Moving away from the high-performance achievements in organometal halide perovskite (OHP)-based optoelectronic and photovoltaic devices, intriguing features have been reported in that photocarriers and mobile ionic species within OHPs interact with light, electric fields, or a combination of both, which induces both spatial and temporal changes of optoelectronic properties in OHPs. Since it is revealed that the transport of photocarriers and the migration of ionic species are affected not only by each other but also by the inhomogeneous character, which is a consequence of the route selected to deposit OHPs, understanding the nanostructural evolution during OHP deposition, in terms of the resultant structural defects, electronic traps, and nanoscopic charge behaviors, will be valuable. Investigation of the film-growth mechanisms and strategies adopted to realize OHP films with less-defective large grains is of central importance, considering that single-crystalline OHPs have exhibited the most beneficial properties, including carrier lifetimes. Critical factors governing the behavior of photocarriers, mobile ionic species, and nanoscale optoelectronic properties resulting from either or all of them are further summarized, which may potentially limit or broaden the optoelectronic and photovoltaic applications of OHPs. Through inspection of the recent advances, a comprehensive picture and future perspective of OHPs are provided.

1. Introduction

Undoubtedly, organometal halide perovskite (OHP) materials have become one of the most appealing research topics in materials science and engineering. The desirable properties, such as appropriate direct bandgap, high absorption coefficient, balanced ambipolar charge transport, etc., enabled the solar-to-electrical power conversion efficiency of OHP solar cells to exceed 22% even before a decade has passed since their emergence, proving that OHPs can be developed into the competitors or complementary light harvesters to existing solar-cell materials.[3]

Since OHP-based polycrystalline thin films (ABX₃ where A = MA⁺ (CH₃NH₃)⁺, FA⁺ ((NH₂)₂CH⁺), B = Pb₂⁺, Sn₂⁺, and X = I⁻, Br⁻, Cl⁻) were demonstrated to realize outstanding photovoltaic (PV) cells, it is natural that researchers have first concentrated on revealing the correlation between the microstructures of OHP films and the photovoltaic performance. Following the achievement of compact films, while satisfying the undisputed prerequisite of complete coverage to forbid any photocurrent leakage, the focus has been devoted to finding out how the different nanostructures and corresponding defect structures are mutually coupled, and to reveal their influences on the behavior of photogenerated charge carriers. Since freestanding OHP single crystals have demonstrated one of the longest-lived photocarriers and outstanding diffusivity, methods to reduce the structural disorder and electronic traps have attracted significant interest, resulting in successful optical and optoelectronic properties. The insight into the nanostructures is further highlighted especially in most OHP-based optoelectronic and photovoltaic applications where thin-film technology is utilized: the aforementioned advantageous characters of OHPs guarantee high performance at sub-micrometer thickness, and, thereby, the focus has lain in controlling the lateral dimension and the grain boundaries in OHP films, which are mainly governed by nucleation, crystal growth, and grain coalescence mechanisms.

However, considering the myriad of synthetic routes suggested up to now for controlling the OHP film growth, it is not surprising that it has not been possible to explain the photovoltaic performance of OHP solar cells solely from the macroscopically observed morphological features of the OHP films. It is obvious now that the inherent nanostructural properties from each specific synthetic route have veiled distinctive and anomalous history-dependent optoelectronic features, complicating the performance of the resultant device being assessed simply from the apparent topological and chemical features. These observations first invoke the need of a deeper understanding of the nature of the defects in OHP films, and, second, necessitate the examination of the optoelectronic properties on the
nanoscale, often realized in conjunction with local structural/elemental mapping, to finally resolve the nanoscopic origins affecting the PV performance. The distinguishing properties of OHP PVs, like the hysteresis in the current density–voltage ($J$–$V$) characteristics, are understood to result from the recently investigated ion/defect migration, and thereby demand sophisticated approaches with regard to both spatial and temporal resolution of the defect characteristics.

Here, we summarize the essential efforts that have been made with regard to OHP materials in the aforementioned perspectives: the efforts to elucidate the nucleation/growth kinetics of OHP films with the methods to prepare robust PVs, investigations regarding the electronic/atomistic structures of various traps/defects in OHP materials, nanoscopic characterizations affecting the OHP solar-cell operation, and thereby their further utilization for potential applications.

2. Microstructural Evolution and Electronic Disorder in OHPs

2.1. Phase Diagram and Mechanisms of Thin-Film Formation for OHPs

Various processing conditions such as precursor compositions,[2,3] additives,[4,5] deposition methods,[6–10] annealing protocols,[11,12] etc. have been applied for the deposition of OHP thin films with the chemical formula of ABX$_3$ (A = MA$^+$ (CH$_3$NH$_3$)$^+$, FA$^+$ ((NH$_2$)$_2$CH)$^+$, B = Pb$^{2+}$, Sn$^{2+}$, and X = I$^-$, Br$^-$, Cl$^-$, for common compositions of OHPs). A plethora of deposition attempts has achieved high-quality films with significant tuning of each processing condition. The underlying phase diagram will extend the understanding of the OHP microstructural evolution under various synthetic environments, and thereby enables the systematic engineering of the synthesis routes. From the pseudobinary temperature-dependent processing diagram (Figure 1a),[13] MAPbI$_3$ has an $I4/mcm$ tetragonal structure (β phase) at room temperature, and the $P4mm$ tetragonal structure (α phase) becomes stable above 60 °C owing to the reduction of the degree of distortion in the unit cell at stoichiometric composition.

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Although the high-temperature phase is commonly considered as a $Pm\overline{3}m$ cubic structure, several reports have demonstrated that the direct phase transition from tetragonal to cubic structure does not occur. Stoumpos et al. reported that the tetragonal $P4mm$ is a stable phase at 400 K with little difference in lattice parameters ($\approx 0.005$ Å) along the a- and c-axes, which is difficult to resolve.\[14\] Also, Baikie et al. showed that the X-ray diffraction pattern of MAPbI$_3$ single crystals obtained at 343 K is well indexed by tetragonal $P4mm$ and rhombohedral $R3\overline{m}$ or $R3m$ structures, which compiles accurate characterization among these structures.[15] In addition, computational results have demonstrated that the free energy increases from tetragonal $I4_1/mcm$ to tetragonal $P4mm$ to cubic $Pm\overline{3}m$ with respect to the unit cell volume (i.e., temperature rise).\[16\] To resolve the ambiguity concerning the phase transition, further study is necessary, and the utilization of high-resolution synchrotron X-ray diffraction is suggested as a possible method.[15]

In the case of PbI$_2$-rich precursors, the OHP is stable with the presence of PbI$_2$ up to the MAI composition reaching $\approx 0.2$. In the MAI- rich compositions, where the amount of intercalated species (MA$^+$ and I$^-$) increases in the corner-sharing PbI$_4$ metal halide octahedrons, the transitional phase between 2D and 3D OHP (stacked perovskite sheet (SPS)) appears near the stoichiometric composition. Further increment of the amount of MAI at temperatures below 120 °C dominantly yields low-dimensional perovskite (LDP) due to additional insertion of MA$^+$ between the metal halide layers,[17] whereas the increased evaporation rate of MAI above 120 °C results in SPS, even at a high composition of MAI. As inferred from the phase diagram, the characteristic stable near-stoichiometric perovskite phase under 190 °C allows a decent OHP thin film to be synthesized by a variety of deposition approaches.

To achieve high photovoltaic efficiencies, OHP thin films with pinhole-free optimal microstructures are prerequisite. Therefore, understanding the fundamental mechanisms of nucleation and growth of grains and coalescence is of significant importance to allow control over the film evolution. In a normal one-step solution process, which includes spin-coating and annealing, OHP films typically grow by the Volmer–Weber mode, in which the condensed phase is formed on the substrate as separate islands due to the interfacial tension, and thus a high density of nucleation is essential for a uniform film morphology.\[18,19\] According to the LaMer model, solutes in the precursor solution are expended by nucleation competitively by nucleation and growth, and increased supersaturation accelerates the nucleation rate compared to the growth rate, thereby enabling dense nucleation during the film formation (Figure 1b).\[20,21\] For the solvation of OHP precursors, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), or γ-butyrolactone (GBL) is commonly used. However, solvents of high boiling point reduce the evaporation rate and suppress the nucleation, producing a nonuniform and rod-shaped film morphology. To overcome this intrinsic problem, external approaches to augment the supersaturation, such as introducing an antisolvent for immediate precipitation,\[7,22\] increasing the substrate temperature over the solvent boiling point,\[10,23\] flowing heated gas during spin-coating,\[24\] and vacuuming for rapid solvent evaporation,\[25–27\] have been applied to enable the formation of pinhole-free and uniform thin films.

