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Metal-Halide Perovskite Semiconductors

From Physical Properties to Opto-electronic Devices and X-ray Sensors

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About the Editors

Wanyi Nie graduated from Wake Forest University with a Ph.D. degree in physics in late 2012. Her Ph.D. thesis was on the optimization of organic photovoltaics. She later joined Los Alamos National Laboratory (LANL) in Material Physics and Application Division (MPA) as a postdoc associate and director's funded postdoc fellow from 2013 to 2016 working on interfacial charge transfer states of organic electronics. Since 2016, she has been working as a staff scientist at LANL leading a team to develop novel semiconductors and opto-electronic devices. The main research projects at her group include perovskite photovoltaics, light emitting diodes, X-ray/Gamma-ray detectors and imagers. She is also a scientist at Center of Integrated Nanotechnology at LANL, a DOE user facility. Wanyi is an active reviewer for peer-reviewed journals, such as *Nature*, *Nature Energy*, *Nature Electronics*, *Nature Communications*, *Science Advances*, *JACS*, *Advanced Materials* etc.; she also serves as a reviewer for several funding agents (LANL Laboratory Directed Research Direction Office, DOE office of science and other international grant offices).

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Perovskite Materials: Application Perspective

Krzysztof (Kris) Iniewski, Wanyi Nie, Yuki Haruta, and Makhsud Saidaminov

1 Introduction

Perovskite is a calcium titanium oxide mineral, with the chemical formula of $CaTiO_3$. The mineral was discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after the Russian mineralogist Lev Perovski (1792–1856). The terms "perovskite" and "perovskite structure" are often used interchangeably, but while true perovskite (the mineral) is formed of calcium, titanium, and oxygen in the form $CaTiO_3$, the perovskite structure is anything that has the generic form ABX_3 and the same crystallographic structure as perovskite mineral. The simplest way to describe ABX_3 perovskite structure is as a cubic unit cell with B in the center, X on the faces, and A in the vertices of the unit cell. In halide perovskites, X is a halogen (Cl^-, Br^-, I^-), B is a divalent cation typically Pb^{2+} and/or Sn^{2+}, and A is a large monovalent cation such as Cs^+, $CH_3NH_3^+$. From here on, we will focus on halide perovskites.

Perovskite's potential applications include catalyst electrodes, solar cells, lasers, memory devices, X-ray and gamma ray sensors, and spintronic applications. The book covers these applications in more depth in the following chapters, so the intent here is to provide some general guidance. Several chapters in various books and review papers can be referenced for earlier reports on perovskite materials [1–8].

Depending on the composition, perovskites can have an impressive array of interesting properties including wide bandgap tunability, nonlinear optics,

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ferroelectricity, charge ordering, spin-dependent transport, and others. Perovskites, therefore, hold exciting opportunities for physicists, chemists, and material scientists. Over the last two decades, halide perovskites (HPs) have been identified as one of the most promising materials in photovoltaic and light-emitting devices. This has led to major breakthroughs in materials science.

Recent advances in halide perovskite materials have resulted in impressive gains in solar cells, photon detectors, and light-emission diodes. This chapter briefly reviews recent advancements in perovskite materials for high-energy photon sensing and contrasts them against state-of-the-art semiconductors, as well as conventional scintillators. A new startup company Actinia is described as a case study.

Although the first halide perovskite ($CsPbX_3$) was already reported in 1893 [9], this class of materials received widespread attention only in the last 10 years. The technology development has been driven by the solar cell field since 2009 [10], and its X-ray detection capability has been recently recognized as a possibility to adopt. The development of the process to fabricate mm-scale perovskite single crystals paved the way for X-ray detection applications.

Halide perovskites do not perform well under very high-flux conditions, creating a barrier to entry into applications like computed tomography (CT); therefore, perovskite is not a significant threat to traditional semiconductor devices at the moment. But due to unique material properties, perovskites will likely find some entry points where low cost, ease of manufacture, and mechanical flexibility are attractive. They will likely displace some low-end scintillator solutions and perhaps with time applications like mammography/breast imaging where the flexible shape might be of premium.

It is challenging to forecast how this technology will move forward as every day new perovskite research papers are published. The citations of the first perovskite solar cell paper [10] have reached over 14,000 in 12 years, and the research on perovskite X-ray detectors is also accelerated (Fig. 1). Things can change quickly as perovskite materials have been very successful in raising research funds from both state and private sectors. Therefore, this chapter offers a sampling perspective in 2022. An example of recent government funding activity is Peroxis, an EU-funded research consortium (https://peroxis-project.eu/consortium/). Its objective is to develop a groundbreaking highly sensitive and high spatial resolution direct X-ray detection technology that will greatly improve the diagnosis of major diseases such as cancer, infectious, degenerative, or cardiovascular diseases. The consortium partners are CEA, Trixell, Siemens, University of Jaume (Spain), Philips and TNO, and Neel. Similar grant initiatives have been announced in the USA and other countries.

1.1 Perovskite as a Photovoltaics

Solar cells are currently the most prominent perovskite application, as perovskites are recognized as potential inexpensive base materials for high-efficiency commercial photovoltaics. Perovskite photovoltaics (PVs) are constantly undergoing

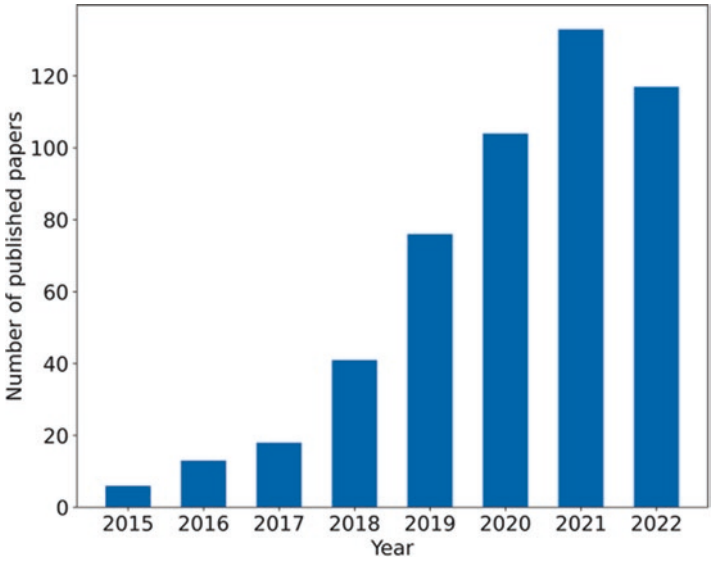

Fig. 1 Number of "perovskite X-ray detector" papers retrieved from *Web of Science* as of October 24, 2022

research and improvement, going from just 3.8% efficiency in 2009 to over 25% in 2022. Market research forecast that the market for perovskite PV will reach $214 million in 2025 [11].

