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Effect of the Microstructure of the Functional Layers on the Efficiency of Perovskite Solar Cells

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The efficiencies of the hybrid organic–inorganic perovskite solar cells have been rapidly approaching the benchmarks held by the leading thin-film photovoltaic technologies. Arguably, one of the most important factors leading to this rapid advancement is the ability to manipulate the microstructure of the perovskite layer and the adjacent functional layers within the device. Here, an analysis of the nucleation and growth models relevant to the formation of perovskite films is provided, along with the effect of the perovskite microstructure (grain sizes and voids) on device performance. In addition, the effect of a compact or mesoporous electron-transport-layer (ETL) microstructure on

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the perovskite film formation and the optical/photoelectric properties at the ETL/perovskite interface are overviewed. Insight into the formation of the functional layers within a perovskite solar cell is provided, and potential avenues for further development of the perovskite microstructure identified.

1. Introduction

Hybrid organic–inorganic perovskite-based solar cells (PSCs) have attracted a high level of research interest over the past seven years.^[1-11] The power conversion efficiencies (PCEs) of PSCs have improved steadily from $\approx 3\%$ ^[12] to $\approx 22\%$,^[13] which is outperforming conventional polycrystalline silicon solar cells. The high performances achieved by perovskite-based devices are mainly due to the impressive light-harvesting efficiency and high charge-carrier mobilities of the hybrid perovskite materials, such as methylammonium lead iodide. Another interesting feature of such perovskite materials is their ambipolar nature, which allows transport of both electrons and holes within the photoactive layer.^[1,14] This property makes the perovskite material suitable for a simple p–i–n planar architecture. Significant effort has been invested into the improvement of the PSC performance, including the development of new electron-transport-layer (ETL)/hole-transport-layer (HTL) materials.^[15,16] However, the most fruitful developments have come about from improving the microstructure of the perovskite layer itself.

When solid-state PSCs were first reported in 2012, the cell efficiencies were approximately 10% and had relatively poor reproducibility.^[1] This was mainly due to the inferior perovskite film coverage as a result of conventional spin-coating fabrication methods. This was overcome by the development of a two-step sequential deposition method, which produced a full surface coverage, with the capping

layer consisting of 100–200 nm-wide, randomly packed perovskite grains.^[9] This variation of the perovskite morphology using the two-step method achieved a maximum device efficiency of 15%, with a significantly improved cell-to-cell reproducibility. The newly developed two-step method was successfully employed in a mesoscopic PSC architecture; however, the perovskite microstructure is equally important for improvement of planar architectures. When using the conventional spin-coating method in a planar assembly, the poor surface coverage of the perovskite film leads to direct contact between the adjacent n-type and p-type materials. This promotes charge recombination and thus impairs the overall performance of the device. This problem was remedied by changing the perovskite morphology and grain structure. Large perovskite grains may successfully minimize the effects of defect-rich grain boundaries on both charge transport and recombination kinetics. Perovskite films comprising large grains have exhibited significantly longer charge diffusion lengths, up to 1 μm , relative to smaller grain devices.^[2] Ideally, a single-crystal perovskite film would provide the highest light-harvesting efficiency, as it is expected that this morphology would allow extremely long charge-diffusion lengths. In addition to varying the morphology of the light-absorber layer, the microstructure of the other functional layers, especially the n-type semiconductor layer, may also be varied in order to optimize the material interfaces. It is commonly accepted that the morphology of the perovskite layer is largely influenced by the microstructure of the material directly beneath it.^[17] Herein, the effects of the perovskite and ETL microstructure are discussed in relation to the overall efficiency of the final PSC devices.

