Planar vs Mesoscopic Perovskite Microstructures: the Influence of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Morphology on Charge Transport and Recombination Dynamics

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ABSTRACT

Perovskite solar cells (PSCs) employing planar and mesoscopic architectures have both resulted in high efficiency devices. However, there is presently a limited understanding of the inherent advantages of both systems, particularly in terms of the charge transport and recombination dynamics. In the present study we characterize the relative benefits of the two most prominent $\text{CH}_3\text{NH}_3\text{PbI}_3$ morphologies, primarily through time-resolved microwave conductivity (TRMC) and time-resolved photoluminescence (TRPL) measurements. The comparatively large perovskite grains, typical of planar assemblies, exhibited higher charge mobilities and slower trap-mediated recombination compared to the mesoscopic architectures. These findings reveal the injurious influence of grain boundaries on both charge transport and recombination kinetics, and suggest an innate advantage of planar morphologies. However, through impedance spectroscopy (IS) measurements, mesoscopic architectures were found to limit the interfacial recombination at the transparent conductive oxide (TCO) substrate. The lessons learnt through the characterization measurements were subsequently utilized to produce an optimized cell morphology, resulting in a maximum conversion efficiency of 16%.

KEYWORDS: Perovskite, solar cells, time-resolved microwave conductivity, time-resolved photoluminescence.

1. Introduction

Hybrid organic-inorganic perovskite-based solar cells (PSCs) have garnered significant attention since first reported six years ago.[1] Over the same period, PSC conversion efficiencies have improved from below 4% to values presently exceeding 20%, and are rapidly approaching the benchmarks set by leading thin-film technologies. In association with their impressive performance, PSC devices boast immense potential for low material and manufacturing costs compared to other photovoltaic technologies. To date, high efficiency PSCs have successfully employed both mesoscopic and planar architectures, with no clear standout. However, the microstructure of the perovskite layer within both these device structures is markedly dissimilar. In the mesoscopic assembly, the perovskite grain growth is restricted by the pore size of the mesoporous scaffold. While in the planar architecture, the perovskite grain growth is relatively uninhibited, and is solely limited by the growth of neighbouring perovskite grains. However, it is yet to be established whether one of these two architectures is inherently superior, particularly in relation to charge transport and recombination kinetics.

Varying interpretations of planar and mesoscopic perovskite morphologies have complicated objective comparisons between the two cell architectures. Early reports of PSC technologies represent the perovskite material in mesoscopic architectures as a quantum-dot style sensitizer,[1-3] or as a dense layer coating the mesoporous scaffold.[4] Additionally, high efficiency PSC devices have been produced through the combination of both planar and mesoscopic architectures.[5] Hybrid mesoporous/planar assemblies comprising micron-sized perovskite cuboids on top of a mesoscopic TiO_2 /perovskite film have produced efficiencies exceeding 16%.[6] The high efficiencies achieved with these PSC architectures further complicates any correlation between the perovskite morphology and the device performance.

Control of the perovskite morphology in planar PSCs is strongly influenced by the fabrication technique employed. The perovskite grain size and structure varies widely depending on whether films are formed using ‘fast-crystallization’ or two-step methods, as well as the nature of these fabrication steps. Fast-crystallization techniques utilize either an inert gas flow (gas-assisted method) or anti-solvent (anti-solvent method) to rapidly induce the supersaturation of the perovskite material within the precursor solution, leading to the fast nucleation and crystallization of the perovskite layer.[7-9] Two-step fabrication methods entail the initial spin-coating of a PbI_2 layer and the subsequent reaction with a $\text{CH}_3\text{NH}_3\text{I}$ solution.[10, 11] This process is achieved via submersion in a diluted $\text{CH}_3\text{NH}_3\text{I}$ solution,[12, 13] through a vapor based reaction,[14, 15] or through a second spin-coat and heating step.[6] Gas-assisted and anti-solvent fast-crystallization techniques typically result in single $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals that span the entire thickness of the perovskite layer, with a uniform layer thickness.[7, 8] In contrast, two-step fabrication methods using planar architectures have been shown to produce perovskite grain sizes ranging from ~ 75 nm to ~ 1 μm , with a broad variety of crystal shapes.[5, 6, 13, 14] Despite the resulting differences in perovskite morphologies, both fabrication techniques have been shown to produce high efficiency PSC devices.