The original perovskite photovoltaics started as a simple variant of dye-sensitized solar cells (DSSCs) in which a perovskite was just a dye [10] but the device structure has been evolving toward the planar architecture. Perovskites offer a significant advantage over silicon in PV applications since perovskites react to a broader range of visible light frequencies. In addition, perovskite PVs offer additional attributes like flexibility, semi-transparency, lightweight, and low processing costs [12].

Besides, the bandgap of perovskites can be tuned widely (~1.2 to ~3.0 eV). This creates an opportunity in pairing them up with low bandgap PV technology like silicon PVs, which will result in improved efficiency as tandem solar cells and will matter in a highly competitive market where system costs and performance levels depend on efficiencies.

The technology is, however, not fully commercially ready yet, and perovskite PVs will need to face several challenges before commercialization. Among these issues are the cells' long-term durability and toxicity (the risk is that these devices may release lead, a highly toxic element, into the environment). To avoid these issues, encapsulation technologies are being developed. A number of chapters in this book address photovoltaic applications.

1.2 Perovskite in X-ray Imaging

In addition to application in solar cells, the realization of perovskite-based X-ray imaging devices is expected as they show some promising properties such as a high X-ray sensitivity. Market research predicts that perovskite X-ray detectors will open new applications for X-rays, expanding what is already a multibillion-dollar industry [13]. More efficient imagers would draw less power, lending themselves to portable machines that run on batteries. Researchers have demonstrated a variety of tunable, color-emitting perovskite nanocrystals. That work could lead to multicolor X-ray displays, which are impossible with today's scintillator X-ray machines. Research continues in both indirect detection scintillator materials and direct conversion semiconductors. And because they use flexible substrates, perovskite imagers could conform to whatever is being scanned. Faster, more sensitive imagers might also reduce the radiation from dental and medical X-rays and airport security scanners.

One of the biggest issues in PV application, which is instability against the moisture, is not significant for X-ray imagers application because the environmental conditions they will face are more benign. In addition, one can wrap the detector in different materials while still seeing good X-ray penetration into it, which is not necessarily the case with a PV system that needs to absorb solar radiation efficiently. Solar panels need to perform even after 20 years, typically exposed to heat and light, both of which can degrade the perovskite compound. X-ray machines, by contrast, are typically used in climate-controlled settings. For these reasons, many researchers including us believe perovskite X-ray detectors will be commercialized much more quickly than other perovskite applications.

A big obstacle to the market is the lack of a scalable fabrication process for perovskite X-ray imagers. Although X-ray imagers require enough area comparable to the imaging area for the X-ray absorbing layers, the fabrication of such a large perovskite single crystal is still challenging. Polycrystalline perovskite thick films prepared by some scalable processes have been reported, but the X-ray detection performance is not enough compared to the single crystal-based devices and so needs to be improved [14].

1.3 Perovskite Quantum Dots and Lasers

Perovskite quantum dots (PQDs) are a class of quantum dots based on perovskite materials. While these are relatively new, they have already been shown to have properties matching or surpassing those of the metal chalcogenide QDs: they are more tolerant to defects and have excellent photoluminescence quantum yields and high color purity. Such attractive properties are extremely suited for electronic and optoelectronic applications, and so PQDs have significant potential for real-world applications, some of which are already emerging, including LED displays and quantum dot solar cells [15].

As direct bandgap semiconductors, perovskites exhibit the unique optical properties of bandgap tunability, charge-carrier mobility, defect tolerance, photoluminescence quantum efficiency, and power conversion efficiency. These properties make them promising light-emitting materials for high optical gain, low-threshold, and multicolor laser applications. The fact that they can be fabricated from low-cost precursors via simple processes makes them attractive as well.

Researchers have found that organometal halide-based perovskites (a combination of lead, organics, and halogens arranged into a perovskite crystal structure in the solid state) could be very suitable for making optoelectronic devices since they can be processed in solution and do not need to be heated to high temperatures. This means that large-area films of these materials can be deposited onto a wide range of flexible or rigid substrates. The perovskites also have an optical bandgap that can be tuned in the visible to infrared regions, which makes them very promising for a range of optoelectronic applications. These materials also emit light very strongly, which makes them very suitable for making LEDs. The wavelength of the light emitted by the perovskites can be easily tuned, which could make them ideal for color displays and lighting and in optical communication applications.

However, a major obstacle is that electrons and holes only weakly bind in perovskite thin films. This means that excitons (electron-hole pairs) spontaneously dissociate into free carriers in the bulk recombination layer, leading to low photoluminescence quantum efficiency (PLQE), high leakage current, and low luminous efficiency. This obviously impairs perovskites' ability to create high-performance LEDs, and for perovskite materials to make a comparable impact in light emission, it is necessary to overcome their slow radiative recombination kinetics. Researchers will have to find ways of effectively confining electrons and holes in the perovskite so that they can "recombine" to emit light. Major progress is already being made in this field, and it seems that perovskites might indeed open the door to a low-cost, color-tunable approach to LED development. One chapter in this book is devoted to this exciton problem.

2 Perovskites for X-Ray and Gamma-Ray Detection

2.1 Motivation

The interest in perovskites started with highly efficient photovoltaic cells. Researchers were also exploring perovskites' potential in transistors and LED lighting. There is yet another use for halide perovskites, likely the most promising of all: as X-ray and gamma-ray detectors. What makes perovskites so useful for X-ray detection is the same thing that makes them good for solar cells: they are excellent at converting photons into electrical charge. In a direct detector, X-ray photons are converted into electrons inside a semiconductor. In a scintillator imager, the X-ray photons are first converted into visible photons, which are then converted into electrons by a photodiode array. Interestingly, perovskites can be manufactured and

used as either direct conversion detectors (like silicon, CdTe, or CZT) or as traditional indirect scintillator materials (incumbent technology for X-ray detection) [6].

Many companies exploring this area and major X-ray imaging manufacturers are considering perovskite for their next-generation X-ray machines. Compared with today's X-ray imagers, detectors based on perovskite compounds can be more sensitive and use less power. And for certain applications, the materials can be tuned to emit color when irradiated.