2. Effect of Microstructure of the Perovskite Layer

The morphology of the perovskite film is widely recognized as being essential to the fabrication of high-efficiency solar cells. The perovskite structure is most commonly directed by the film-

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fabrication process. For example, when a $\text{CH}_3\text{NH}_3\text{PbI}_3$ film is deposited onto a compact TiO_2 -layer-coated substrate via a conventional spin-coating process, the resulting perovskite layer forms a dendritic microstructure. When a p-type semiconductor such as spiro-OMeTAD is coated on this perovskite layer, the presence of large voids ($\approx 1 \mu\text{m}$) in the perovskite layer lead to direct contact between the ETL and HTL semiconductors, resulting in severe current leakage. The performance of such devices is very poor, $\approx 4\%$, and the performance reproducibility is comparatively low.^[18] In order to prevent the formation of voids inherent to the dendritic morphology, various film-fabrication methods have been developed. Thermal co-evaporation of PbCl_2 and methyl-ammonium iodide (MAI) was first employed to produce a homogeneous perovskite film with a uniform thickness.^[10] The devices formed using this method showed a maximum efficiency of 15.4%, significantly better than the cells comprising solution-processed perovskite films (8.6%).^[10] However, as solution-based processes present the potential to reduce manufacturing costs and simplify mass production, research has generally focused on the development of solution-based processes to develop the microstructure of the perovskite films. In order to achieve dense perovskite films, an understanding of the perovskite nucleation and crystal growth is required.

2.1. Perovskite Nucleation and Growth Models

Research into the understanding of perovskite nucleation/growth mechanisms has been helpful for film formation and device optimization. As efficiencies strive to approach the theoretical limits for energy conversion, a deep understanding of the nucleation and growth dynamics will be vital to improve cell efficiencies. Presently, classical nucleation and growth models have been used to

provide a broad description of the perovskite film formation.^[19] These models are generally interpreted in the context of solution-based materials processing, where the film formation takes place via successive nucleation and growth stages.^[20-23] In a typical one-step method, both homogeneous and heterogeneous nucleation is expected to occur. For hybrid organic–inorganic perovskite thin films, the complete coverage of the underlying substrate and control of the material morphology is achieved primarily through regulation of the heterogeneous nucleation rate.^[24,25] The surface roughness and microstructure of the underlying substrate are considered paramount to understand heterogeneous nucleation at the precursor/substrate interface, as they have a direct influence on the heterogeneous nucleation energy barrier. Mesoporous metal-oxide scaffolds are commonly believed to accelerate the formation of heterogeneous nucleation sites, leading to an enhanced film coverage.^[25,26] Furthermore, the crystallographic orientation of the substrates may impact nucleation and growth mechanisms in solution-processed perovskites. Previous studies have noted that the orientation of the perovskite layer is strongly correlated with the nature of the underlying material, indicative of topotactic perovskite crystal growth.^[17,27,28]

Determining the nature of these nucleation sites is nontrivial, and, in addition, to the formation of perovskite single-crystal nuclei, it is expected that adducts of $\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{DMSO}$ ^[29-33] and $\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{DMF}$ ^[34,35] play a key role in the perovskite film formation. In the case of two-step methods, it has been reported that the intercalation of DMF within the PbI_2 scaffold regulates the growth rate of the perovskite material.^[36] Previous studies have also reported the formation of crystalline lead halide aggregates in solution prior to film formation, which serve as further heterogeneous nucleation sites.^[25] This observation, supported by in situ grazing-incidence wide-angle X-ray scattering data,^[20] signifies a departure from classical nucleation theories,^[37] and are akin

to nonclassical pathways involving pre-nucleation clusters^[38,39] of ions or primary particles.^[40] It is likely that nonclassical growth mechanisms entailing oriented-attachment^[41-43] play a significant role in the formation of perovskite thin-films, given the aforementioned existing evidence for nanoparticle agglomerations and recent evidence for preferential crystallographic orientation.^[44] A complete description of hybrid organic–inorganic perovskite nucleation dynamics is further complicated by the intricate relationship between the precursor solubility and temperature.^[24,45] Despite a limited understanding of the nature of heterogeneous nucleation dynamics, there appear to be many possible pathways toward establishing a suitable density of nucleation sites required for the complete coverage of the underlying substrate.