After spin-coating, thermal annealing is conducted to activate the transformation of the intermediate phase into the OHP phase or to promote grain coarsening. Thermally activated grain boundaries migrate to reduce the total Gibbs’ free energy.\[28\] As shown in Figure 1c, solid-state grain coarsening occurs, depending on the number of neighboring grains, and it proceeds until the grain size becomes comparable to the film thickness, and abnormal/secondary grain growth can occur for further coalescence.\[28,29\] Specific grains having low surface or interfacial energy can additionally grow at the expense of neighboring grains. During this intermediate stage, a bimodal distribution of the grain size is clearly observed, and, subsequently, a unimodal distribution of the lateral grain size exceeding the film thickness is achieved.\[29\] OHP thin films typically exhibit a [110] texture on a TiO$_2$ or poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS) substrate, and secondary growth is expected to occur.\[30,31\] Abnormal grain growth in OHP films has been reported for processes adopting a Cl-containing precursor.\[32\] Ostwald ripening also dominates the OHP thin-film growth through a liquid-mediated process. A compact MAPbI$_3$ film was obtained by an antisolvent dripping method at first, and an solution of either MAI or MABr in isopropyl alcohol was spin-coated onto the film, resulting in an enlarged grain morphology.\[33,34\] In solution-annealing methods, significant coalescence took place during annealing under DMF and DMSO vapor, whereas grain growth was limited in typical thermal annealing.\[35,36\] It is thought that the solvent dissolving the OHP acts as a liquid mediator promoting grain-growth processes. However, improper thermal stress after film formation induces the degradation of the perovskite film. Volatile iodine species such as MAI and HI diffuse out from the surface, resulting in the formation of PbI$_2$ during excess annealing. Therefore, the annealing temperature and time should be optimized considering the conflicting effects on the grain coalescence and perovskite decomposition.

In a two-step process, high-coverage OHP films can be attained by dipping the uniformly coated metal halide film into an organohalide solution.\[9,37\] With competition between nucleation and growth, the concentration of the MAI dipping solution controls the degree of supersaturation with the resultant nucleation density, and the final grain size estimated as

$$\ln Y = \frac{32\sigma_3^3}{3kT V_m} \left[ \frac{\chi X}{\text{ln} X - \text{ln} C_0(T)} \right] + C'$$

where $Y$ is the grain size, $\sigma_3$ is the average surface tension, $V_m$ is the volume of nuclei, $X$ is the MAI concentration, $C_0$ is the equilibrium concentration of MAI, and $C'$ is a constant.\[38\] The experimental grain sizes as a function of MAI concentration match well with Equation (1) (Figure 1d). During the dipping step, volume expansion accompanies the insertion reaction of the organohalide into the PbI$_2$ framework, which may retard the reaction and induce incomplete conversion. Actually, replacement of the pre-deposited layer of PbI$_2$ with PbI$_4$(DMSO)}
enables rapid transformation and negligible volume change, owing to the ease of substitution of intercalated DMSO molecules with the organohalide.[9] Comprehensive insights of the nucleation and growth mechanisms enable the microstructural evolution of OHP thin films to be elucidated, and therefore the processing parameters can be experimentally tuned to deposit a desirable morphology more systematically.

2.2. Effect of Microstructures on the Structural Disorders and Electronic Traps

Recombination of charge carriers is the main detrimental factor limiting photovoltaic efficiency, and the trap states stemming from deep-level defects serve as major recombination centers.[39–42] In this sense, the grain boundaries are commonly suspected to work against photovoltaics based on crystalline thin-film materials by accompanying high defect concentrations. This perspective has led to a major stream of OHP studies, which were devoted to minimizing the detrimental effect of defect-containing grain boundaries in OHPs by enlarging the grain size or providing appropriate treatments to passivate the trap sites in the grain boundaries.

Augmentation of the OHP grain size has been realized utilizing various strategies, such as the introduction of additives in the precursor solution,[43,44] posttreatment after the spin-coating step,[33,34] temperature/atmosphere control of the annealing process,[11,35,36,45] and adoption of a nonwetting substrate.[46] Figure 2a presents the enlargement of the grain size as the hydrophobicity increases through different substrates.[46] Especially in the comparison between the substrates PEDOT:PSS and crosslinked N-N′-bis(4-(6-((3-ethyloxetan-3-yl)methoxy)hexyl)phenyl)-N-N′-diphenylbiphenyl-4,4′-diamine (c-OTPD), grain growth with annealing time was more significant on the nonwetting substrate than that on the wetting one (Figure 2b). When the average grain size reaches the film thickness, grain coarsening is limited by the surface-tension-driven dragging force at the boundaries. However, growth on the nonwetting substrate can further proceed due to the reduced dragging force.

The trap density of states (tDOS) was extracted by admittance spectroscopy at each substrate,[46] and values 2–3 orders of magnitude lower were observed for the OHP film on the c-OTPD substrate than that on PEDOT:PSS, owing to the larger OHP grains and improved interfacial properties (Figure 2c). The effect of the grain size on the charge transport has been verified by comparing the photocarrier diffusion length of ≈175 μm for single-crystal OHPs with that of ≈1 μm for polycrystalline thin films, and also the carrier mobility (either electron or hole) shows values several times higher for single crystals.[47–49] These enhancements in charge transport can be ascribed to the reduced trap density in the single crystal, which is a few orders of magnitude lower compared to the polycrystalline film, as shown in Figure 2d. These results reveal the

Figure 2. Perovskite microstructures and trap density. a) The surface tension experiments of various substrates by contact angle measurement of water, and the as-grown MAPbI3 grains on each corresponding substrate. b) Grain growth of perovskite during thermal annealing at 105 °C on different substrates (PEDOT:PSS or c-OTPD). c–f) Trap density of states (tDOS) for various perovskite microstructures estimated from admittance spectroscopy. Eω represents the energy with respect to the valence band maximum. c) Comparison between MAPbI3 films grown on PEDOT:PSS and c-OTPD substrates, corresponding to the scanning electron microscopy (SEM) images in (b). a–c) Reproduced with permission.[46] Copyright 2015, Nature Publishing Group. d) MAPbI3 single crystal and thin film. Reproduced with permission.[47] Copyright 2015, AAAS. e) MAPbI3 films with and without surface passivation using a Lewis base. Reproduced with permission.[53] Copyright 2016, Wiley-VCH. f) FAPbI3 films with (blue) and without (red) Cs doping. Reproduced with permission.[54] Copyright 2015, Wiley-VCH.
potential for improving the optoelectronic quality of polycrystalline OHP thin films by applying trap-passivation strategies. In addition to the increased grain size, defect-healing strategies have been progressively investigated to passivate Pb–I antisite defects and undercoordinated Pb by forming Lewis adducts (Figure 2e)\cite{50–53}.

Also, alloying (or doping) of cations with Cs, Rb, or Na, and anions with Br or Cl has been widely introduced to reduce the structural defects (Figure 2f)\cite{54–59}. Ghosh et al. calculated the effect of Rb- and Cs-doping into FAPbI₃, confirming that doping of these smaller cations leads to improved phase stability\cite{60}. With Rb or Cs doping, the lattice parameters of FAPbI₃ were reduced with the relaxation of the inorganic bond angle (angle of Pb–I–Pb), which results from the PbI₆ octahedra tilting. Distorted inorganic cage strongly captures the cation by hydrogen bonding, leading to a stable perovskite structure, and, in addition, vibration spectra reveal that the trembling frequency of the cation was largely reduced, indicating that the bonding strength of N–H···I is increased.\cite{60}

On the other hand, anion doping with Br or Cl works in different ways. Nagabhushana et al. reported the tolerance-factor-related formation enthalpy of various OHPs with different halides.\cite{61}

Regarding the tolerance factor, MAPbI₃ is in the tetragonal structure due to the large ionic radius of the iodine. By incorporating smaller halides such as Br or Cl, the MAPbI₃ crystal structure transforms into cubic with stronger bond strengths and lower formation enthalpies, leading to stable perovskites.\cite{62}

Zheng et al. revealed that the substitution of MAbr in FAPbI₃ causes strain relaxation of the lattice, which was confirmed by using a Williamson–Hall plot. The strain relaxation reduced the lattice and increased the Coulomb interactions within the structure, suppressing the formation of structural defects.\cite{63}

Another perspective on the effect of grain boundaries is that they are inert or even helpful regarding the photovoltaic performance. Theoretical analyses suggest that Σ3(111) and Σ5(310) grain boundaries consisting of typical defects do not generate gap states.\cite{64,65} These calculations are further supported by experimental results, in which the photovoltaic performance of conductive atomic force microscopy (cAFM) at the grain-boundary region exhibits a higher value than that at the grain interior.\cite{66,67} However, major results in this field have addressed that the grain size of OHPs and passivating the grain-boundary-related defects by doping or posttreatment improve the charge transport, recombination properties, and the resulting solar-cell efficiency.\cite{68,69,70,71}

Therefore, the efficacy of reducing the grain boundaries can be considered positive for outstanding cell performances. Furthermore, even though the absence of defects serving as deep traps within the MAPbI₃ bandgap has been argued, other studies have suggested that a grain-boundary-assisted detrimental effect on the photovoltaic performance can be established even without forming deep trap sites. It has been reported that shallow trap states form near the valence-band maximum (VBM) of MAPbI₃, prohibiting hole diffusion, which can be relieved by inclusion of Cl at the grain boundaries.\cite{64,72}

More recently, Long et al. argued that, at the grain boundaries of MAPbI₃, the nonadiabatic coupling between electron–phonon pairs is increased and the bandgap is decreased, creating fast recombination paths at the grain boundaries, which also can be recovered by Cl inclusion by spatially separating the highest occupied molecular orbital (HOMO) wavefunctions from those of the lowest unoccupied molecular orbital (LUMO).\cite{70} These reports imply that, even though grain boundaries can be beneficial for a photovoltaic performance given their benign properties, such can be realized only by appropriate strategies to mediate possible deficiencies.