Even though a variety of successful PSC architectures have emerged, little analysis has been afforded to the objective comparison of planar and mesoscopic perovskite morphologies. Of particular interest is the comparison of charge transport and recombination kinetics within mesoscopic and planar devices. The present study utilizes correlated electro-optical transport measurements, including time-resolved microwave conductivity (TRMC) and time-resolved photoluminescence spectroscopy (TRPL), to accurately map charge transport and recombination dynamics within both planar and mesoscopic perovskite materials. Impedance spectroscopy (IS) is used to explore interfacial recombination rates and

the characteristically slow response of the two perovskite morphologies. Together, these characterization techniques provide insights that enable an improved cell design over both the conventional architectures. Wide-field fluorescence spectroscopy is also used to affirm the optimized perovskite layer used in the complete PSC devices. This analysis provides a valuable link between the role of perovskite crystal morphology and the ensuing device performance.

2. Material and Methods

Materials Synthesis: Unless otherwise specified, all materials were purchased from either Alfa Aesar or Sigma-Aldrich and used as received. spiro-OMeTAD (2,2',7,7'-tetrakis(*N,N*-di-*p*-meth-oxyphenylamine)-9,9-spirobifluorene) was purchased from Luminescence Technology Corp. The synthesis of CH₃NH₃I was performed using the same previously reported method.[8] Al₂O₃ (Aldrich, 642991) and TiO₂ (Hydrothermal Synthesis) nanoparticle pastes used for characterization measurements were formed by suspending ~ 45 nm and ~ 20 nm particles in a solution of ethanol, terpineol and ethyl cellulose.

Device fabrication: The perovskite solution was prepared by dissolving CH₃NH₃I (111 mg) and PbI₂ (329 mg) in dimethyl sulfoxide (150 μ L) and gamma-butyrolactone (350 μ L). ~ 25 μ L cm⁻² of the perovskite solution was deposited on the substrate. Mesoporous Al₂O₃ and TiO₂ scaffolds were produced by spin-coating the nanoparticle suspensions at 6000 rpm and 3000 rpm respectively for 60 s to produce a scaffold thickness between 250 – 300 nm. Planar films were fabricated using a spin-coating step at 4500 rpm for 50 s. Gas-assisted and solvent-assisted perovskite films were formed by introducing an inert gas flow or toluene solvent, respectively, after a given duration. Conventional spin-coated films were formed by spin-coating without any introduced gas-flow or solvent. Mesoscopic perovskite films were formed by spin-coating at 6100 rpm for 50 s. Perovskite films were heated at 85 °C for 10

min, unless specified. The spiro-OMeTAD solution was formed by dissolving 41.6 mg Spiro-OMeTAD in 7.5 μL of a stock solution of 500 mg mL^{-1} lithium bis(trifluoromethylsulphonyl)imide in acetonitrile and 16.88 μL 4-tert-butylpyridine in 500 μL chlorobenzene. The spiro-OMeTAD layer was formed by spin-coating at 2000 rpm for 30 s. Compact TiO_2 layers were deposited through spray pyrolysis of a bis(isopropoxide)-bis(acetylacetonate)titanium(IV) solution at 450 $^{\circ}\text{C}$ prior to the deposition of the perovskite film. Complete devices were formed on fluorine-doped tin oxide (FTO) coated glass (Dyesol). Glass substrates were cleaned using a three step sonication process of hallmanex, distilled water and ethanol. For the optimized devices, the c.a. 50 nm TiO_2 layer was produced by spin-coating a commercially sourced (CCIC) 18 nm TiO_2 paste diluted in ethanol (1:9 wt) at 11,000 rpm for 30 s. The counter-electrode was deposited through the thermal evaporation of an 80 nm Au contact.

Current-voltage characteristics: A solar simulator (Oriel) fitted with a filtered 1,000 W Xenon lamp was used to provide solar simulated irradiation (AM1.5, 1000 Wm^{-2}). The light source was calibrated using a reference silicon photodiode (Peccell Technologies). Current-voltage measurements were performed using a Keithley 2400 source meter. Solar cells were masked using a non-reflective metal aperture of 0.16 cm^2 which defined the active area.

Electron Microscopy: SEM cross-section images were obtained by a FEI Nova NanoSEM 450 FEG microscope using a 5 kV accelerating potential. Samples were prepared on glass substrates and fractured to produce the cross-section.

Time-resolved Microwave Conductivity Measurements: Samples were excited using a 500 nm source with 5 ns laser pulses from an optical parametric oscillator (Continuum Panther) pumped by a 355 nm harmonic of a Q-switched Nd:YAG laser (Continuum Powerlite) at a frequency of 10 Hz. The perovskite films were probed using an X-band ($\sim$

9GHz) microwave source, while held within a corresponding microwave resonance cavity. All samples were deposited on a quartz-glass substrate of approximately 2 cm² in size. Details of the TRMC decay fits are outlined in the supporting information.