Both crystal nucleation and growth dynamics are largely dependent on the fabrication technique employed. In the case of the two-step method, it is generally understood that perovskite formation occurs initially at the interfacial region between the inorganic and organic precursor materials.^[46,47] This growth transpires at a solid–liquid,^[9,48] solid–solid,^[49] or solid–gas^[35,46,50] interface, depending on the nature of the two-step fabrication method used. However, the crystalline perovskite formed at this interface is believed to impair further migration of methylammonium ions toward the unreacted PbI_2 .^[47,51] Another feature of the two-step method is the significant volume expansion concomitant with perovskite crystallization and intercalation of adducts within the PbI_2 template.^[52-55] In the case of a one-step method, crystal growth is believed to adhere to non-epitaxial Stranski–Krastanov or Volmer–Webber growth, where perovskite clusters or islands grow three-dimensionally in order to minimize the free energy of the system.^[56] This growth mechanism is characterized by a strong interaction at the precursor–perovskite interface relative to the precursor–substrate interface.^[57] Thus, the perovskite islands expand laterally until their growth is impinged upon by the growth of an

adjacent domain. Diffraction patterns from transmission electron microscopy (TEM) cross-sections have provided good evidence to suggest that these fully formed, sub-micrometer islands comprise a single perovskite crystal.^[18,58]

Coarsening and coalescence dynamics also play a key role in establishing the final film morphology. The rate of grain coarsening is largely a function of the annealing temperature and duration,^[59,60] however, this process may also promote the concurrent degradation of the perovskite structure.^[61] A high degree of grain coarsening has been noted in systems using an excess of CH_3NH_3^+ in the precursor solution,^[44,62,63] which may partially account for the smoother films produced under these conditions.^[64,65] However, it is expected that the extended annealing required to drive out this excess organic component may promote CH_3NH_3^+ and PbI_2 deficiencies.^[63] Solvent-assisted annealing, as part of a one-step^[66] or two-step^[67] fabrication procedure, has also proven to be an effective way to coarsen $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, ultimately resulting in the formation of perovskite grains in excess of 1 μm in diameter. It is likely that grain-growth mechanisms prevalent in the solvent-annealing studies adhere to well-documented Ostwald ripening.^[68]

2.2. Effect of the Grain Size of the Perovskite

High-efficiency PSCs have been produced via both one-step and two-step techniques, comprising planar, mesoscopic, and hybrid planar–mesoscopic structures.^[5,32,49,69,70] Thus, it is yet to be shown conclusively what an optimized perovskite microstructure might entail. There is a growing body of literature, however, to suggest that certain morphological features are more desirable than others. Previous studies have identified the beneficial properties of large-grain perovskite microstructures, both in terms of efficiencies and charge-transport kinetics,^[7,71-79] although these findings are

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contrasted by some reports describing favorable^[80,81] or benign^[82] effects at grain boundaries. The majority of these studies imply that planar perovskite morphologies have an innate advantage over mesoscopic morphologies, yet a mesoporous scaffold can offer select advantages over a planar architecture, such as interfacial charge separation,^[83] which is an established limitation of some planar assemblies.^[84] Presently, it appears that an optimal perovskite morphology would encompass a combination of various architectures.^[85]

The most effective route toward microstructure control, particularly in the case of a one-step deposition, is through optimizing the ratio of the nucleation and growth rates. This process is well accounted for through the classical LaMer growth curve (**Figure 1a**).^[86] The formation of an inhomogeneous perovskite film resulting from a conventional spin-coating procedure is due largely to the comparatively low density of the heterogeneous nuclei and the diffusion-limited growth of the dendritic or other intrinsic perovskite structures. The low density of nucleation sites is fundamentally a result of the limited degree of supersaturation achieved during the conventional spin-coating procedure. Due to the comparatively fast crystal growth rate as a function of the solution supersaturation, the solute material precipitates rapidly at regions of relatively high surface energy. The imbalance between the required nucleation and growth rates results in rapid growth of large dendritic or other intrinsic perovskite structures on the limited number of nuclei. The key for the development of densely covered thin films from hybrid perovskite solutions is to promote a high nucleation rate before the rapid growth onset. The most common way of addressing the nucleation–growth imbalance has been through regulating the nucleation kinetics. This is primarily achieved via altering the chemistry of the precursor solution,^[4,63,87-92] modification of the underlying substrate^[93,94] or by controlling the precursor supersaturation rate, such as the gas-assisted or the