To deal with the atomic origin of defects in OHP thin films, there have been various theoretical studies calculating the effects of point defects on the electronic disorders. Typical MAPbI₃ can have vacancies of VMA, VPb, VI, interstitials of MA, Pb, and I, and antisite defects of MAPb, MAZ, PbMA, PbI, MA, and IPb. Figure 3a exhibits the representative charged vacancies in the crystal structure,\cite{73} and the transition level of each point defect enables whether it acts as a deep trap, a shallow trap, or a dopant to be determined (Figure 3b).\cite{74}

Also, the equilibrium defect density can be deduced from its formation enthalpy (ΔH) as a function of the Fermi energy (E_F) (Figure 3c). The common consequence of theoretical calculations from numerous groups is that most point defects act as shallow states, and deep level defects have high formation enthalpies.\cite{75–78} These results are consistent with the experimentally observed stable electronic structure in MAPbI₃ even for the 1/Pb ratio down to 2.5\cite{79} and elucidate the high open-circuit voltage of solar cells approaching the bandgap in spite of the polycrystalline nature of OHP thin films.\cite{80}

The role of intrinsic defects on the unintended doping in perovskites is an intriguing feature that significantly affects the photovoltaic ability. Shallow point defects having in-gap states near the band edge can act as dopants at room temperature (~25 meV). Theoretical calculations have suggested that the major acceptors are Ii, MAPb, VMA, and VPb in an I-rich growth condition, and donors are MA, VI, and MA in a Pb-rich growth condition, with their low formation energies in the MAPbI₃ phase.\cite{81,82} Therefore, the majority of carrier type should be changed depending on the growth conditions of the perovskite film. In experimental studies, Wang et al. showed that the doping type and concentration of dopants can be altered by controlling the ratio of PbI₃ and MAI in the precursor.\cite{83} In MAI-rich conditions, the perovskite film exhibits p-type behavior due to VPb, which has a lower formation energy than other possible point defects like MAI and VI, while VI contributes an n-type property in PbI₂-rich conditions, which is confirmed by Hall effect measurements and ultraviolet photoelectron spectroscopy. It is worth noting that each growth condition is not exactly identical to the ratio of PbI₂ and MAI in the precursor.

Furthermore, the doping type is changed from p- to n-type after thermal annealing at 150 °C for 45 min in the case of an MAI-rich precursor, since MAI becomes deficient upon annealing. Similar results have been reported by Song et al., showing that the changes of doping type and concentration in sequentially deposited perovskite films depend on the annealing temperature.\cite{85}

The perovskite has a p-type property owing to intrinsically MAI-rich growth condition in the sequential deposition where the postannealing temperature is lower than 60 °C. On the other hand, it intrinsically exhibits n-type behavior with increased annealing temperature, since the removal of MAI at high temperature gives rise to Pb-rich conditions.
This unintentional doping influences the photovoltaic performance by altering the work function of the perovskite, affecting the built-in potential at the interface, which manages the transport and separation of charge carriers in the device, and by increasing the number of scattering centers, which reduces carrier mobility.\textsuperscript{[80,81]} However, it is challenging to deduce a correlation between the doping type/concentration and the photovoltaic properties experimentally, while other parameters such as the grain size and crystallinity of the perovskite remain constant. Furthermore, changes in the type of point defect (intrinsic dopant) and their density affect the ion-migration kinetics, resulting in different $J$–$V$ hysteresis in solar cells, which will be further discussed in Section 3. For example, Yu et al. reported that devices from MAI-excess conditions show a lower hysteresis index compared to stoichiometric and PbI$_2$-rich cells, owing to the reduced concentration of V$_{\text{MA}}$, which facilitates migration of iodine ions.\textsuperscript{[82]}

On the other hand, low defect-formation energies with considerable deep trap density are calculated for I$_{\text{Pb}}$, V$_i$, and Pb$_i$ in Pb-rich growth conditions and I$_{\text{MA}}$, Pb$_i$, and I$_i$ in I-rich conditions.\textsuperscript{[74,77,83]} Several researchers have proposed that the ionic nature of MAPbI$_3$ gives rise to the absence of gap states within the bandgap for Schottky disorder (PbI$_2$ and MAI vacancies) and dopants from Frenkel defects.\textsuperscript{[73,75,76]}

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**Figure 3.** Atomic defects and electronic traps in MAPbI$_3$. a) Calculated PbI$_6$ octahedral framework in MAPbI$_3$, containing charged MA$^+$, Pb$^{2+}$, and I$^-$ vacancies. The corresponding vacancy site is shown in black for each case. Reproduced with permission.\textsuperscript{[73]} Copyright 2015, Wiley-VCH. b) Energy levels of defect states for vacancies (V$_{\text{Pb}}$, V$_i$, and V$_{\text{MA}}$), interstitials (Pb$_i$, I$_i$, and MA$_i$), and antisites (Pb$_i$ and I$_{\text{MA}}$), with their neutral and charged states in MAPbI$_3$. c) Defect-formation energy as a function of Fermi level for iodine-rich (left) and iodine-poor (right) growth conditions, between the valence band maximum (VBM) and conduction band minimum (CBM). b,c) Reproduced with permission.\textsuperscript{[74]} Copyright 2014, American Chemical Society.
On the other hand, Agiorgousis et al. have reported that Pb cations and I anions located in the neighborhood of some intrinsic defects exhibit relatively strong covalent behavior to form Pb dimers (with V I\(^+_1\), Pb I\(^+_2\), and Pb\(_{\text{MA}}\)\(^+_1\)) or I trimers (with I\(_{\text{MA}}\)\(^-_2\)), which contribute to the undesired deep traps.\(^{[77]}\) Uratani et al. examined the chemistry of surface defects in MAPbI\(_3\) with different stoichiometries and types of dominating terminations, reporting that the I-rich condition is less desired due to the lower formation energy for deep traps.\(^{[83]}\) Even though correlating the behavior of specific defect sites with the photovoltaic performance has not been fully achieved, theoretical studies provide insight toward improving the synthetic routes for OHP absorbers by minimizing the recombination sites and/or the actions of them.

3. Photoinduced Charge Carrier Dynamics in OHPs and Nanoscopic Characterization

3.1. Transport and Recombination of Photocarriers in OHPs: General Features

It is known that OHP materials are able to solely serve as a medium through which photogenerated carriers can individually be conveyed to each carrier-selective contact.\(^{[84]}\) This feature distinguishes OHP photovoltaics from the dye-sensitized solar cells from which prototype OHP photovoltaic cells were derived, where the monolayer of organic dye molecules and the photoelectrode serve, respectively, as the light absorber and the electron pathways, further emphasizing the importance of the photoanode architecture in nanostructural engineering for effective light harvesting.\(^{[85–88]}\) Current OHP photovoltaic cells operate based on the OHP light-absorber layer with a thickness of hundreds of nanometers with ambipolar carrier transport within OHPs. Accordingly, understanding the diffusion and the drift characteristics of photogenerated charge carriers in OHP films has become a subject of paramount importance, as knowledge of them should pave the way to further enhancing the charge collection from OHP materials.

In such a perspective, researchers have focused on the effect of composition, crystallinity, defects, etc. on the charge-carrier diffusion in OHP films. The diffusivity ranging from 0.05 to 10 cm\(^2\) s\(^{-1}\) for thermalized carriers and that of \(\approx 450\) cm\(^2\) s\(^{-1}\) for energetic hot carriers have been reported.\(^{[47,84,89–95]}\) Guo et al. measured the temporal evolution of a laser-pump-induced Gaussian population of photocarriers by transient absorption microscopy imaging techniques, estimating a diffusion coefficient of \(< 0.08\) cm\(^2\) s\(^{-1}\) and a diffusion length of \(\approx 1.2\) µm.\(^{[89]}\) Hill et al. reported nearly constant ambipolar diffusivity between 0.74 and 1.77 cm\(^2\) s\(^{-1}\) at photocarrier densities between \(\approx 10^17\) and \(\approx 10^19\) cm\(^{-3}\), with a significant domain-to-domain variation over a 10–100 nm scale.\(^{[91]}\) It was also reported by confocal photoluminescence microscopy by Handlos et al. that higher diffusivity up to 5–10 cm\(^2\) s\(^{-1}\) can be observed with OHP films that have undergone light soaking, probably due to the photoinduced filling of trap-like carrier-quenching sites.\(^{[95]}\) For single-crystal OHPs having a low density of grain boundaries, the carriers generated inside the bulk of the crystal exhibited lifetimes of around microseconds by optical analyses, with values exceeding 100 µs from impedance spectroscopy measurements.\(^{[96,97]}\) Magneto-optical analyses revealed that the exciton binding energy and reduced effective mass of orthorhombic MAPbI\(_3\) are independent of grain size (\(\approx 16\) meV and 0.102–0.109m\(_0\), respectively, for grain sizes in the range between tens of nanometers and sub-micrometers), further emphasizing the importance of photocarrier kinetics for optoelectronic and photovoltaic applications.\(^{[98]}\)

