoltaics, provided the replacement of metal electrodes with semitransparent ones. One of the main drawbacks of these material is their degradation under voltage bias due to ion migration, an effect strongly dependent on the amount of defects in the material.³¹

The efficiency gap between the best performing single crystals and polycrystalline cells has been attributed to the high surface charge trap density that results from the contamination of residual crystal growth solution, strongly affecting the surface quality and charge recombination. In this context, N. Liu et al. suggested that the addition of self-assembled amphiphilic long-chain organic amine (CTAC) can induce hydrophobicity and allows for a self-cleaning of the surface.³² In this work, the cell efficiency was found to increase from 20.9% to 23.4%, in particular related to an increase in J_{sc} and FF and also to a longer photocarrier lifetime, evidence for a reduced carrier density. Besides the performance improvement, another reported effect of surface cleaning is an increased stability, in fact the efficiency drop after 10 days of use was reduced with respect to the control cell without surface treatment.

Another factor considered to explain the limit of PSC-TF efficiency is the presence of methylammonium (MA) as an organic cation, which makes the material highly vulnerable to thermal stress due to the tendency of MAI to decompose into methylamine and hydrogen iodide at temperatures above 60 °C. The approach of Lintangradipito et al. starts from this observation: in a very recent work they developed a space limited inverse temperature crystallization (ITC) method to produce $\text{Cs}_{0.05}\text{FA}_{0.95}\text{PbI}_3$ single-crystal perovskite solar cells. Notably, they achieved a PCE above 24%, overcoming the record of 23.1% previously achieved on $\text{FA}_{0.6}\text{MA}_{0.4}\text{PbI}_3$.^{29,30} Thanks to the improved stability, the cells were capable to preserve 90% of their initial efficiency after 900 h of heat test above 50 °C, largely exceeding the durability of polycrystalline films.

With respect to the growing interest of 2D PSC-TF in photodetectors, there is still a lack of evidence of advantages in photovoltaics. This can be attributed to the challenge to grow large area thin crystals with full control of the thickness and layer orientation and to the intrinsic efficiency limit due to the wide bandgap of phase-pure 2D, cutting out the low-energy radiation, thus restricting the possible application field. Despite the undeniable role of 2D perovskites as additives for the passivation and stabilization of 3D cell surfaces, it remains to be assessed whether 2D single-crystal solar cells will bring any significant advantage. According to current understanding of 2D perovskites, their strong excitonic feature in optical absorption and high exciton binding energy only apparently limit their optoelectronic properties, due to an unexpected abundance of unbound excitons. One of the first explanations

was based on polycrystalline grain edge-assisted exciton dissociation, resulting in an effective presence of free carriers in polycrystalline thin films, suggesting that their formation process actually requires a defective material. However, fundamental studies performed on single crystals by resonant exciton injection showed that exciton dissociation into unbound carriers is an intrinsic phenomenon, taking place also in single crystals with low defect densities.¹⁸ This can enable more possibilities for 2D PSC-TFs for optoelectronic applications, including photovoltaic ones.

4. FUTURE OUTLOOK AND CONCLUSIONS

PSC-TFs show significant potential for enhancing the optoelectronic device performance. Their superior properties, including high charge carrier mobility, extended carrier diffusion lengths, and better environmental stability, address many limitations associated with polycrystalline perovskites. The crescent understanding and development of novel growth techniques, such as top-down methods, vapor phase epitaxy, and various space-confinement methods, are pivotal in producing high-quality PSC-TFs with diverse compositions. Future challenges to be addressed include the full comprehension of single crystal growth mechanisms, to enable precise control of the thickness in the submicrometer regime, which is currently difficult to achieve, and overcoming the limitations in the lateral size of the crystals. Dedicated computational and experimental efforts are required to refine the synthesis process and understand the mechanisms behind the ion precursors/substrate surface interactions, which are considered to be key factors affecting thin SC growth. Although the optimization of device fabrication techniques suitable for perovskite processing is still ongoing, recent advances in device integration, patterning, surface treatments, and encapsulation methods are paving the way to reliable PSC-TFs integrated optoelectronic devices such as photodetectors, solar cells, and field-effect transistors. Notable achievements include improved photodetector sensitivity and stability, high mobility and reduced hysteresis in transistors, and enhanced stability of solar cells. The results obtained so far demonstrate the enormous potential of these materials across various fields, with the possibility of advancement toward cutting-edge applications. A fundamental aspect still requiring investigation is achieving control over defect state dynamics and contact engineering. Enhancements in this area, combined with the exploitation of internal gain mechanisms, could lead to the development of highly advanced devices such as single-photon detectors operating at room temperature, without the need for intense voltage bias that would be detrimental for the material. Moreover, exploring the possibility of varying defect filling through electrostatic gating or high irradiances could enable real-time operation with an ultrafast dynamic response. However, achieving high-performance field-effect transistors remains challenging, with current results still falling short of expectations for single crystal perovskites, with large room for improvement in the next years. By addressing current challenges, PSC-TFs can play a crucial role in the advancement of next-generation optoelectronic devices, offering a path toward more reliable and high-performance technologies.

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