anti-solvent methods (Figure 1b).^[18,29,58] Both hot-casting^[8,56,95] and vacuum flash-assisted^[96] techniques present comparable ways of modifying the solvent-evaporation rate, and hence, the degree of supersaturation. Although some of these fabrication techniques have successfully regulated the density of heterogeneous nucleation sites, and extended the size of crystalline regions beyond 100 μm (Figure 1c), it is unclear whether these large crystalline areas comprise a single perovskite crystal. Evidence for the growth of large ($>100\text{ }\mu\text{m}$) single crystals as part of a perovskite thin-film has been limited to polarized-optical-microscopy measurements,^[8] whereas transmission electron microscopy (TEM) or electron backscatter diffraction (EBSD) measurements may be helpful in further substantiating these conclusions.

Despite correlations between the charge-transport kinetics and perovskite grain sizes, benchmark perovskite solar cells still typically comprise grains of less than 1 μm in diameter.^[32,70] Charge-diffusion lengths in solution-processed hybrid organic–inorganic perovskite single crystals have been observed to be in excess of 10 μm ,^[97,98] while path lengths in excess of 1 μm have been measured in polycrystalline thin-films.^[2,3] These relatively long charge-carrier diffusion lengths may already be sufficient for $\sim 100\%$ of the charge carriers to be collected at the respective material contacts on either side of the perovskite layer. Hence, the performance gains concomitant with increasing the perovskite grain size may prove trivial compared to other gains obtained through material substitution or enhanced photon harvesting. The charge-concentration gradient within the perovskite film perpendicular to the substrate forms the primary driving force for charge diffusion. As long as the number of perovskite grain boundaries parallel to the substrate can be avoided or reduced, it is possible that there will be no significant benefit gained from increasing the in-plane grain diameter beyond 1 μm .

2.3. Effect of Voids in the Perovskite Layer

Large voids in the dendrite perovskite film severely impair the performance of PSCs even if the film is composed of large grains. Voids that penetrate the depth of the perovskite layer promote shunting due to direct contact between the HTL and ETL semiconductors (**Figure 2a**). If these voids do not extend throughout the profile of the perovskite layer, the performance may be improved significantly, as electron-hole recombination would be reduced. Chemical additives have been introduced into the perovskite precursor solution toward this end, including small ions/molecules that facilitate homogeneous nucleation, such as Cl^- ,^[99,100] 1,8-diiodooctane (DIO),^[90] and N-cyclohexyl-2-pyrrolidone (CHP).^[101] The coverage of the perovskite layer is improved greatly by both introduction of Cl^- into the perovskite precursor and annealing-temperature control.^[99] With the addition of DIO, the size of the large pores (Figure 2b) can be further decreased to hundreds of nanometers (Figure 2c). Although the performance was not completely optimized as pores were still present, a much improved PCE was achieved increasing from 9% to 12%.^[90] Other groups of additives including polymers such as poly(vinylpyrrolidone) (PVP)^[102] and poly(ethylene glycol),^[103,104] have been incorporated into the perovskite precursor solution. It is reported that these polymers induce perovskite nucleation during film formation and fill pores within the perovskite structure. The addition of PEG reduced the average pore size to ~ 100 nm and few pores perforated the perovskite film (Figure 2d), minimizing direct contact of the HTL and ETL materials. These measures improved the PCE to 16% and the cells exhibited an enhanced resistance to water corrosion.^[104]

Fabrication methods have been developed in an attempt to completely remove voids in the perovskite film, including antisolvent engineering^[29,58] and gas-assisted methods.^[18] PCEs up

to $\approx 21\%$ have been achieved using these fabrication techniques, which indicate the relatively low interfacial recombination rates achieved in these systems.^[105] However, nanometer-sized pores still occur in such perovskite films.^[63] Different lead salts have also been shown to alter the film morphology, as reaction by-products may influence the nucleation and crystallization dynamics.^[63,106] When PbCl_2 or PbI_2 was used as a lead source, the perovskite films were relatively dense but contained some nanometer-sized pores. However, when $\text{Pb}(\text{CH}_3\text{COO})_2$ was employed as a lead source the perovskite films showed no evidence of parasitic pinholes.^[63] The PSC devices prepared using $\text{Pb}(\text{CH}_3\text{COO})_2$ achieved a PCE of 14.0%, significantly higher than those formed with PbCl_2 (12.0%) or PbI_2 (9.3%).