The effects of surface/interface, phonon/impurity, and/or polarizations (by organic molecule/noncentrosymmetric inorganic frameworks) on the carrier dynamics have been studied in depth.\(^{[99–103]}\) Importantly, it has been reported that the polycrystalline character limits the diffusivity. Random diffusion of carriers is influenced by structural disorder, like grain boundaries and charged defects, which causes scattering with a corresponding length of \(\approx 0.1\) nm and also trapping by recombination.\(^{[47,89,91,92]}\) Figure 4 shows the variations in the optoelectronic response from OHP films by controlling the grain size or composition in MAPbI\(_3\).\(^{[59,104]}\) Grains with high crystallinity guarantee the reduction of scattering centers, and cAFM with noise analysis was utilized to characterize the nanoscale behavior of photogenerated carrier transport with controlled applied bias and/or light.\(^{[105–107]}\) Increase in the grain size by the MAI-excess precursor actually enhanced the photovoltaic performance, with improved photocurrent at short-circuit conditions, as shown by the mapping images in Figure 4a.\(^{[104]}\) Dependence of photocurrent on each grain boundary is highly complicated due to several factors, such as dangling bonds, active channels for ion/defect migration, band bending from chemical doping, and passivation by a segregated second phase with a different energy level.\(^{[106,108,109]}\) The power spectral density for noise quantification is proportional to the trap density along the carrier path,\(^{[105,106]}\) and the photocurrent noise with \(1/f\) behavior indicates that the carrier transport in OHPs is influenced by multiple isolated traps. The reduction of noise and thereby the decrease of trap density was clearly observed for the cases of increased grain size and Cl incorporation, as shown in Figure 4b,c, respectively.\(^{[59,104]}\) It was reported that the introduction of Cl led to an order-of-magnitude increase in diffusion length, i.e., from \(\approx 100\) nm to \(\approx 1\) µm, of the photoexcited electrons, and such a beneficial role is expected to originate from the decreased nonradiative recombination, even with a few atomic percent of Cl.\(^{[70,110,111]}\) By utilizing cAFM and noise-mapping techniques combined with structural analyses, direct evidence for the effects of nanostructures, polarization, phonon scattering, etc. on the carrier transport can be obtained.\(^{[101,106,112]}\)

In addition, diffusivity, lifetime, and trap density have shown inhomogeneities among grains. Even at an identical composition, the nanoscale optical inhomogeneity, either lateral (grain-by-grain variation) or vertical (from surface to bulk), is attributed to the spatial variation of disorder and trap densities.\(^{[108,113,114]}\) Furthermore, the polycrystalline character of OHPs results in different photocurrent and open-circuit voltages among the grains, leading to facet-dependent photovoltaic performance.\(^{[103]}\) The distinctive local performance among different grains is attributed to the crystal orientation-dependent defect concentrations and the effective masses of the electrons/holes. Similar changes of effective masses and dark drift
currents are linked to the orientation-dependent polarization regarding the electronic structure of OHPs, i.e., the alignment of methylammonium ions and the concomitant displacement of lead ions relative to the iodine octahedrons by the electric field.\[^{103}\] Different photocarrier kinetics by distinctive measurement techniques should be considered for understanding the diffusion parameters, for example, the different depth profiles of carrier-generation rates by the incident photon energy, which may result in different recombination kinetics of photocarriers, different charge-injection efficiency at the metal electrode for electronic analysis, and so on.\[^{96,97}\] Anyway, the observation of grain-by-grain differences has led to a common conclusion that varying OHP qualities by different preparation pathways for distinctive crystallographic orientations, trap densities, spatial inequality of additional ions, etc. are the origins of such inhomogeneities, further necessitating nanoscale approaches for understanding photocarrier dynamics.\[^{71,103,104,110,114}\]

Figure 4. Optoelectronic properties by controlling grain size and composition. a) Topography (left column) of MAPbI\(_3\) films synthesized either from PbI\(_2\):MAI = 1:1 (upper row) or nonstoichiometric 2:3 (lower row) for grain-size and defect control, and the corresponding photocurrent at 0 V under 80 mW cm\(^{-2}\) illumination obtained from conductive atomic force microscopy (cAFM) (middle). Local photocurrent variations along the perovskite microstructures of the white straight lines, with the grain boundaries marked by pink dashed lines in the height/photocurrent profile (right). b,c) Current-normalized power spectral densities (S/I\(^2\)) for the quantification of photocurrent noise. The reduced 1/f noise by the incorporation of iodine (in (b)) or chlorine (in (c)) is clearly observed, confirming the decreased defects of recombination centers for the perovskites. The inset in (b) is the photocurrent as a function of time for the analysis of noise spectroscopy by cAFM. a,b) Reproduced with permission.\[^{104}\] Copyright 2016, American Chemical Society. c) Reproduced with permission.\[^{59}\] Copyright 2016, Elsevier.
conductors demands consideration of the unexpected physical/chemical parameters. The photoinduced giant dielectric constant, dipole alignment change of organic cation under light/bias, light-induced diffusion-length alteration, photoluminescence, etc. all have potential contributions to the optoelectronic/photovoltaic properties in OHPs.\(^{[115–121]}\)

### 3.2. Photoinduced Phase Separation and Ion Segregation in OHPs

Photoinduced phase separation is commonly observed in mixed-cation and/or mixed halide OHPs, for example \((\text{Cs}_x\text{FA}_{1-x}\text{MA}_{2-x-y})\_\text{Pb}_x(\_\text{Br}_z\_\text{I}_{3-x-y})_\text{I}_{3-y}\), where the mixing entropy contribution stabilizes mixed-cation/anion-based OHPs by compensating the energetic penalty of different atomic radii between constituents. The transition temperature from the photovoltaic-applicable and high-temperature-stable \(\alpha\) phase (trigonal FAPbI\(_3\)) to \(\delta\) phase (hexagonal) is therefore reduced by approximately 200–300 K from structural and thermodynamic arguments, leading to a homogeneous solid solution.\(^{[122]}\)

Interestingly, Hoke et al. reported the photoinduced reversible phase separation of MAPb\(_{1-x}\text{Br}_x\_\text{I}_{3-x-y}\) into MAPb\(_{1-x}\text{Br}_x\_\text{I}_{3-y}\) phases, and Brivio et al. proposed the corresponding phase diagram of I–Br OHP exhibiting a miscibility gap from thermodynamic calculations.\(^{[123,124]}\)

Beal et al. showed the photoluminescence peak shift in the phase-separated \(\text{CsPb}(\_\text{Br}_{z-x}\_\text{I}_{x})_3\) with \(x > 0.4\).\(^{[125]}\)

Wang et al. utilized the spinodal decomposition and resultant coarsening of I- and Br-rich phases in MAPb\(_{1-x}\text{Br}_x\_\text{I}_{3-y}\) for the development of epitaxial perovskite heterostructures, and showed that the phase separation did not originate from heating by photon absorption.\(^{[126]}\) Other studies, such as phase evolution through aging under inert/dark conditions with reduced disorder and increased crystallinity by Sadhanala et al.\(^{[127]}\) identification of different timescales for halide segregation under illumination (less than a minute) and its recovery in dark conditions (for a few minutes) by Yoon et al.\(^{[128]}\) et al. have evidently implied the dynamic equilibrium of OHPs under specific environments with concurrent variations of material properties.\(^{[129]}\)

**Figure 5a,b** represents the phase separation in \((\text{FAPbI}_3)_{0.85}\_\text{MAPbBr}_3\_0.15\) into I- and Br-rich phases using the state-of-the-art nanoscale elemental-mapping technique by secondary-ion mass spectroscopy (SIMS) with 10 nm lateral resolution.\(^{[130]}\)

I-prevalence spots with sizes of at least 100 nm were observed, as shown in the elemental map of Figure 5b, and the possibility of these spots indicating PbI\(_2\) was excluded as the carbon spots originating from organic cations in OHPs were found in the same locations. This inhomogeneity was further demonstrated by mapping the photoluminescence peak, and a peak shift of \(+10\text{ nm} (0.02\text{ eV})\) was observed between domains, which were averaged by a diffraction-limited spot size of 300 nm, further supporting the halide redistribution in the range of a few hundred nanometers. They suggested that the segregation of \((\text{FAPbI}_3)_{0.85}\_\text{MAPbBr}_3\_0.15\) resulted in three phases: \((\text{aFA}_{x}\text{MA}_{1-x}\text{PbI}_3) + \text{bFA}_{x}\text{MA}_{1-x}\text{PbL}_{1-x-y}\_\text{I}_{y} + \text{cFA}_{x}\text{MA}_{1-x}\text{PbBr}_{1-x-y}\_\text{I}_{y}\) where \(b\) dominated while \(a \neq 0\) and \(c = 0\) (probably from the resolution limitation of SIMS). Interestingly, a high work function (deeper Fermi level) corresponding to the low contact potential difference (dark spot which was \(+0.1\text{ eV}\) lower than the average value among the grains from Kelvin probe force microscopy, as shown in Figure 5c) led to the high photovoltage under illumination.