Photoluminescence measurements: Time resolved photoluminescence spectroscopy (TRPL) decays were performed using a 500 nm excitation source from a high-powered broadband fiber laser (Fianium WhiteLase Supercontinuum SC400-2-PP) with a 0.5 – 2 MHz repetition rate produced by a dual output acousto-optic tuning filter. The laser pulse width was ~ 6 ps. The spot size was measured to be ~ 150 μm in diameter, and each pulse had an energy density of ~ 50 nJ cm⁻². Emissions were transmitted through a 715 nm long-pass filter and were selected at 770 nm via a monochromator and detected by a cooled photon counting photomultiplier tube (TBX-07C) using the time-correlated single-photon counting technique. The detector unit included a HFAC-26 wideband amplifier and a SPC-140 TCSPC module (Becker & Hickl). PL decay measurements were stopped when the peak intensity reached 10⁴ counts. Decay curves were analyzed using OriginPro 8 SR0 software (OriginLab Corporation). Details of the TRPL decay fits are outlined in the supporting information. Steady-state PL measurements were performed using a luminescence spectrometer (Fluorolog 3, Horiba Yvon, Japan) comprising a monochromator (iHR320) and cooled CCD camera (Group Spectrum One G35 SPEX Instruments). Samples were illuminated using a 500 nm excitation source with an intensity of ~ 800 μW. Widefield fluorescence maps were performed using a Nikon 3D N-STORM instrument. Samples were excited using a 647 nm laser source (Nikon LU4A) over an area of approximately 40 μm in diameter. The fluorescence was captured using an oil immersion objective lens and imaged through an Andor DU-897 X-6926 camera. All fluorescence intensity maps comprised 2000 frames with an exposure times of 45 ms/frame, and were performed under equivalent laser excitation intensities.

Impedance spectroscopy measurements: Impedance spectroscopy measurements were performed under illumination using a 435 nm LED powered by a PP210 potentiostat. Cells were measured using a 10 mV perturbation under an illumination intensity of 250 Wm^{-2} with an applied potential. A Zahner Zennium electrochemical workstation ECW IM6 was used as a frequency response analyzer, and impedance measurements were performed in the 4 MHz to 50 mHz frequency range. Impedance data were analyzed using Zview equivalent circuit modeling software (Scribner).

3. Results and Discussion

3.1 Planar and Mesoporous Perovskite Morphology

High performance perovskite-based solar cells have successfully comprised both small and large perovskite grain structures. Mesoscopic architectures typically contain smaller grains that are limited by the pore size within the nanoparticle scaffold. While planar devices, formed through fast-crystallization (both gas-assisted and anti-solvent) methods, typically exhibit relatively large grains. Diffraction patterns of films fabricated using fast-crystallization methods also provide evidence that these relatively large grains are comprised of single crystals.[7] For the purposes of this study, contrasting small and large crystal sizes were produced to analyse transport and recombination kinetics as a function of the perovskite morphology. Using the gas-assisted crystallization method, relatively large perovskite grains were formed as part of a planar assembly. Small perovskite crystals were fabricated via the use of a nanoparticle Al_2O_3 layer, which restricted grain growth within the mesoporous scaffold. The inert nature of the Al_2O_3 scaffold allowed for the observation of charge transport and recombination kinetics within the perovskite phase alone.

Scanning electron microscope (SEM) cross-sections of the two perovskite morphologies are shown in Figure 1 (and Figure S1, Supporting Information). SEM surface

images for the gas-assisted planar and mesoscopic films are presented in Figure 2(a) and 2(b), respectively (and Figure S2, Supporting Information). The relatively large-scale grains of the planar perovskite material are depicted in Figure 1(a), which is in contrast with the mixed perovskite and Al_2O_3 phases shown in Figure 1(b). As has been reported previously, planar perovskite films formed through the fast-crystallization technique exhibit grains that typically span the entire thickness of the perovskite layer.[7, 8] It has also been shown that planar films produced through fast-crystallization methods can result in grains exceeding 1 micron in width.[7] The Al_2O_3 nanoparticles constituting the mesoscopic assembly impede the perovskite grain growth, unlike the homogenous film produced by the fast-crystallization method. This results in relatively small perovskite grains residing within the Al_2O_3 scaffold, as depicted in Figure 1(b).

Figure 1. SEM cross-sections of (a) a planar perovskite layer and (b) a mesoscopic Al₂O₃/perovskite layer deposited on a glass substrate. CH₃NH₃PbI₃ and CH₃NH₃PbI₃/nanoparticle-Al₂O₃ form the material layers at the top of Figures (a) and (b), respectively. The glass substrates are shown at the bottom of the SEM images.