Micrometer- or sub-micrometer-sized pores undoubtedly decrease the PCE of the devices. However, the presence of nanometer-sized-pores that do not perforate the perovskite film have little bearing on the PCE. For a ≈ 300 nm-thick perovskite film, the recess caused by a pore has little effect on light absorption and electron-hole recombination, and is a common feature of some textured morphologies. A textured $\text{CH}_3\text{NH}_3\text{PbI}_3$ morphology formed on a thin mesoporous TiO_2 seeding layer has been shown to comprise a dense bottom perovskite layer and a porous perovskite upper layer (Figure 2e). Thus, spiro-OMeTAD can infiltrate the perovskite pores to increase the interfacial contact at the perovskite/HTL interface, which allows significant improvements in the charge extraction. In addition, the rough interface presents a scattering effect that lengthens the light path and improves the light-harvesting efficiency. PSCs based on such textured perovskite morphologies have obtained PCEs of 16.3% with a J_{sc} exceeding 22 mA cm^{-2} .^[26]

3. Effect of the Microstructure of the ETL

In addition to the perovskite layers, the microstructural features (morphology, thickness, porosity, and crystallinity) of the ETLs are also critical for the device performance and stability. To date, various n-type semiconducting metal oxide materials (i.e., TiO_2 , ZnO , SnO_2 , WO_3 , SrTiO_3 , Zn_2SnO_4 , and BaSnO_3)^[9,107-112] have been employed as the ETLs for PSCs. The microstructure of the ETL plays an important role that invariably affects the perovskite infiltration, light trapping and harvesting, and charge injection, transportation, and collection at the ETL/perovskite interfaces. Therefore, an understanding of the relationship between the ETL microstructure and device performance provides a useful guide for developing efficient perovskite-based photovoltaic devices.

3.1. Effect of Compact ETL

Most state-of-the-art PSCs have used TiO_2 as the ETL. The fabrication of a conventional PSC commences typically with the deposition of a TiO_2 compact layer as a hole-blocking layer (HBL) on top of the transparent conducting oxide (TCO) substrate. It is critically important to ensure that this HBL is both uniform and dense to conformally coat the TCO substrate. This prevents charge recombination at the interface between the perovskite layer and the TCO. Moreover, the thickness of the TiO_2 blocking layer also plays a crucial role in the solar-cell performance.^[113] In addition to TiO_2 , other metal oxide blocking layers such as ZnO ,^[107] SnO_2 ,^[108] or Zn_2SnO_4 ,^[110] have also been employed to construct efficient planar PSCs. The effective use of these materials shows their potential as promising alternatives to the commonly used TiO_2 blocking layer. These ETL materials typically

possess a higher electron mobility and a relatively lower refractive index than TiO_2 , which can ensure rapid transport and collection of photoinjected electrons and good optical transmittance.^[107,108,110] However, if the conduction-band edge of the ETL is situated comparatively closer to the perovskite valance-band edge, then electron–hole recombination may be increased at the ETL/perovskite interface.^[114] To remedy this issue, bilayered ETLs (i.e., TiO_2/ZnO ,^[115] $\text{SnO}_2/\text{TiO}_2$, or $\text{Zn}_2\text{SnO}_4/\text{TiO}_2$) have been used. These bilayered structures comprise a metal oxide underlayer with high electron mobility and a secondary metal oxide upper layer with an improved energy-level alignment relative to the perovskite layer. Bilayered ETLs exhibit the synergistic advantages of improved electron transfer and better hole-blocking for enhanced electron extraction and suppressed interfacial recombination (Figure 3a). Conduction-band misalignment between the ETL and the perovskite material may cause undesirable consequences, such as accumulation of photogenerated charges, which could hamper the device performance. It is important to either match the ETL with a suitable perovskite material, or vice versa. For instance, a conduction-band misalignment between a TiO_2 ETL and a mixed perovskite material (i.e., $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$) may hinder electron injection. In contrast, there is no such misalignment between SnO_2 and the same mixed perovskite, and thus this combination is more favorable toward electron injection (Figure 3b). The conduction band of the mixed perovskite is ≈ 300 meV below that of TiO_2 , and only ≈ 30 meV below that of SnO_2 (Figure 3c).^[116]