The exact match of the high work function of these nanodomains to the work function at the MAPbI\(_3\) surface indicated phase separation into \(\text{FA}_{x}\text{MA}_{1-x}\text{PbI}_3\) on the surface of \((\text{FAPbI}_3)_{0.85}\_\text{MAPbBr}_3\_0.15\). The high photovoltage in the I-rich perovskite was attributed to the accumulation of photogenerated holes, which was supported by the establishment of energy levels between MAPbI\(_3\) and MAPbBr\(_3\). The transport and accumulation of photogenerated holes into MAPbI\(_3\) from MAPbBr\(_3\) are explained by favorable valence-band alignment (\(-5.9\) and \(-5.4\text{ eV}\) vs. vacuum for MAPbBr\(_3\) and MAPbI\(_3\), respectively) while the conductance-band levels are similar (\(-3.7\) and \(-3.6\text{ eV}\) for MAPbBr\(_3\) and MAPbI\(_3\), respectively).\(^{[128]}\)

The observation of photobrightening in I-rich MAPbBr\(_3\_\text{I}_{x}\_\text{Br}_{1-x}\) nanocrystals (embedded in a Br-rich MAPbBr\(_3\_\text{I}_{x}\_\text{Br}_{1-x}\) matrix), which is supported by the numerical kinetic model of emission growth and decay, further demonstrated the above charge transfer between OHPs and, thereby, the funneling of optical excitation.\(^{[131]}\)

To construct a precise phase diagram and understand the experimental aspects above, strains by lattice mismatch, Coulombic interactions by electronegativity differences, photoinduced polaron formation, etc. should be further considered.\(^{[131,121,124]}\) The film composition may differ from the solution composition due to the dissimilar complexation affinity among halogen anions to Pb cations, and also the possible phase separation and/or ion segregation even in a single composition (e.g., MAPbI\(_3\)). The physical phenomena occurring in solid thin films should be investigated considering the external stimuli such as bias and light. Ion/defect migration is indicated as the origin of such anomalous behavior in various OHP-based devices, which is supported by theoretical and experimental evidence.\(^{[132]}\)

The calculated formation enthalpies of the Schottky defects in MAPbI\(_3\) are 0.14, 0.08, and 0.22 eV per defect for \((\text{VMA}^+ + \text{VBr}^- + 3\text{VI}^- + \text{MAPbI}_3), (\text{VMA}^- + \text{VI}^- + \text{MAI}), \) and \((\text{VPS}^- + 2\text{VI}^- + \text{PbI}_3)\), respectively, and that of the Frenkel defect is 0.31 eV per defect for \((\text{VI}^- + \text{I}^-)\).\(^{[132,133]}\) These values are sufficiently less than the photon energies used for various optoelectronic/photovoltaic applications, and the defect formation energy becomes smaller when the entropy contribution is included.\(^{[133]}\) The activation barriers for the diffusion of defects/interstitials are experimentally and theoretically obtained, and the results are summarized in **Tables 1** and **2**. Facile diffusion of I (either vacancy or interstitial) is expected for its lower activation barrier compared to others, and the diffusivity may be in the range of \(\approx 10^{12}\) to \(10^{14}\text{ cm}^2\text{ s}^{-1}\), with the assumption of the attempt frequency of \(\approx 10^{12}\) Hz and the molecular dynamic simulations of point defects by the random walk model.\(^{[133–139]}\)

Similar activation energies are actually driven by temperature-dependent physical quantities in various experiments.\(^{[133,134,137,140–145]}\) Variation of the photocurrent-relaxation rates at different temperatures, originating from the dynamic alteration of energy levels, reveals an activation energy of 0.60–0.68 eV for \(\text{VI}^-\), where the diffusional transport of iodine vacancies is studied in computational research.\(^{[134]}\)

The time-dependent charge-collection efficiency is suggested to originate from the redistribution of mobile ionic species, concomitant with the partial compensation of the built-in electric field in perovskites, i.e., the accumulation of mobile ionic species at the interfaces and the corresponding screening of the field (e.g., ionic screening).\(^{[134,135]}\)
Light-induced photoluminescence enhancement with its dependency upon temperature, which is possibly due to the photoinduced annihilation of iodine Frenkel defects, will be further discussed in the last part of Section 3.4, and suggests an activation energy of 0.19 eV for $V_{I}^{+}$. Several research reports have shown two distinctive activation energies, indicating the presence of two thermally activated fast and slow ions along their reflection in reversible photovoltaic performance decay. These ionic motions exhibit stabilization times of one for less-than minutes and one for hours respectively, which is assigned to the migration of iodine and organic cations. Besides the effect of temperature in overcoming the transition state for diffusion, the thermal stress-induced structural changes of OHPs should be considered, in that they alter the environmental conditions of the diffusion channel, such as the lattice parameters, local dipole moment, vacancy-formation energy, and so on. It has been demonstrated that the phase transition and lattice expansion by light-induced heating (3.66% volume expansion for the tetragonal to cubic transition in MAPbI$_3$) resulted in a discontinuity of the Arrhenius plot, where it is claimed that the activation energy

Figure 5. Nanoscale elemental mapping of mixed cation/halide perovskite film. a) Secondary-ion mass spectroscopy (SIMS) with nanoscale mapping revealing the phase segregation into iodine- and bromine-rich perovskites in (FAPbI$_3$)$_{0.85}$(MAPbBr$_3$)$_{0.15}$. Typical surface image from SEM, and $^{127}$I (blue), $^{79}$Br (red), and $^{12}$C (green) mappings across 10 µm × 10 µm from SIMS. b) Overlaid images of Br and I mappings (with the magnification of the gray square) for the combined Br and I in (1) and Br alone in (2). Line profiles of I (blue) and Br (red) from the dashed lines in (1–2). Overlaid images of Br and C that exclude the possibility of pure PbI$_2$, as the origin of Br deficiency. c) Kelvin probe force microscopy (KPFM) of the perovskite surface under dark conditions (left), with suitable magnification of the square region (middle + right). Average contact potential difference (CPD) of ≈600 mV, with low CPD of the dark grain (480 mV) marked by the yellow arrow (middle). Photovoltage buildup under illumination of the grain indicated by the yellow arrow is probably due to the hole accumulation in the iodine-rich perovskite (right). The three yellow arrows are for the same position. Reproduced with permission. © 2016, American Chemical Society.
Table 1. Experimentally reported activation energies for ion migration. Values are classified by the migrating species as suggested, or assigned as unidentified (U) if the origin of estimated activation energy is not suggested in the original paper. Detailed atomistic origins of migrating species are not specified. The morphologies of examined samples (grain/particle size) and/or sample-dependent illumination conditions are accompanied (if available).

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Migrating species</th>
<th>Activation energy [eV]</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI₃</td>
<td>I</td>
<td>0.10–0.18[102] 0.137 ± 0.028[113] 0.341 ± 0.042[117] 0.314 ± 0.048[113] 0.3.0[121] 0.42 ± 0.09[103]</td>
<td>Thin film</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.19 ± 0.05[142]</td>
<td>Thin film (~760 nm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1 ± 0.001[147]</td>
<td>Thin film (~200 nm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.26 ± 0.03[144]</td>
<td>Thin film (&lt;100 nm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.21 ± 0.02[196]</td>
<td>Platelet (&gt;2 µm)</td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>MA</td>
<td>0.36 ± 0.019[141] 0.58 ± 0.045[145] 0.17 ± 0.10[119] 0.110–0.179[196]</td>
<td>Thin film</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4 ± 0.02[147]</td>
<td>Thin film (~200 nm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.27[135] 0.08[155]</td>
<td>Thin film (~300 nm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5[135] 0.14[155]</td>
<td>Thin film (~1 µm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.05[135] 0.4[155]</td>
<td>Single crystal</td>
</tr>
<tr>
<td>MAPbI₃,Cl₃</td>
<td>I</td>
<td>0.60–0.68[134] 0.55[197] 0.42–0.58[198]</td>
<td>Thin film</td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>MA</td>
<td>0.68[198]</td>
<td>Thin film</td>
</tr>
<tr>
<td>FAPbI₃</td>
<td>FA</td>
<td>≈0.22[141]</td>
<td>Thin film</td>
</tr>
<tr>
<td>MA,FAPbI₃</td>
<td>MA/FA</td>
<td>≈0.63[145] 0.43[195]</td>
<td>Thin film</td>
</tr>
<tr>
<td>MAPbBr₃</td>
<td>Br</td>
<td>0.168 ± 0.043[137]</td>
<td>Thin film</td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>I/Br</td>
<td>0.197 ± 0.04[199]</td>
<td>Platelet (&gt;40 µm)</td>
</tr>
<tr>
<td>MAPbI₃,Br₃</td>
<td></td>
<td>0.27 ± 0.06[123]</td>
<td>Thin film</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Migrating species</th>
<th>Activation energy [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI₃</td>
<td>I</td>
<td>0.05–0.08[115] 0.08[115] 0.19–0.33[116] 0.24[116]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.09–0.15[115] 0.38[116] 0.08[115] 0.32–0.45[116]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.28–0.45[115] 0.26–0.34[116] 0.1[116] 0.372[116]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.342[199] 0.29–0.30[199]</td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>MA</td>
<td>0.38–0.48[134]</td>
</tr>
<tr>
<td>FAPbI₃</td>
<td>V</td>
<td>0.84[114] 0.46[115] 0.55–0.89[116] 0.70–1.12[117]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.62–0.89[114] 0.735[200]</td>
</tr>
<tr>
<td>FAPbI₃</td>
<td>V</td>
<td>2.31[114] 0.8[115] 1.39–1.78[117]</td>
</tr>
<tr>
<td>FAPbI₃</td>
<td>V</td>
<td>0.42–0.55[116] 0.25[116]</td>
</tr>
<tr>
<td>FAPbI₃</td>
<td>V</td>
<td>0.57–0.6[116]</td>
</tr>
<tr>
<td>MAPbBr₃</td>
<td>Br</td>
<td>0.09[115] 0.20–0.46[115] 0.23[201]</td>
</tr>
<tr>
<td>MAPbBr₃</td>
<td>V</td>
<td>0.56[115] 0.80–1.13[117]</td>
</tr>
<tr>
<td>MAPbBr₃</td>
<td>V</td>
<td>1.35–1.80[117]</td>
</tr>
<tr>
<td>MAPbI₃,Br₃</td>
<td>V</td>
<td>0.456–0.522[200]</td>
</tr>
<tr>
<td>MAPbI₃,Br₃</td>
<td>V</td>
<td>0.326[200]</td>
</tr>
<tr>
<td>FAPbI₃</td>
<td>V</td>
<td>0.801[200]</td>
</tr>
</tbody>
</table>

3.3. The Effect of Ion Migration on Carrier Dynamics and Its Implications

Ions and defects move through the vacant sites in a crystal lattice, and thus the open character of grain boundaries provides an effective path for ion/defect migration in polycrystalline OHP thin films. Shao et al. examined the ion-migration channel regarding whether the grain or grain boundary is the dominant migration path, and the results are presented in Figure 6. Following identification of the grain boundary (the blue square in the topography map of Figure 6a) and the grain interior (the red triangle in the corresponding figure), the dark-current measurements at the relevant locations revealed that the hysteresis occurred at the grain boundary, whereas the grain interior exhibited negligible hysteresis (Figure 6b).