Other researchers have demonstrated perovskites in direct X-ray detectors with superior performance to that of commercial imagers, but low-performing silicon or selenium is typically used in these comparisons. Research into perovskite materials for X-ray detection remains fertile. At the recent 2021 IEEE NSS MICS RSTD conference, there were more research papers on perovskites than on traditional CdTe and CZT semiconductor detectors [16–30]. Interestingly, there was a lack of any big original equipment manufacturers (OEMs) or startups presenting, which is an indication that the technology development is still in the research phase, with no clear indication of technology transfer or attempts to build commercially viable devices. We expect this trend to continue at the 2022 IEEE NSS MICS RSTD conference which at the time of this writing is about to start in Milano.

In addition to the ongoing material research activity that may benefit the development of new ionizing radiation detectors, it is attractive that the Pb-halide perovskites can be grown and processed in solution at relatively low temperatures and that the basic raw materials are earth-abundant. Furthermore, the $APbX_3$ perovskites have reasonably high density and high-Z elements (e.g., Pb, Cs, I), which are helpful in a radiation detector to stop and convert the incident X-ray or gamma photon to electron-hole pairs.

The lead-halide perovskites exhibit so-called defect tolerance, which is partly credited for transport properties beneficial in solar cells and high quantum yield from nanocrystals in LEDs. Defect tolerance is taken here to mean that defect trap levels lie within the bands rather than in the bandgap or are shallow if within the bandgap. Reviews and explanations have been offered in the literature and further in this book. The attractive properties of metal halides are accompanied by the fact that such salts generally are soft insulators prone to point and line defects. Many of the electron trap levels that would appear within the bandgaps of most other halide insulators become enveloped within the Pb-derived conduction band that is mainly responsible for narrowing the gap from typical metal halide insulators to $APbX_3$ semiconductors [31–33].

As suggested by the branching in the lower part of Fig. 2, it appears that lead-halide perovskites may be poised to furnish radiographic detectors by two different routes, one depending on defect tolerance-associated carrier lifetime in semiconductor mode for direct radiographic detection and the other depending on high quantum-yield light emission from excitons in semiconducting quantum dots (QDs). The following two sections examine these two paths separately. Section 2.2 focuses on the right branch seeking to exploit scintillating light emission for indirect radiography. Section 2.3 focuses on examining progress along the left branch using charge collection.

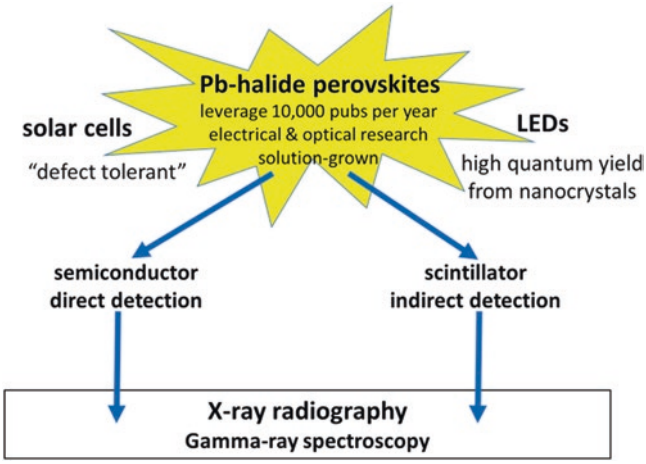

Fig. 2 Activity in photovoltaic and LED research on perovskites may be leveraged for two corresponding routes to radiation detection, particularly X-ray radiography and gamma ray spectroscopy [6]

2.2 Perovskites as Scintillators

Prospects for making room-temperature perovskite scintillators benefited from research and development on perovskite light-emitting diodes (LEDs), where it had been found that perovskite nanocrystals as light emitters avoid the room-temperature quenching of luminescence that occurs in extended 3D bulk crystals. The retention of light emission at room temperature in nanocrystals is generally attributed to the quantum confinement of electrons and holes together. Inorganic $CsPbBr_3$ or hybrid $(CH_3NH_3)PbBr_3$ (=$MAPbBr_3$) might attain a scintillation light yield as high as 156 photons/keV [6]. To realize them, an understanding of how the thermal quenching in microscopic and macroscopic crystals occurs and how quantum confinement defeats room-temperature quenching would be helpful. Although various strategies have been proposed to solve these fundamental perovskite scintillator problems, the applications in the industry are still challenging. On the other hand, the second path of using perovskites as direct detectors looks more promising as discussed below.

2.3 Perovskites as Direct Detectors

The research on perovskite direct X-ray detectors was triggered by the development of facile growth methods which provide high-quality mm-scale perovskite single crystals. In 2015, high-quality, hybrid perovskite single-crystal growth was first published using a low-cost, rapid growth technique, now known as inverse temperature crystallization (ITC) [34–37]. Soon thereafter, large, ongoing research efforts

have been placed in a variety of areas in solution-based hybrid perovskite single-crystal growth. There are a variety of other efficient solution-based growth techniques that have been successfully demonstrated to produce high-quality single crystals of hybrid and non-hybrid perovskite single crystals. These include anti-solvent vapor diffusion, temperature-lowering methods, and slow solvent evaporation [38].

Although the solution-based methods have been the most popular method for perovskite single-crystal growth, some groups have turned to melt growth methods for high-quality inorganic perovskite crystal growth (e.g., $CsPbBr_3$). This method provides accurate control to produce high-quality single crystals. However, in the realm of hybrid perovskites, this method cannot be used because the organic components in hybrid perovskites will be decomposed or volatilized.

Thanks to those developments in mm-scale single-crystal growth, many perovskites' direct X-ray detectors have been reported. As provided in the recent review paper [39–44], excellent X-ray detectors with high X-ray sensitivities over 10^4 μC Gy^{-1} cm^{-2} and low detection limits below 10 nGy s^{-1} have been reported. The sensitivity and detection limit of the perovskite X-ray detectors are several orders higher and lower than conventional detectors (amorphous Se, HgI_2, and CdTe), respectively. While those reports are supporting the promising future of perovskite-based direct X-ray detectors, further scale-up for imaging devices is still challenging. Therefore, polycrystalline thick films that can be easily scaled up for imaging devices are recently developed and described in one of the chapters in this book.

2.4 Perovskites as Flexible X-Ray Detectors

The world around us consists of a myriad of objects with curved geometries and complex surfaces, yet most sensors and detectors that we use to study them are rigid and planar. Confronting this incompatibility will allow for applications impossible to realize with current technologies. Ultra-flexible, low-cost, and highly sensitive high-energy radiation detectors are of great interest to the fields of medical diagnostics, dosimetry, industrial inspection, security, and defense. Low weight and high conformability of X-ray wearable dosimeters are appealing features for astronauts, nuclear power plants, and laboratory workers, as well as for imagers used in structural inspection and cultural heritage preservation. This research area is part of the major trends in electronics industry of producing flexible electronics/sensors products.