3.2. Effect of a Mesoporous ETL

A mesoporous metal oxide layer may also be deposited on top of the blocking layer in order to provide a porous scaffold for the perovskite precursor loading and promote efficient extraction of photogenerated electrons. The mesoporous ETL/perovskite interface greatly affects the optical light-harvesting and charge-extraction behavior of PSC devices. The development of mesoporous TiO₂ ETLs has matured over the past decades. To date, a wide range of TiO₂ structures such as zero-dimensional (0D) nanoparticles,^[117,118] one-dimensional (1D) nanostructures (nanorods, nanowires, nanotubes, and nanofibers),^[119-123] two-dimensional (2D) nanosheets,^[14,124] and three-dimensional (3D) hierarchical architectures,^[122,125,126] have been employed in PSC applications.

The film thickness, porosity, and crystallinity of the mesoporous TiO₂ ETL play a crucial role in determining the cell performance. The high absorption coefficients and long charge-carrier diffusion lengths characteristic of perovskite materials allow thin mesoporous TiO₂ ETL films (normally <1 μm thick). The optimized thickness should be in the range of 400–600 nm for TiO₂ nanoparticles and 600–900 nm for 1D TiO₂ nanorods in perovskite-sensitized mesoscopic PSCs.^[117,119,120,125] When the thickness of the mesoporous TiO₂ film exceeds 1 μm, this is longer than the charge diffusion length,^[2] leading to a significant loss in V_{oc} and fill factor (FF).^[127]

The most efficient PSCs to date constitute both mesoscopic and planar elements. These structures commonly feature a perovskite-infiltrated mesoporous TiO₂ film (~150–200 nm in thickness) and a perovskite capping layer (300–500 nm in thickness) that contacts the HTL.^[29,70] The perovskite grain structure and thickness depends strongly on the thickness and porosity of the underlying ETL. In general, an ETL with a high porosity and high film thickness would allow more-effective perovskite infiltration, resulting in the formation of a thinner perovskite capping layer consisting of smaller grains and a textured surface, whereas a relatively thin ETL with low porosity may suppress

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perovskite growth within the mesoscopic voids and cavities. This, in turn, allows a greater fraction of perovskite solute to precipitate on top of the ETL, leading to the formation of perovskite films with comparatively large grains and flat surface.^[118,123,126] A macroporous ETL scaffold featuring large pores and a honeycomb structure has been used to template the microstructural growth of the perovskite film. In this system, the domain size and film thickness of the perovskite can be well tuned by controlling the honeycomb structure as well as the perovskite precursor concentration (Figure 3d,e).^[128]

In general, metal oxide ETL films need to be sintered at a high temperature (>450 °C) to enhance their crystallinity and electrical conductivity.^[129] Although PSCs based on such high-temperature-processed ETLs showcase excellent photovoltaic performance, recent research efforts focusing on low-temperature-processed ETLs revealed that the high crystallinity of the ETL may not be required. PSCs based on low-temperature-processed amorphous TiO_x , SnO_2 , or Zn_2SnO_4 ETLs have been shown to yield PCEs approaching 18% for rigid devices and exceeding 15% for flexible devices.^[110,130-133] A high level of optical transmittance, electrical conductivity and charge-separation can be achieved as long as the low-temperature-processed ETL is thin and covers fully the TCO layer.^[132,134] However, the long-term stability of PSCs comprising amorphous ETLs is yet to be shown.