They also identified the grain boundaries as low-angle and high-angle boundaries from the surface potential map by interpreting the surface potential difference between adjacent grains as an indicator of a difference in the work function by different crystallographic directions (Figure 6c). Thereby, the grain boundary between grains with a large surface potential difference was identified as the high-angle boundary, and the low-angle boundary was also assigned similarly. Photocurrent–voltage (I–V) curves showed that the magnitude of the photocurrent hysteresis was larger at the high-angle grain boundary (Figure 6d), which was expected to have more vacancies (dangling bonds). The chemical mapping by energy-dispersive X-ray spectroscopy (EDS) demonstrated that a change in iodine concentration along the boundary occurred after the bias application between both ends of the grain boundary,
further identifying that the grain boundary is the dominant migration path. In addition, the trap densities in OHP polycrystalline films (≈10^{16} \text{ cm}^{-3}, which corresponds to one trap per ≈10^6 unit cells, compared to 10^8 to 10^{10} \text{ cm}^{-3} for single crystals) are largely dependent on the crystallization routes, and therefore the extent of ion/defect migration is dominated by the nanostructures of the OHPs\textsuperscript{[84,153,154]}. The electromigration of mobile ionic species was also influenced by light illumination.\textsuperscript{[155]} It was reported that, both for poly- and single-crystalline OHPs, light exposure promotes ion movement by more than an order of magnitude than in the dark by reducing the activation energy. This result provides an insight that light illumination also modifies the kinetics of ion/defect migration, which will be further discussed in the last part of Section 3.4.

As evidently revealed by theory and experiments, OHPs are mixed ionic/electronic conductors so that the photocurrent from optoelectronic analysis inevitably includes the contribution of the mobile ionic species directly or indirectly. Bias between the contact electrodes causes both the electronic current by photogenerated carriers and the inherent ionic current. Normally, the contacts with OHPs are ion-blocking layers (e.g., Au), such that the electronic current is initially influenced by the ion/defect movement until full accumulation of the mobile ionic species at the ion-blocking layers. Consequently, the current evolves as a function of time, exhibiting the characteristics of the initial decay or rise, depending on the bias history followed by the saturation from electronic current.\textsuperscript{[82]} The overturn of the current direction is therefore expected at short-circuit conditions. Flipping of the current direction is caused by the diffusion of the accumulated mobile ionic species at the interface toward the bulk for the concentration equilibrium: positive (negative) species which have been attracted to the cathode (anode) under the bias return into the bulk when the bias is removed.\textsuperscript{[156]} Interfacial effects have been experimentally verified by measuring the capacitance as a function of the OHP thickness.\textsuperscript{[143,157]} The capacitance corresponding to the electrode polarization does not change regardless of the OHP thickness, indicating that the low-frequency polarization (<1 Hz) of a few µF cm^{-2},

---

**Figure 6.** Ion migration along grain boundaries in a polycrystalline perovskite. a) Topography image of an MAPbI\textsubscript{3} film with the typical grain interior (red triangle) and grain-boundary (blue square) regions. b) Current–voltage curves under dark conditions obtained at a grain boundary (left) and at an intragrain (right), corresponding to the marked regions in (a). c) Height (left), amplitude (improved resolution by a tapping feedback-off mode, middle), and CPD (right) from the MAPbI\textsubscript{3} film. The average grain size in (c) is identical to that of the grains in (a). d) Photocurrent–voltage curves under white-light illumination of 20 mW cm\textsuperscript{-2} obtained at the locations indicated by the triangle, square, and circle in (c). Reproduced with permission.\textsuperscript{[152]} Copyright 2016, The Royal Society of Chemistry.
which is a corresponding scale for the electrical double-layer capacitance, originates from the interfacial mechanisms (due to the migration of mobile ionic species) rather than the bulk polarization of OHPs, while the intermediate-frequency polarization (=1 kHz) of the nF cm⁻² regime by dipolar polarization shows inverse proportion to the thickness.[143]

An electric field is formed by the accumulated interfacial mobile ionic species, and thereby they modify the built-in potential, which is originally established by the different work functions of each contact material. Interestingly, for contacts with similar or identical work functions, the holography development (p-i-n or n-i-p) in OHPs enables switchable photovoltaics through electronic manipulation near the interface by chemical doping via DC-bias poling or light-induced self-poling (LISP).[135,141,143,156,158–162] Even though the ferroelectric polarization in the OHP domain is not negligible, difficult poling at low temperatures further supports the temperature-activated defect migration, and this is the opposite aspect against the expectation of ferroelectricity enhancement at low temperatures from the reduction of thermal disorder.[159,163] (Further details regarding the photovoltaic effects in ferroelectric perovskites (beyond OHPs) can be found in ref. [164]).

Actually, various elemental and structural characterizations reveal evidence for either halide anions (or positive halide vacancies), organic cations (or corresponding vacancies), or their combined migration, with speculation of the dominant ionic-transporting species as iodine (vacancy and/or interstitial), which is further supported by low activation energies from theoretical calculations, as compared in Section 3.2 for different ionic species.[119–141,144,145,138,159,165,166] Even besides the ion/defect migration by applied bias, electron- or light-induced OHP degradation (segregation), quenching facilitated by the migration of photoexcited charges, etc., imply the existence of additional nanoscale driving forces for the ion/defect migration.[167–169] In addition to the OHP’s constituent ions, the extrinsic ions, such as H, Li, Na, etc., can diffuse across the OHP channel, and thereby have potential to modify the interfacial properties and extractability of photogenerated carriers.[170,171]

Unlike other solar cells based on dyes, quantum dots, polycrystalline GaAs, Si, etc., OHP-based photovoltaic devices significantly suffer from anomalous hysteresis, which is largely dependent on the scan direction/rates and preconditioning of illumination/bias.[172] To provide a theoretical framework for understanding the hysteresis behavior, the ion/defect migration in the bulk for the charged compositional elements, the charge (ionic/electronic) accumulation at surface/interfaces, recombination of photocarriers with accumulated charges, etc., have been considered. In this perspective, there have been efforts to explain the J–V hysteresis in the OHP-based solar cells by the superposition of capacitive current contributions both from linear capacitance (which is proportional to the voltage scan rate) and nonlinear capacitance.[157,173–175] The capacitive current derived from the interfacial charge accumulation was modeled to explain the characteristic features of hysteresis, like the current bump (at voltages between short-circuit and open-circuit conditions) and the overestimation of the short-circuit current at increased scan rates.[13,173] The hysteresis inversion, even in the same sample (inversion of J–V curves by voltage scan directions, which depends on the prepoling bias), is also supported by the capacitive term accounting for the nonlinear polarization effects.[176] It has been commonly shown that the polarization model is effective for describing hysteresis by assuming a single time constant involved with the relaxation of nonlinear polarization. The linear component (geometric capacitance derived from the dielectric polarization of the OHP itself) was argued to have less influence on the capacitive current than the nonlinear term.[143,173] The working environments of solar cells, such as light illumination and applied electric field, however, also have a potential to change the linear term of the capacitive current by modulation of the molecular orientation.[115,116]

The experimental results demonstrated that the capacitive behavior is much more severe in TiO₂/OHP/TiO₂ than in the 2,2',7,7'-tetrakis(N,N-bis(p-methoxyphenyl)amino)-9,9'-spirobirofluorene (spiro-OMeTAD)/OHP/spiro-OMeTAD structure, due to the reversible formation of Pb–I–Ti bonds at the TiO₂ interface and the irreversible redox reaction of iodide coordination to the oxidized spiro-OMeTAD.[157] This result implies that, in TiO₂/OHP/spiro-OMeTAD-based solar cells, the TiO₂/OHP interface is the major source of charge-accumulation-induced hysteresis, and the OHP/spiro-OMeTAD interface is more associated with the long-term irreversible degradation and the open-circuit voltage loss in cell performance than the hysteresis behavior.[177] Furthermore, Pockett and Carnie recently reported that OHP solar cells with a compact TiO₂/OHP/spiro-OMeTAD structure exhibit negative transient behavior in transient photovoltage measurements (i.e., initial drop of V oc upon laser-pulse incidence), which is absent for the TiO₂-free cell. They observed that the initial negative transient cannot be eliminated by using laser pulses with different penetration depths or varying the hole-transporting medium, emphasizing that accumulated charges near the TiO₂/OHP interface participating in the recombination process are responsible for the hysteresis behavior.[178] In this perspective, surface treatments of TiO₂, such as Li-doping for fast charge transfer at the interface or the replacement into other oxides to overcome the charge-transfer imbalance (e.g., SnO₂, Zn₃SnO₄, etc.), would effectively reduce the hysteresis in the J–V curve by diminishing the interfacial charge buildup.[179–181] How the kinetics of ionic constituents affect the transient behavior of photocarriers, such as electronic/ionic charge accumulation at the interface, charge trapping/detraping and surface polarization, recombination kinetics of photocarriers, etc., should still be scrutinized, possibly with a simple and universal model. Anyway, the fact is that the realization of hysteresis-free J–V curves through reducing the trap-assisted recombination at the interface/grain boundary, which occurs via trap states in the bandgap, does not guarantee the absence of ion migration in the OHP layer. This emphasizes the significance of insight on the mobile ionic species and its impact on the photocarrier dynamics, such as recombination by charged (or neutral from photocarrier capture) traps, transport by band bending at the interface, charge transfer by the injection barrier at the interface, etc., under various photovoltaic working conditions.[132,182,183]