State-of-the-art solid-state X- and gamma ray detectors for large-area applications based on silicon (Si), amorphous selenium (a-Se), and cadmium (zinc) telluride (CdTe/CdZnTe) are mechanically stiff, difficult to scale up, and require high operating voltage. Organic semiconductors were the first group of materials that was able to overcome these issues, offering liquid phase, low-temperature, and low-cost deposition techniques that are scalable to large flexible substrates. Mechanical

flexibility, high X-ray sensitivity (up to 1.3×10^4 μC Gy^{-1} cm^{-2}), and low limit of detection (down to 0.29 μGy s^{-1}) have been demonstrated for both organic single-crystal and thin film direct X-ray detectors. Despite these encouraging results, organic semiconductors are intrinsically low-Z materials, therefore resulting in subpar high-energy photon absorption. Blends of organic semiconductors and heavy inorganic nanoparticles or lead-based quantum dots have been proposed to overcome such issues. On one hand, this approach offers a strategy to improve the material attenuation fraction, but on the other hand, it is intrinsically limited by the maximum nanoparticle concentration that can be dispersed in the blend before clustering and agglomeration occur, resulting in electronic transport degradation.

Recently, lead-halide perovskites emerged as an auspicious novel material family for X- and gamma ray detection. Their success can be attributed to strong absorption of ionizing radiation due to the presence of heavy atoms (e.g., Pb, I, and Br), high charge carrier mobilities, long exciton diffusion, long charge carrier lifetime, and excellent optical properties. Single-crystal and thick-film perovskite X-ray detectors have been the focal point of current research, often incorporated in a lateral photoconductor radiation detector architecture. This kind of device shows outstanding sensitivity as well as fast, stable, and reproducible responses. Increasing the thickness of crystals or films has been the primary way to raise the total radiation absorbance and thus improve the detector efficiency. Nevertheless, limited attention has been devoted to thin-film perovskite ionizing radiation detectors. Vertical configuration photodiode architecture based on thin films allows for lower dark current and faster response and stands out as the only viable candidate for flexible device implementation.

2.5 *Case Study: $CsPbBr_3$*

Actinia (https://actiniadetectors.com/) is developing one of the most studied perovskite materials, $CsPbBr_3$, that features a large bandgap of 2.3 eV which ensures low dark currents and robust performance well above room temperature. $CsPbBr_3$ has a pseudo-cubic perovskite structure (Fig. 3). Compared to organic-inorganic hybrid perovskites, the all-inorganic $CsPbBr_3$ perovskite features great advantages in chemical and device stability, due to the lack of organic molecules, while also exhibiting top-of-the-line performance that rivals the best room-temperature semiconductors. Unlike such materials, however, detector-quality $CsPbBr_3$ is inexpensive to synthesize, uses readily available starting materials, and tolerates crystal defects well.

Actinia has developed proprietary growth methods for high-quality crystal growth of $CsPbBr_3$. Growing crystals of $CsPbBr_3$ using Actinia's techniques has the advantage of producing size-controllable high-purity single crystals and provides a feasible path to mass production for commercial X-ray detection applications. Actinia's proprietary technology and methods produce large, high-performing $CsPbBr_3$ crystals. Actinia's $CsPbBr_3$ devices exhibit high-energy discrimination

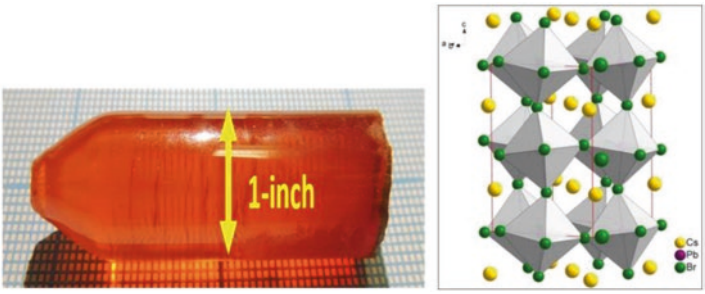

Fig. 3 $CsPbBr_3$ ingot produced by the other Actinia (middle) and three-dimensional (3D) perovskite structures of $CsPbBr_3$ (right)

ability and high X-ray sensitivity under a variety of X-ray sources with a continuum energy spectrum. The details of the performance can be found in these published papers [27–30]. The performance of the Actinia detectors can be summarized using *Nature Photonics* Abstract [27]: "Halide perovskite semiconductors are poised to revitalize the field of ionizing radiation detection as they have done to solar photovoltaics. We show that all-inorganic perovskite $CsPbBr_3$ devices resolve ^{137}Cs 662-keV γ-rays with 1.4% energy resolution, as well as other X- and γ-rays with energies ranging from tens of keV to over 1 MeV in ambipolar sensing and unipolar hole-only sensing modes with crystal volumes of 6.65 mm^3 and 297 mm^3, respectively. We demonstrate the scale-up of $CsPbBr_3$ ingots to up to 1.5 inches in diameter with an excellent hole mobility–lifetime product of 8×10^{-3} cm^2 V^{-1} and a long hole lifetime of up to 296 μs. $CsPbBr_3$ detectors demonstrate a wide temperature region from ~2 °C to ~70 °C for stable operation. Detectors protected with suitable encapsulants show a uniform response for over 18 months. Consequently, we identify perovskite $CsPbBr_3$ semiconductor as an excellent candidate for new-generation high-energy γ-ray detection."

3 Perovskite Material Properties

3.1 Perovskite Material Characterization

Once single crystals are grown and harvested from the solution, it is important to characterize them to ensure high quality, proper composition, and desired properties. In principle, this is not different than for CZT. There are abundant characterization techniques developed in the literature to understand the properties of hybrid perovskite single crystals, but the most important properties belong to structural, optical, and electronic categories for semiconductor device development.

When single crystals are first grown and harvested from solution, a well-utilized tool to initially characterize the quality of the growth is a visual inspection. When

the bromide- and chloride-based crystals are grown, they are transparent. When visually inspecting a single crystal, it is important to look for various signs. The most common visual inspection for these types of single crystals among the community relies on the transparency of the crystals without distortion of imagery or graphical lines placed underneath the crystal. However, if the crystal is not transparent or cloudy or even slightly distorts the image below, one can speculate on the quality of the crystal growth through a relative concentration of defects or microcracks in the bulk of the crystals. In the case of nontransparent single crystals, like the black, iodide-based single crystals, transparency cannot be utilized for quality checks. Instead, the quality inspection here comes from the smoothness and mirror-like finishes of the crystal faces. Other visual inspections include checking for smooth parallel sides without curvature for cubic crystals and sharp edges.