The morphology of mesoporous ETLs also affects the photoelectrical properties of the ETL/perovskite interface. A family of well-defined TiO_2 nanostructured thin films including 0D nanoparticles, 1D nanowires, and 2D nanosheets on fluorine-doped tin oxide (FTO) glass have been employed recently in PSCs.^[123] The highly porous networks of 1D nanowires or 2D nanosheets facilitate enhanced charge extraction at the ETL/perovskite interface due to improved infiltration of the perovskite material within the ETL. This increased interfacial contact establishes a more direct

electron pathway for faster electron transport compared to cells featuring 0D titania-nanoparticle ETLs (Figure 3f).^[123] Other 1D oxide structures, including SnO₂ nanowires or ZnO nanorods, have also been employed as efficient ETLs in PSCs.^[135-137]

3D branched TiO₂ nanowire films are able to provide a higher surface area and porosity compared to conventional TiO₂ nanoparticles. Such 3D structures afford efficient perovskite infiltration, superior light scattering for enhanced light collection by the perovskite, improved electron transport, and suppressed charge recombination for efficient charge collection.^[122,125,126] Recently, various branched TiO₂ nanowire architectures have been developed for use in PSCs, showing improved photovoltaic performances and largely suppressed *J*-*V* hysteresis owing to the enhanced light harvesting and charge-collection efficiency (Figure 3g,h).^[122,125,126] Several reports have demonstrated heterostructured nanoarrays such as core-shell ZnO@TiO₂ nanorod^[138] or SnO₂@TiO₂ nanowire arrays.^[135] These arrays exhibit advantages, including favorable charge separation and reduced charge recombination, when employed in PSCs. 3D branched architectures comprising two or more energetically matched semiconductors may ultimately serve as ideal ETLs for PSC applications. Other ETLs have been designed with different morphologies or compositions, such as mesoporous TiO₂ or SnO₂ single crystals,^[139,140] well-organized mesoporous TiO₂,^[141,142] inverse-opal-like TiO₂,^[143] nanohelical TiO₂ arrays,^[144] and WO₃ nanowires and nanosheets,^[109] providing many choices for constructing highly efficient perovskite-based photovoltaic devices. A balance is inevitably required between the cost and ease of manufacture of the high-precision nanoarchitectures, the stability of these advanced ETLs, and the associated performance gains.

In a mesoporous structured PSC, the porous nanoparticle ETLs can be replaced by an insulating material (Al₂O₃ or ZrO₂).^[1,4] Such insulators do not take part in the electron extraction due to their

comparatively large bandgap. In this regard, the electron quasi-Fermi level is determined chiefly by free electrons in the perovskite phase, and thus results in a high V_{oc} . More importantly, the stability of PSCs using an insulating scaffold is enhanced since electron trapping does not occur in these devices.^[145]

4. Conclusions and Outlook

As a low-cost, solution-processable photovoltaic technology, hybrid organic–inorganic PSCs present very promising prospects for commercial applications. Within this technology high efficiencies have been obtained by optimizing the microstructure of the perovskite films and other functional layers. Various fabrication techniques have been employed to improve the perovskite film quality and device reproducibility. Regardless of whether a one-step or a two-step process is used during fabrication, the primary focus of perovskite-film optimization has been to control the material microstructure, which is governed by the nucleation and crystal growth process. By regulating the nucleation and crystal growth rates it is possible to obtain dense perovskite films without deleterious pinholes. The grain size of the perovskite layer can also be controlled by subsequent annealing processes. Furthermore, controlling the microstructure of other functional layers, like the electron-transport material, also plays an important role in constructing high-efficiency solar cells.