The transport of photogenerated carriers is governed by the energy levels in OHP solar cells, and it should reflect the dynamic...
equilibrium by mobile ionic species (ions and charged defects). The proposed hypothetical energy-level models mirroring the temporal changes caused by the movement and accumulation of mobile ionic species, and the corresponding electric-field screening are supported by the photocurrent transients and the hysteresis characteristics in the $J$–$V$ relationships.[134,182,184,185] The details for the evolution of electric charge accumulation at the interface and its influence on the transient electronic current can be understood following the valley formation at the interface or the wiggly band model: just after the deposition of the hole- or electron-transport layer on the OHP (e.g., conventional TiO$_2$/OHP/spiro-OMeTAD or PEDOT:PSS/OHP/PCBM), the built-in field ($E_{\text{box}}$) is established along the OHP layer with a constant Fermi level.[159] The ionic and electronic charges respond to the $E_{\text{box}}$, so is $J_{\text{phot}}$ direction of the photocarriers is governed by the direction of $E_{\text{box}}$ at short-circuit conditions. (For clarity, $E_{\text{box}}$ is set as in the positive direction pointing from n- to p-type selective contacts, and therefore so is $J_{\text{phot}}$.) The drift direction of mobile ionic species is identical to that of $J_{\text{phot}}$ (positive $J_{\text{ionic}}$) until equilibrium is reached ($J_{\text{ionic}} = 0$), and the accumulated mobile ionic species at the ion-blocking interfaces contribute to the space-charge regions at each charge-selective contact. As a result, the field screening ($E_{\text{screen}}$) of the originally established $E_{\text{box}}$ is induced by those accumulated charges, and, accordingly, it leads to a constant potential in the middle of the OHPs, by the field formation of $E_{\text{box}}$ and $E_{\text{screen}}$ having equal magnitude but opposite directions. Thus, photogenerated electrons and holes transport by diffusion in the bulk, and drift govern the transport at each interface. Immediately after the external bias is applied ($E_{\text{app}}$, corresponding to the working condition of photovoltaics, that is, negative bias at an n-type and positive bias at a p-type contact), where the drift of mobile ionic species is negligible ($J_{\text{ionic}} = 0$), a band valley occurs near the interface since $E_{\text{app}}$ opposes the original $E_{\text{box}}$ ($E_{\text{app}}$ as negative). (The band profile resembles the tilde symbol (~), where the band summit and valley lie near the n-type and p-type interfaces, respectively.) Due to the characteristic shape, this band profile is called the “wiggly band” in results.[184] In the wiggly band, the direction of the field-induced photocarrier drift in the middle region of the OHP layer (the region between the band summit and valley) is opposite to that in the space-charge layer near the charge-accumulated interfaces. The wiggly band is maintained until the new electric field in the middle region is compensated by field-induced migration of mobile charges, and, accordingly, a plateau forms again.

Belisle et al. elaborated the temporal evolution of wiggly bands in OHPs and provided experimental proof for this phenomenon.[184] Their reasoning was that, as long as the width of the interfacial space-charge layers is sufficiently thin, most of the photocurrent would be generated within the middle region of the wiggly band and overrides that from the space-charge layers. As the direction of the drift current in the space-charge layers governs the direction of the net photocurrent in equilibrated OHP films (without bias), the above speculation predicts that a “flip” of the photocurrent direction would be measurable if the photocurrent transient were to be recorded within a sufficiently short timescale after applying a forward bias. They also estimated the thickness of the space-charge layers to account for approximately 10% of the OHP thickness (~5% at each interface) in mesoporous-TiO$_2$/MAPbI$_3$/spiro-OMeTAD architectures (~17 nm space-charge layer for 350 nm OHP). However, the width would depend on the concentration of mobile ionic species available in the OHP films, and therefore will be variable by synthetic methods. The numerical device model based on ionic theory, which concerns the ion accumulation, resultant interfacial recombination, and the formation of a photocarrier injection barrier, also accounts for the characteristics such as the S-shaped $J$–$V$ curve, the enhancement of the transient photovoltage, and the behaviors of both normal and inverted hysteresis (hysteresis inversion) in a single device.[176,185,186]

3.4. Potential Applications of Ion/Defect Migration

The demonstration of power-conversion-efficiencies exceeding 20% in OHP-based solar cells and their applications into tandem architectures with the other types of light harvesters like Si and copper indium gallium selenide (CIGS) prove that there is no concern about realizing OHP-based solar cells with sufficiently high efficiency.[31] Ion/defect migration during the operation of the solar cell, however, causes dynamic modification of the materials properties, as typically observed in hysteresis. This point raises questions regarding the performance stability of OHP-based photovoltaics in long-term operations, even though the well-known detrimental factors such as humidity, oxygen, ultraviolet exposure, etc., can be successfully resolved by providing complete encapsulation. The degradation of OHP solar cells consists of two parts, one (decay) with permanent degradation due to the decomposition of the materials and the other with reversible decay. Reversible decay is demonstrated to originate from the migration of mobile ionic species with two timescales: $10^1$ to $10^2$ s for halide vacancies and above $10^3$ s for cation vacancies in (FA$_{0.83}$MA$_{0.17}$)Pb(I$_{0.83}$Br$_{0.17}$)$_3$.[31] Fortunately, a recent report has indicated that well-prepared OHP cells are suitable for long-term use by the degradation mechanisms being limited to the reversible one.[140] Even though the cell performance deteriorates by ~10% over several hours by migration and consequent accumulation of mobile ionic species, a full recovery of the initial performance is demonstrated when the device is left under dark conditions for a sufficiently long time. This performance recovery was observed over several cycles of illumination and dark conditions, which resembles a succession of the day-and-night sequences in daily life, proving the stability of the OHP-based solar cells to be suitable for long-term use under native working conditions.[146]

These distinctive characters by mixed ionic/electronic conduction, in other ways, provide an additional avenue for new applications, such as switchable photovoltaics, memristors, artificial synapses for neuromorphic devices, etc.[158,187–189] Switchable photovoltaics utilize the formation of a homojunction (p–i–n or n–i–p) by poling-induced self-doping in a symmetric structure (e.g., Au/OHP/Au) as aforementioned, and the open-circuit voltage ($V_{OC}$) is determined by the extent of poling, the distance between the electrodes, the concentration of mobile ionic species, etc.[141,146,188] A lateral photovoltaic device, which is composed of serially connected individual photovoltaic units,
yields $V_{oc}$ accounting to the sum of each $V_{oc}$ from all the units, and therefore the $V_{oc}$ of lateral photovoltaic devices can sequentially be varied by the number of photovoltaic units. By regulating the self-doping extent in each unit and the number of units for a lateral photovoltaic device, a value of $V_{oc}$ as high as 70 V has been demonstrated.\[141\]

Rather than achieving high $V_{oc}$ from serially connected photovoltaic units, a single photovoltaic unit has also been demonstrated to reach a similarly high value of $V_{oc}$. Figure 7 illustrates this situation, representing the “anomalous photovoltaic effect” in a lateral-structure MAPbBr$_3$-based device.\[180\] It was shown that an Au/MAPbBr$_3$/Au unit device can achieve $V_{oc}$ up to 15 V (depending on the electrode spacing and the extent of poling bias), which necessitates an unconventional interpretation since $V_{oc}$ in a vertical-structure solar cell is known to be restricted by the bandgap of the light harvester (2.3 eV for MAPbBr$_3$). The formation of a tunneling junction at the grain boundary was proposed, working as an interconnecting metallic layer for the accumulation of photovoltages from each local photovoltaic unit formed by poling-induced self-doping of individual MAPbBr$_3$ grains. The build-up of positive and negative mobile ionic species along the grain boundary (perpendicular to the applied electric field) causes the accumulation of each charge, resulting in $n^+$ and $p^+$ doped regions at opposite sides of the grain boundaries and the formation of interfacial $n^+/p^+$ “local tunneling junctions” between the adjoining grains. The surface potential profile along the two electrodes supports the accumulation of photovoltages under light illumination (Figure 7a–c).

The absence of clear and abrupt potential changes at each grain boundary is attributed to the resolution limit of the measurement technique (tens of nanometers) and the formation of a discontinuous and random distribution of tunneling junctions (labeled as “dispersed tunneling junction” in Figure 7d) from polycrystallinity.

To further verify the tunneling-junction formation, the grain boundaries are intentionally broadened using electron-beam irradiation (~100 nm in width), which leads to the decomposition of OHP and allows the accumulation of mobile ionic species at designated positions. The e-beam-patterned area therefore will form an “aligned tunneling junction”, as shown in Figure 7e, with magnification of the “local tunneling junctions” in Figure 7f and the e-beam-damaged region in Figure 7g. Artificially formed boundaries lead to the surface potential showing an abrupt increase at the $Z$-patterned lines, as shown in Figure 7h,i, with the boundaries confirmed in the topography profile (Figure 7j).