The visual inspection is a first, simple step to initially speculate on the quality of the bulk material; however, phase and defect concentration are very important properties in these materials for semiconductor applications and must be quantified properly. Powder X-ray diffraction (XRD) is commonly used to study the crystal structure of single crystals. In this method, the single crystal is finely ground into powder and an XRD pattern is collected. The data is then matched to the pure compound from a crystallographic database to ensure that the material is in the proper phase (i.e., $MAPbBr_3$ = cubic, $MAPbCl_3$ = cubic, $MAPbI_3$ = tetragonal for room-temperature structures). Other X-ray diffraction techniques can be used to understand imperfections in the crystallographic structure throughout the material such as Laue diffraction patterns to characterize the alignment of the crystal faces and high-resolution XRD (such as rocking curves) to see any deviations in the crystal structure. Temperature-dependent XRD can also be used to understand structure transitions such as in $MAPbI_3$ which undergoes a transition from cubic to tetragonal phase around 330 K and another transition to the orthorhombic phase around 160 K.

The next common characterization deals with quantifying defect concentration and characterizing the types of defects that directly play an important role in semiconductor optoelectronic applications. There are a wide variety of experimental techniques including secondary ion mass spectrometry, positron annihilation spectroscopy, X-ray measurements, electrical measurements, and optical measurements. Electrical measurements such as space charge limited current (SCLC) and Hall measurements can be also used to quantify defect concentrations. Meanwhile, other common techniques include the time of flight and temperature-modulated techniques to determine the levels of traps within the bandgaps, which helps to understand the roles of traps in charge transport processes. Again, similar techniques are used in the CZT world so there is little new here.

The following techniques to continue characterizing As-grown perovskite single crystals use optical spectroscopy. Absorption is used to directly measure the bandgap and states that below the gap, photoluminescence can be a close substitute for estimating the bandgap and trap density of the material. When they are excited by an absorbable wavelength, the excited states relax from the conduction band to the valence band, and the corresponding energy is released via light such as photoluminescence.

3.2 Perovskite Electronic Properties

The electronic band structure, charge transport, traps, and defects depend on the perovskite compositions and the crystal growth conditions. Here, we discuss the general electronic properties of perovskites relevant to radiation detection applications. Lead-halide perovskites have a strong radiation stopping power due to their high effective atomic number (consists of heavy elements like Pb, Cs, halides, etc.) and high density. The linear attenuation coefficients of hybrid perovskite materials ($MAPbI_3$, $CsPbBr_3$, 2D perovskite, and double perovskite) are comparable to conventional CZT and much higher than Si. Therefore, the quantum efficiency of a $MAPbI_3$ crystal with a 2 mm thickness (density 4.15 g/cm^3) for a radiation photon with an energy of 100 keV is about 99.9% (assuming the photon deposits all its energy in the crystal and all the electron-hole pairs generated are collected). Even at an energy of 300 keV, photoelectric absorption is the dominant interaction mechanism and Compton scattering is much smaller. The inorganic $CsPbBr_3$ perovskite has an even higher attenuation coefficient. Due to the tunable nature of the material compositions, other high atomic number elements can also be incorporated into the perovskite materials to further increase the stopping power. $Cs_2AgBiBr_6$ double perovskite is one example of high detection efficiency. Moreover, using the optical bandgap (E_g), one can estimate the ionization energy or the free electron-hole pair creation energy (W) using empirical relation $W = \sim 3E_g$. The bandgap for common perovskites falls within the range of 1.1–2.5 eV, which translates to ionization energies in the range of 3.3–7.5 eV comparable to 4.6 eV in CZT.

3.3 Perovskite Charge Transport Properties

Due to strong spin-orbit coupling, the electron and hole effective mass in $MAPbI_3$ is reduced to 0.1–0.3 of m_0. These effective mass values are comparable to Si. However, the carrier mobilities in halide perovskites are lower than that of Si. Depending on the measurement technique used and the quality of the single crystal, the chaptered electron and hole mobility values for $MAPbI_3$ are in the range of 24–800 cm^2/Vs. This range is large, indicating that many samples at the low end of reported mobilities were likely inferior, e.g., containing many trapping centers that lower the measured mobilities. In addition, the temperature dependence of mobility measurements indicates that these modest mobility values are mainly due to the scattering of electrons with longitudinal-optical phonons. Notably, the reported electron and hole mobilities are in the same range, which is consistent with effective mass. Therefore, ambipolar charge transport in lead-halide perovskites is ideal for the efficient extraction of both electrons and holes.

On the other hand, the perovskites have long carrier lifetimes and diffusion lengths [20]. The reported lifetimes of $MAPbI_3$ are around 10–17 μs while a record lifetime of $CsPbBr_3$ which is more than 25 μs has been reported [27]. The long

lifetimes also make up for the modest mobility values and result in mobility-lifetime ($\mu\tau$) products comparable to CZT materials. It might be worth noting here that some of these materials, $CsPbBr_3$ for example, are hole-dominant materials. The reported $\mu\tau$ product values for $MAPbI_3$, $MAPbBr_3$, and $CsPbBr_3$ are 0.8×10^{-3} cm^2/V, 1.2×10^{-2} cm^2/V, and $1.33–1.69 \times 10^{-3}$ cm^2/V, respectively [1–8]. In addition, a high $\mu\tau$ product of 1.8×10^{-2} cm^2/V for mixed-halide $MAPbBr_{2.94}Cl_{0.06}$ has been obtained by doping $MAPbBr_3$ with Cl.

Low trap state densities in the range 10^9–10^{10} cm^{-3} have been reported for solution-grown halide perovskite single crystals, again comparable to CZT. Using Bridgman melt growth method, centimeter-sized $CsPbBr_3$ crystals with impurity levels below 10 ppm for a total of 69 elements have also been obtained. The experimental results are consistent with theoretical studies which indicate that dominant intrinsic defects are shallow traps while deep defects located near the middle of the bandgap are unlikely to form due to high enthalpy of formation. This "defect tolerance" in perovskites has been attributed to the strong lone pair in Pb s-orbital, antibonding coupling in I p-orbital. Due to the low density of electrically active defects in halide perovskites, charge carriers excited by radiation can be extracted without being trapped. Moreover, the defect tolerance nature of perovskites also gives rise to radiation hardness.

4 Looking Ahead

What is ahead for perovskite materials? Research funds will likely continue to pour into this technology. Perovskite materials, after all, exhibit intriguing and unusual physical properties that will be extensively studied for both practical applications and theoretical modeling, and the materials science and applications of perovskites have already been a broad research area open to many revolutionary discoveries for new device concepts. At least 10,000 research papers have been published on this topic already.