Although PSCs have reached some impressive efficiencies, there are still significant obstacles to overcome before this photovoltaic technology can warrant commercialization. Firstly, most high-efficiency results reported are based on small-scale laboratory-based devices ($<1\text{ cm}^2$). To scale-up the technology, perovskite-film deposition should move beyond spin-coating-based procedures, which are unlikely to meet the large-area or high-throughput requirements of a mass-production

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process. The nucleation and crystal growth processes under these conditions might be considerably different. For example, during a spin-coating procedure the solvent dries relatively quickly compared to that in a slot-die-printing process. Additionally, the drying process of a large film is different to that of a small film. Thus, future research will need to consider perovskite nucleation and crystal growth for comparatively large-scale devices in order to improve the cell efficiency and reproducibility. The long-term stability of the cell performance is another important issue that overlaps with morphological control. Disregarding encapsulation, the microstructure of the perovskite film is linked strongly to the cell stability. Questions correlating the perovskite film microstructure to stability in the field of PSC research include: how will defects within the perovskite film affect the cell stability and will the grain size be an important parameter in improving the long-term stability? These issues, and others, must be addressed before perovskite-based technologies are ready for market deployment.

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Figure 1. a) Nucleation and growth dynamics as modeled by the LaMer curve. C_s , C_{min}^* and C_{max}^* represent the solution solubility limit, and the minimum and maximum supersaturation

concentrations, respectively. The curve is broadly divided into three regions describing: I) the initial increase in solution concentration as solvent is removed, II) the formation of nuclei as the solution reaches a state of supersaturation, and III) the associated reduction in concentration as nuclei grow through precipitation. b) Nucleation (red trace) and growth (blue trace) rates as a function of the solution supersaturation. Dendritic morphologies occur when the rate of nucleation < growth, while dense films are formed when the rate of nucleation > growth. c) Large-grain perovskite morphology

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Figure 2. a,b) Cross-sectional SEM image of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSC device fabricated by a conventional spin-coating method (a) and a cross-sectional TEM image of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ PSC device fabricated by a gas-assisted spin-coating method (b). a,b) Reproduced with permission.^[18] Copyright 2014, Elsevier. c,d) SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films without 1,8-diiodooctane additive (c) and with the additive (d). c,d) Reproduced with permission.^[90] Copyright 2014, Wiley-VCH. e) SEM images of the perovskite films with PEG, scale bar 1 μm . Reproduced with permission^[104] Copyright 2016, Nature Publishing Group. f) SEM surface image of the textured perovskite morphology. Reproduced with permission.^[26] Copyright 2016, Wiley-VCH.

Figure 3. a) Schematic diagram of band alignment and charge recombination in the cells with TiO_2/ZnO bilayered ETL. Reproduced with permission.^[115] Copyright 2015, Royal Society of Chemistry. b,c) Schematic electron-injection characteristics (b) and energy-level diagram (c) of mixed perovskite $((\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15})$ materials and different ETLs (TiO_2 and SnO_2). c,d) Reproduced with permission.^[116] Copyright 2015, Royal Society of Chemistry. d,e) SEM image of honeycomb-like TiO_2 scaffold filled with 20 wt% perovskite precursor solution (d) and color enhanced cross-sectional SEM image of a complete device fabricated from the oxide honeycomb with the 20 wt% perovskite precursor solution (e). d,e) Reproduced with permission.^[128] Copyright 2015, Royal Society of Chemistry. f) Schematic showing the different electron-transfer pathways and charge collection at the TNP-, TNS-, and TNW- $\text{CH}_3\text{NH}_3\text{PbI}_3$ interfaces. Reproduced with permission.^[123] Copyright 2016, Wiley-VCH. g,h) Cross-sectional SEM image of a PSC prepared using a 3D branched TiO_2 nanowire ETL, scale bar 500 nm (g) and $J-V$ curves of PSCs based on 3D branched TiO_2 nanowire ETL, showing largely suppressed hysteresis (h); the inset shows a top-view SEM image of the branched TiO_2 morphology. g,h) Reproduced with permission.^[125] Copyright 2015, American Chemical Society.

The performance of perovskite solar cells is greatly affected by the microstructure of the functional layers, especially that of the perovskite film. By controlling the nucleation and crystal growth process, desirable microstructures (grains and voids size) of the perovskite films, such as dense films with large grains, can be achieved for high-efficiency solar cells.

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Effects of the Microstructure of the Functional Layers on Perovskite Solar Cell Efficiencies

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