The grain-boundary-governed anomalous photovoltaic effect is further verified by altering the measurement atmosphere from inert to oxygen exposure. Compared with N$_2$ conditions, oxygen may participate in grain-boundary doping: a continuous decrease of $V_{oc}$ is observed with O$_2$ injection and its partial recovery is observed from O$_2$ removal, further confirming the origin of the anomalous effect through grain-boundary chemistry. Oxygen leads to the reduced band bending of $n^+/p^+$ at the grain boundaries, supported by the disappearance of the abrupt potential change with the oxygen exposure.

A light harvester is a mediator that converts photon energy into electrical energy. Compared to conventional light harvesters for photovoltaic applications, OHPs show unique and intriguing properties, as demonstrated from the ion/defect migration, along with its potential applications for different concepts of photovoltaic devices. Regarding the operation and working principles in OHP-based solar cells, the drift of mobile ionic species under an electric field is straightforwardly understandable, as expressed in the schematic energy-level diagram in Figure 7k. Light illumination, however, gives variations in the optoelectronic/photovoltaic, optomechanical, and electromechanical properties, which further sheds light on the insights into the interactions between photons and semiconductors, at least on the nanoscale.\[115,121,190\] Actually, photoinduced effects bring compelling phenomena such as LISF, light-promoted ion migration in both polycrystalline films and single crystals, light-induced increase of carrier diffusion length, photoinduced phase separation, and strong lattice–phonon coupling. These intrinsic phenomena yield further implications regarding the interactions between mobile ionic species and photogenerated carriers.\[117,126,155,160,190\]

In the photoinduced photoluminescence from polycrystalline OHPs, an increase of the intensity and lifetime is observed, while this effect is negligible in single crystals. The origins are deduced from the photoluminescence kinetic model, and the trap density is actually reduced by an order of magnitude (from ~10$^{17}$ to ~10$^{16}$ cm$^{-3}$) by illumination,\[142\] as attributed to the annihilation of iodine Frenkel defects.\[11\] The photoluminescence after prolonged storage in the dark does not recover its original value (irreversibility), i.e., the trap density is reduced after a cycle of illumination and dark conditions, which is the so-called “photoinduced cleaning” effect. It is speculated that the reason for the brightening after the cycle arises from the difference between the annealing temperature for OHPs (~100 °C) and the photoluminescence temperature (room temperature), leading to different defect concentrations from different entropic contributions by temperature after the annihilation of traps by the photogenerated carriers.\[113\] The correlation between the photoluminescence increase and the structural composition is examined as shown in Figure 8.\[142\] The light-illuminated region shows a decrease of the iodine concentration from SIMS, while an increase of the iodine concentration is observed both near and underneath the illumination region (Figure 8a–c). The photogenerated carrier density exponentially decays along the depth (Figure 8c, where the theoretical calculation for the absorption coefficient of $\alpha \approx 1 \times 10^6$ cm$^{-1}$ is reported at an incident photon energy of 2.5 eV, which corresponds to a sub-micrometer absorption length$^{393}$), and a positive relation between the light intensity and the iodine concentration change is observed. As inferred from the photoluminescence enhancement, the traps are reduced by photogenerated carriers, and also, the iodine atoms migrate away from the illumination area in both lateral and vertical directions.

The proposed mechanism for iodine migration by light illumination is schematically illustrated in Figure 8d. The defect concentration among the grains may vary by regions, especially at the surface and at a grain boundary with a high concentration of defects (low photoluminescence grains), which could arise from the iodine Frenkel defect ($\delta^+$ for the iodine vacancies and $I^−$ for the iodine interstitials in Figure 8d-I). Under illumination, the concentration of photogenerated carriers is the highest at the surface of the OHP and exhibits an exponential
Figure 7. Anomalous photovoltaic effect (APV) in a lateral-structure MAPbBr₃ PV device. Surface potential of MAPbBr₃ film. a) Illustration of KPFM setup for the lateral MAPbBr₃ device. b) Surface potential maps of MAPbBr₃ measured under dark conditions (top) and under white-light illumination of 100 mW cm⁻² (bottom) in a N₂ atmosphere after electric poling. c) The corresponding potential profiles along the red dashed lines. d–f) Mechanisms of tunneling-junction formation between sub-micrometer-sized polycrystalline perovskite grains (corresponding dark-blue polygons with yellow empty spaces for the substrate) through ion migration, followed by accumulation at the grain boundaries. d,e) Schematic images illustrating the “dispersed tunneling junction” (d) (vs. local tunneling junctions expressed as bright-blue dotted curves along the grain boundary), and “aligned tunneling junction” (e). (Iₚ stands for the photocurrent.) f) Magnification of local ionic charge distributions with microstructures at the tunneling junction. g–j) Surface mapping from the intended formation of an “aligned tunneling junction” by e-beam damage. g) SEM image of the intentionally broadened grain boundary in the MAPbBr₃ film by e-beam (~100 nm width using 10–20 keV). h,i) Two artifacts of “Z” shapes on the MAPbBr₃ film, confirmed by topography (h), and the corresponding surface potential map by KPFM (i). j) Topography (top) and potential profile (bottom) along the red dashed line in (i). k) Proposed energy-level diagram illustrating the band bending around the grain boundary due to the n⁺/p⁺ heavy doping (downward/upward bending) by the buildup of positive/negative ionic charges, and working mechanisms for the “dispersed-tunneling-junction”-induced APV. Electrons (blue spheres) and holes (yellow) are schemed with the corresponding moving directions by arrows. Reproduced with permission.[189] Copyright 2017, AAAS.
decay along the depth of the film. Carriers (electrons or holes) will be trapped at oppositely charged defects, and, in particular, near the surface, due to the high concentrations of both traps and photogenerated carriers. Trap filling causes the perturbation in the system by redistributing the established local equilibrium between the defects, and thereby provides the driving force for the iodine migration laterally and vertically in various ways, with Coulombic repulsion between unscreened iodide ions (Figure 8d-2). From the iodide vacancy and iodide interstitial migration, the originally dark region becomes brightened, which is the photoinduced cleaning effect (Figure 8d-3). After the removal of the illumination, the iodide ion may slowly migrate back laterally or vertically to establish a new equilibrium, and thereby lead to a partial reversibility of the photoluminescence (Figure 8d-4).\[142\]

4. Perspectives and Conclusions

A huge leap has been achieved in the performance of OHP-based optoelectronic and photovoltaic devices, with the aid of nanostructural engineering for the synthesis of robust OHP materials and photophysical approaches. Various factors, ranging from geometrical pinholes at the OHP surface to structural disorder in the unit cells, give rise to electronic traps, resulting in performance deterioration but also intriguing mixed ionic/electronic conducting characteristics.

It has been proposed that grain boundaries and point defects can be electronically benign in OHPs, but extensive experimental results and meticulous calculations have verified their negative influences on the optoelectronic properties. The interplay between nanostructures and the photocarrier behavior reveals that the optoelectronic properties are far enhanced in single-crystalline OHPs, overwhelming those of polycrystalline OHPs. However, the main approach to incorporate OHPs for optoelectronic/photovoltaic devices still remains the use of polycrystalline OHP thin films. This necessitates investigations as to the nature of defects and/or traps in OHPs, from which strategies to control the nanostructural evolution of OHPs can guarantee high crystallinity and passivate the grain boundaries and interfaces, thereby reducing either charge scattering or recombination for efficient photocarrier collection. In this sense, the essence of microstructural optimization for OHP films is the construction of less defective materials, i.e., large grains with compact and uniform morphology via a high density of nucleation followed...
by grain coarsening, and this strategy has set a common and universal basis to produce high-quality OHP films.

In conjunction with classical perspectives based on nucleation–growth mechanisms, it is noteworthy that endeavors to elucidate the film formation through a nonclassical particle attachment model have been deliberately conducted. The presence of colloids in OHP precursors is clearly identified by the Tyndall effect, and even though the exact chemistry of the colloids should be further verified, it is suspected that ionic clusters or soft frameworks composed of Pb–I complexes play a major role in the OHP growth mechanisms. Deeper understanding of the chemistry and the role of colloids in precursors will set up a cornerstone to enable systematic control of the atomic defects from the precursors to the films. In fact, the unequivocal results highlight the importance of understanding the mechanisms of thin-film growth regarding the previous results, in that most OHP-based devices adopt submicrometer-thick films that demonstrate excellent properties of energy conversion. Accordingly, aspects in materials science from the nanostructures to the photophysical properties will enable the decoupling of essential factors crucial for realizing the optimal performance, promoting the development of engineering strategies for individual factors and thereby achieving satisfactory optoelectronic qualities.

Different from the normal characteristics as to conventional polycrystalline light harvesters, the intriguing features reveal the inherent variable, which is demonstrated to be the mobile ionic species. Mutual interactions of mobile ions with the nanostructures and photocarrier transport emphasize that the nanoscopic and even the macroscopic properties should be the entangled results from the collective interactions between them. Extrinsic factors, such as light, electric bias, or their combined effect, cause the various complex properties of OHPs to undergo temporal evolution, implying that the history of an OHP material under these factors should be considered for correct scientific interpretation of the observed phenomena, regarding the optoelectronic and even the optomechanical or electro-mechanical properties, as the potential elements behind the observations. Even though the mobile ionic species have raised concerns as to the photovoltaic working conditions, such as the questionable long-term stability of OHP-based photovoltaic devices, the mobile ionic species seem to participate in short-term degradation in a reversible manner, and thus the stability concern is reassured. Rather, it has been demonstrated that the distinctive characteristics from mixed ionic/electronic conduction give additional avenues for the original applications, which may unlimitedly broaden optoelectronic applications with OHP materials.

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Conflict of Interest
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