It is generally recognized that it takes 20–30 years in materials science to reach production maturity although in the perovskite case one might argue it will be shortened, say down to 10–15 years, due to widespread application space and universality of the material solutions offered. That puts 2035 as a year of commercial deployment and 2030 as a year with some product samples being demonstrated. We forecast that low-end scintillator applications will be the first to use perovskite technology on par with some new unique applications that explore perovskites' unique properties like the flexibility of the substrate material. The perovskite mantra will be unique (flexibility in shape), low cost, and easy to manufacture (e.g., in amorphous/polycrystalline shape). But performance needs to follow if this is to become a real contender in the radiation detection space.

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Perovskite Thin Film Growth Techniques

Cheng-Hung Hou and Wanyi Nie

1 Introduction

Perovskite semiconductors are low cost, solution processible materials that have enabled exciting optoelectronic devices. In addition to single crystals, perovskite polycrystalline thin films are widely utilized in optoelectronic devices that adapt a thin-film device architecture. Depositing a uniform perovskite thin film with desirable properties has been an essential task for the development various optoelectronic devices, including photovoltaics, light-emitting diodes, and photo-detectors. Spin coating is a widely used fabrication tool for lab-scale device fabrication. The uniformity and film thickness can be finely tuned by solution concentration, viscosity, and the spin-coating speed. In perovskite photovoltaic research, thin-film engineering approaches have been extensively investigated based on spin-coating methods. However, for building large devices, like solar panels at meter-scales, alternative coating methods need to be explored. And the optimal coating parameters can vary depending on the thin-film deposition mechanisms.

Here in this chapter, we will introduce the thin-film fabrication methods that are mainly used for perovskite photovoltaic development. We will first introduce lab-scale, spin-coating method for building perovskite thin films. One-step, two-step, and antisolvent processing methods are described which are popular way of making perovskite solar cells. Next, we will focus on large-scale solar cell fabrication techniques, such as spin coating, D-bar coating, chemical vapor deposition (CVD), blade coating, and slot-die coating. Among the solution-based approaches, we found that D-bar coating, blade coating, and slot-die coating are popular for building perovskite solar panels. CVD is a dry fabrication method where solvent residual

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would not be not a concern. A precisely controlled deposition rate is possible with CVD which can produce ultra-uniform layer.

2 Lab-Scale Thin-Film Fabrication

Spin coating is the most thoroughly investigated and optimized deposition method for perovskite thin-film fabrication. Briefly, a motor can rotate the substrate from a few hundred to thousands of rams per minute (RPM). Once a small quantity of precursor is dropped on the substrate, the motor starts to spin and the solvent evaporates as the spin speed increases. Once all the solvent escapes from the liquid, a solid film deposition is completed. Normally, a post-annealing step is needed to drive away all the residual solvent which also completes the perovskite crystallization. It is a prevailing approach for making small-area devices. Significant amounts of efforts are invested in thin-film crystallinity and uniformity control via spin-coating methods to produce high-quality optoelectronic devices. Since the perovskite optoelectronics typically have a thin absorber of <500 nm, making a uniform, high-quality film has a direct impact on the efficiency of the devices. Because 3D and 2D perovskites have different transport properties, different film-making strategies are employed. The next sections will introduce the different ways of making high-quality films for each structure.

2.1 3D Perovskite Thin-Film Deposition

The main challenge of making 3D perovskite thin film is obtaining full coverage, high degree of crystallinity, large grain size, and low surface roughness. If defects are not a concern in the thin film, once the correct perovskite phase is fully converted delivering the expected optical band gap and the film is uniformly produced with a low surface roughness (< 10 nm), the solar cells made with these films should output a high-power conversion efficiency. In reality, the pin hole, defects, and grain boundaries often play deterministic roles in the final performances. A perovskite thin-film device is typically made in a "sandwich" device architecture (Fig. 1a) where two doped contacts (called selective contacts) are placed on each side of the intrinsic perovskite layer forming a p-i-n junction. Thin metal films are deposited on top of the selective contacts serving as the metal leads for current signal readout. If a single pin hole is present in the film as illustrated in Fig. 1b, the current will directly flow between the top and bottom electrodes causing a current leakage in the diode.

To eliminate the pin hole problem, extensive thin-film fabrication methods have been reported. The most straightforward method is to directly coat perovskite precursor on the substrate. The precursor contains lead iodide (PbI_2) and organo-halide salt (e.g., methylammonium iodide, MAI) in a common organic solvent, such as

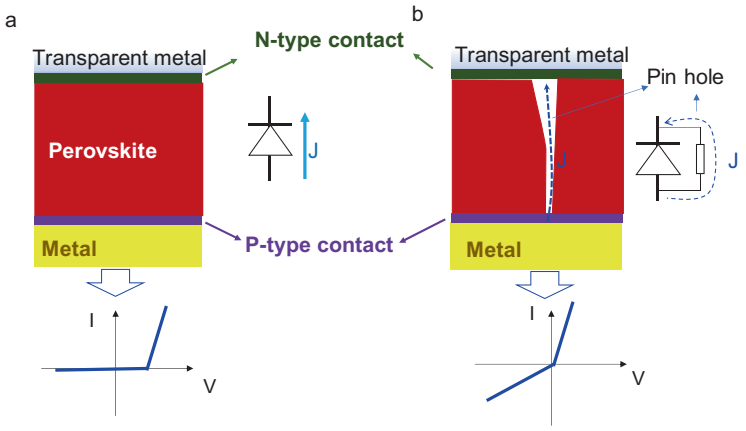

Fig. 1 Schematic illustration of an ideal thin-film device (a) and a device with pin hole (b). Their corresponding typical current-voltage characteristics are drawn below

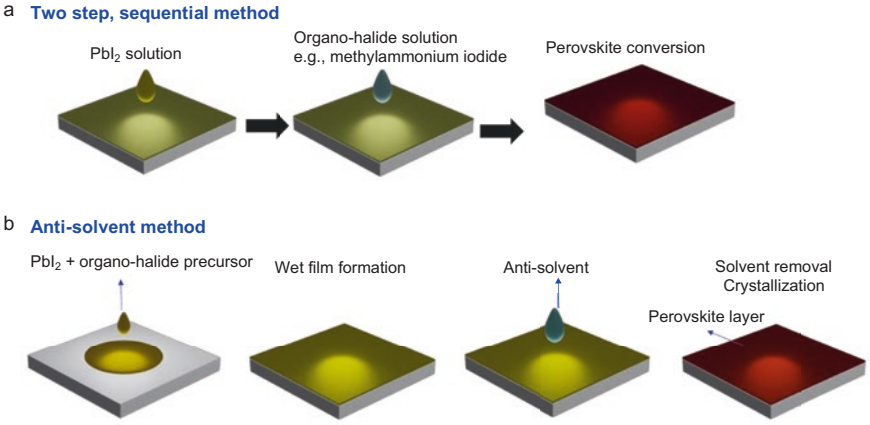

Fig. 2 Schematic illustration of the (**a**) two-step coating method and (**b**) antisolvent spin-coating method for producing uniform perovskite thin films

dimethylformamide (DMF), dimethyl sulfoxide (DMSO), or other polar solvents. Upon solvent removal, PbI_2 makes contact with MAI for perovskite phase conversion, and the perovskite crystalline grains start to grow. However, this method lacks control over the nucleation and reaction rate which often yields porous films. To circumvent this problem, more coating methods have been explored. The next method is called a "two-step" [1] fabrication approach as illustrated in Fig. 2a. In brief, PbI_2 solution is first coated on the substrate producing a pure PbI_2 thin film. After drying, an organo-halide precursor dissolved in a different organic solvent (usually an alcohol) is coated on the PbI_2 forming a double layer. A post-annealing step is performed after the two-step coating, promoting the perovskite phase

conversion in the wet film. And the annealing step also promotes a larger grain growth in the solid phase. This method will allow more control over the reaction and crystal growth rate in solid phase, yielding more uniform coating.

Another popular method that is currently widely employed is called "antisolvent" method. This approach is illustrated in Fig. 2. Briefly, a perovskite solution is first dropped on the substrate and spin coating starts. After the initial spinning stage, the precursor spreads over the substrate, and part of the solvent gets vaporized leaving a wet film. At a certain time stamp, an antisolvent that does not dissolve the perovskite precursor nor coordinate with the materials is quickly dropped onto the wet film. The antisolvent extracts the residual solvent that initiates the crystallization. After the spin-coating process, a post-annealing step is necessary to further promote the crystalline grain to grow. A variety of antisolvents have been investigated, most commonly used antisolvents include ether, toluene, chlorobenzene, etc. [2–5]. A proper choice of antisolvent is critical for making high-performance solar cells.

It is worth mentioning that to achieve the best film quality, a solvent additive such as DMSO is often added in the perovskite precursor in the "antisolvent" method. DMSO coordinates with the lead iodide in the precursor that retards the crystallization rate which is the key to fabricate uniform layers [6]. However, the DMSO-additive coupled with antisolvent method also possesses a narrow time window of producing high-quality film [7]. Specifically, the antisolvent must be dripped at a precise time stamp, i.e., 5–10 seconds after the high-speed coating starts. Once missing this time window, a porous structure can be produced which will harm the device performance [5, 8]. Although the antisolvent engineering and the two-step sequential solution deposition have been widely studied to realize the fabrication of high-performance small-area devices, these two approaches are not necessarily compatible with the high-throughput thin-film fabrications. For instance, the narrow time window of dripping the antisolvent can be a problem when producing larger panels. If the antisolvent does not arrive everywhere on the panel all at the desired time stamp, then high-quality film is not deposited through the full area of the panel. The resulting power conversion efficiency of the solar panel is capped by the poorest sub-cell.

To widen the time window, Zhao et al. [2] attempted to vary the DMSO ratio in the precursor which tuned the time window up to 25 seconds. They attributed it to the intermolecular hydrogen bonding forces in the precursor introduced by adding more DMSO that widened the time window. Similar fine tuning is reported by Chen et al. [9] and many others. Huang et al. reported an alternative solvent additive [5]; instead of using DMSO, the team used sulfolane as the retarding solvent. In this case, sulfolane coordinates with the organo-halide which further slowed down the reaction rate. As a result, the antisolvent dripping window was widened to over 90 seconds after spin coating. This allowed the team to fabricate a perovskite mini-module with a simpler dip-coating method with a high-power conversion efficiency over 16%. Other solvent additives like tert-butyl alcohol [10], 1,4,7,10,13,16-hexaoxacyclooctadecane [11], and others have been explored.

Apart from room temperature coating method, Nie et al. discovered a "hot-casting" method to fabricate crystalline layer with large grains. In particular, the team first preheated the perovskite precursor solution and substrate to coat perovskite thin films, which can produce high-quality, mm-scale large-grain perovskite thin films for reproducible perovskite solar cells [12–16]. This method also turned out to be useful for 2D perovskite thin-film deposition that will be elaborated in the next section.

2.2 2D Perovskite Thin-Film Fabrication

In 2016, Tsai et al. reported nearly single-crystal thin-film growth with controllable orientation for 2D lead halide perovskite materials [17–20]. Interestingly, the hot-cast 2D film showed near single crystalline crystal structures in the film, which is accompanied with a preferential orientation. Controlling the crystal alignment is essential to facilitate the charge transport, suppress the carrier recombination in the semiconductor, as well as improve the device operation stability under light and humidity conditions [17, 21, 22]. In this work, the crystal orientation and crystallinity of the 2D perovskite materials have been characterized by the powerful synchrotron grazing incidence wide-angle X-ray scattering (GIWAXS) [17, 18, 20, 23, 24].

Besides the temperature control, many other methods have been explored to fabricate 2D perovskite thin films with preferential orientations. Additives like molten salt and ammonium chloride have been added to the precursor which assisted the pure phase, vertically aligned 2D crystal growth in the thin film [25–28]. More recently, Chen et al. utilized strain engineering for epitaxial stabilization of halide perovskite thin films, which exhibit enhanced semiconductor device performance [29]. These studies have clearly shown that the quality of the grown perovskite crystals would greatly impact both the stability and performance of the optoelectronic devices.

3 Large-Scale Thin-Film Fabrication

To commercialize the perovskite photovoltaics, large-scale coating methods are needed to build panel scale (m^2) solar modules. While many mini-modules were produced by spin-coating methods, an issue that may result from the spin-coating process is the possible inhomogeneous crystalline structures as the device area increases. To address the inhomogeneity issue, the additive strategy, which can dramatically reduce the surface-property fluctuation, was developed. For example, an upscalable spin-coating manufacturing of perovskite module was found to be enabled by the NH_4Cl-additive strategy, and the high PCE values of 16.35% and 12.14% for modules with active areas of 22.4 cm^2 and 91.8 cm^2, respectively, were successfully demonstrated.

Besides the spin-coating process, D-bar, blade, and slot-die coating are solution-based deposition techniques that are compatible with continuous high-throughput thin-film fabrications. These methods are required for larger-scale (i.e., a few meter squares) panel manufacturing yielding an ultra-high uniformity. As a result, many research groups have tried to optimize this process and develop robust procedures for the fabrication of uniform and large-area perovskite thin films. For these techniques, solvent engineering is found to be crucial for realizing the deposition of a high-quality perovskite film. Besides, the air-knife technique, which enables the fast removal of the residual solvent during thin-film deposition, was also essential because it can significantly improve the film uniformity.

Among all the functional materials used in the module, forming a uniform thin film with desirable properties has been the most challenging for the light-harvesting perovskites. Although the antisolvent engineering and the two-step sequential solution deposition have been widely utilized to realize the fabrication of high-performance small cells, these two approaches are not necessarily compatible with the high-throughput thin-film fabrications.

Spin coating has been the most thoroughly investigated/optimized manufacturing process for perovskite thin-film fabrications. Therefore, it is still a preferable approach for making perovskite mini modules (e.g., modules with a photoactive area ≤ 25 cm^2). The main issue of the spin-coating process is that it results in a rougher and more inhomogeneous perovskite film comparing to those deposited via vapor depositions. In a study conducted by Tong, G. et al. [ref 3], the surface potential mappings obtained from $Cs_{0.05}FA_{0.54}MA_{0.41}Pb(I_{0.98}Br_{0.02})_3$ films fabricated via the two-step spin-coating process and thermal evaporation were compared. According to the Kelvin probe force microscopy (KPFM) images shown in Fig. 3a, the spin cast perovskite film has a more significant potential fluctuation (21.3 mV) than the thermal evaporated film (17.92 mV). To overcome the inherent surface inhomogeneity, Tong, G. et al. have developed an additive strategy to modify the surface morphology of the spin cast film. They demonstrated that if NH_4Cl additive was introduced into the perovskite precursor, the uniformity of the resultant perovskite film would be remarkable improved, yielding the smallest potential fluctuation (9.81 mV). An upscalable fabrication of perovskite module was therefore enabled by the additive strategy, as evidenced by the active area PCE of 16.35% and 12.14% for designated module area of 22.4 cm^2 and 91.8 cm^2, respectively.

D-bar coating is a solution-based deposition technique that is compatible with continuous high-throughput thin-film fabrications. Accordingly, many research groups have tried to replace the spin-coating process with the D-bar coating technique. In a recent study, Lim, K.-S. et al. successfully demonstrated a perovskite mini-module with an impressive PCE value of over 17% based on the D-bar coating technique. They verified that the key to successfully forming a high-quality $(FAPbI_3)_{0.875}(CsPbBr_3)_{0.125}$ film via D-bar deposition is introducing the Lewis base hexamethylphosphoramide (HMPA) additive into the precursor solution. Figure 3b shows the optical microscopy (OM) images obtained from the wet precursor films after different drying times. If dimethylformamide (DMF) was the only solvent used to prepare the perovskite ink, formation of the large precipitates would be

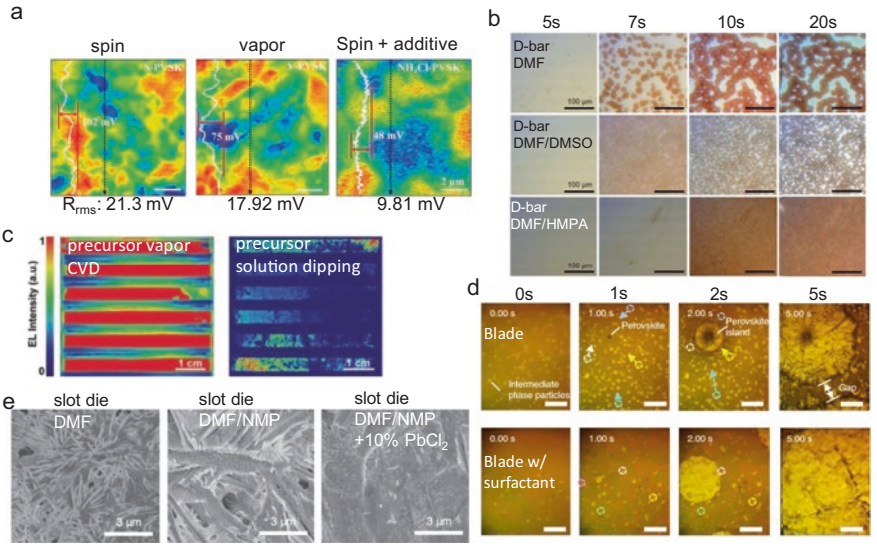

Fig. 3 Morphologies of perovskite thin films fabricated with scalable deposition tools. (**a**) KPFM mapping images showing surface potential fluctuations of the spin-cast and vapor-deposited perovskite films. The introduction of NH_4Cl additive was found to decrease the surface potential roughness from 21.3 mV to 9.81 mV, leading to the smallest surface potential fluctuation. [#3] (**b**) In situ OM images of wet precursor films deposited using the DMF, DMF/DMSO, and DMF/HMPA solutions. The island crystal growth was suppressed by the utilization of DMF/DMSO mixed solvent and eliminated by introducing the HMPA additive. [#8] (**c**) EL mapping images obtained from perovskite modules utilizing CVD and dip-cast perovskite films. The uniformly saturated EL signal in the sub-cell area confirmed the superior quality of the large-area CVD perovskite film. [#12] (**d**) In situ OM images acquired from the blade-cast perovskite films without and with surfactant. The introduction of the LP surfactant was found to remarkably increase the uniformity of the blade-cast film. [#30] (**e**) SEM images of the slot-die cast perovskite films using the DMF, DMF/NMP, and DMF/NMP with excess $PbCl_2$ inks. [#6] Fig. 3(**b–f**) was acquired from the original figures in the references and modified/reprinted with permissions

observed within 7 s. The large precipitates would subsequently lead to significant pinhole areas in the final perovskite film. It was also discovered that the pinhole density could be remarkably decreased by the utilization of DMF: dimethyl sulfoxide (DMSO) mixed solvent. Nevertheless, if a pinhole-free perovskite film is desired, introducing the HMPA additive into the solution would be required so the HMPA molecule could form a stable adduct intermediate phase with the precursor. The film uniformity was found to be dramatically improved due to the presence of the adduct intermediate phase. As a result, by using the HMPA-additive precursor, the D-bar coating technique had enabled the fabrication of a 17% perovskite mini-module with device area up to 25 cm^2.

Another promising perovskite thin-film deposition technique is chemical vapor deposition (CVD) that takes the advantage of forming perovskite films using vaporized precursors. Unlike the thermal evaporation process, which is another