Figure 1(b) also reveals a thin (ca. 50 nm) perovskite capping layer sitting upon the Al₂O₃ nanoparticle film. For the purposes of this study, the thickness of this capping layer was limited to a minor fraction of the total film thickness, in order to confidently ascribe charge transport and recombination characteristics to the mesoscopic portion of the film. This was performed through the high rotational speeds used during the perovskite spin-coating step. The restricted capping layer ensured that the majority of the mesoscopic perovskite layer was defined by the smaller grain sizes residing within the nanoparticle Al₂O₃ pores. The gas-assisted method was also employed for the film shown in Figure 1(b) in order to aid the crystallization of this thin capping layer. From the SEM surface images in Figure 2, it is apparent that the average grain size within the mesoscopic capping layer (Figure 2(b)) is consistently smaller than the average grain size in the planar film (Figure 2(a)).

The gas-assisted crystallization technique, used to produce the planar PSC morphologies in this study, is an effective way of optimizing the surface coverage of the CH₃NH₃PbI₃ on the underlying substrate. The success of the technique relies in the super-saturation of the perovskite precursor as the solvent is evaporated using an inert gas flow. In the absence of the applied gas flow, the perovskite material will form micron-scale dendritic needles (Figure 2(c) and Figure S3, Supporting Information), as the perovskite crystallization rate far exceeds the nucleation rate. Comparative absorbance data has highlighted the poor light harvesting of the dendritic perovskite morphology relative to the fast-crystallization produced films (Figure S4, Supporting Information). The fast-crystallization method rapidly reduces the solubility of the perovskite in the precursor and promotes the formation of

nucleation sites. The increased number of nucleation sites limits the further growth of individual crystals, allowing for a uniform coverage of the underlying substrate and preventing the growth of dendritic grain structures. In this regard, the fast-crystallization technique encourages the forced nucleation and crystallization of the perovskite precursor, unlike the relatively slow nucleation and crystallization of the conventional spin-coat method. The higher efficiencies achieved using the fast-crystallization method versus the conventional spin-coat method are readily attributed to the poor absorption characteristics of the needle-like perovskite morphology.[16] However, the efficiency measurements alone provide little insight into the charge transport and recombination dynamics within this needle-shaped perovskite morphology. In order to elucidate the charge transport and recombination dynamics within these dendritic needles, this study has also analyzed films produced through the conventional spin-coat method.

Figure 2. SEM surface images of (a) a planar perovskite layer and (b) a mesoscopic Al₂O₃/perovskite layer produced using the gas-assisted method, and (c) the dendritic needles produced by the conventional spin-coating. All films are deposited on FTO-glass substrates with a spray pyrolysis TiO₂ coating.

3.2 Time-Resolved Microwave Conductivity (TRMC) Mobilities

TRMC is recognised as a powerful technique to analyse both transport and recombination kinetics in hybrid organic-inorganic photovoltaic technologies.[17-19] Through this technique, changes in the microwave absorption, $\Delta P(t)$, with respect to the steady-state power of the microwave beam, P , are related to the photoconductance of a material, $\Delta G(t)$, by $\Delta G(t) = -K \Delta P(t)/P$, when the sample is excited with a 5 ns laser pulse. In the above equation, K is an experimentally determined calibration factor that depends on the sample and measurement geometry.[20] The photoconductance is proportional to the density of excited charge-carriers as a function of time, and the corresponding mobility of these carriers. For a given material, one of the figures-of-merit typically extracted from TRMC measurements is the product of the quantum efficiency for free carrier generation per photon absorbed during the pulse, ϕ , and the sum of the mobilities of these carriers, $\sum \mu$, given by:[17]

$$\phi \sum \mu = \frac{\Delta G_{peak}}{\beta q_e F_A I_0} \quad (1)$$

In the expression above, ΔG_{peak} is the measured peak photoconductance during the pulse, F_A is the fraction of photons absorbed by the photoactive layer, I_0 is incident photon fluence, $\beta = 2.2$ is a geometric factor for the X-band microwave cavity used and q_e is the elementary charge. In the case of hybrid organic-inorganic perovskites, due to the high dielectric constant of the material[21, 22] free charges are generated upon excitation, i.e. $\phi = 1$. In this case, Equation (1) can be directly used to estimate the sum of mobilities of electrons and holes in the material. Furthermore, the strong microwave absorption of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite material, attributed to the relatively high charge carrier mobilities,[21] also allows for

measurements to be performed at relatively low excitation densities, avoiding high-injection effects and providing a more representative analysis of operating conditions close to one sun illumination.

Figure 3 illustrates the $\phi \sum \mu$ product for both planar and mesoscopic PSC assemblies as a function of the absorbed excitation flux. Measurements have been performed using an excitation intensity spanning approximately two orders of magnitude. As noted above, for materials with high dielectric constants, $\phi = 1$ and the data of Figure 3 can be directly interpreted as the sum of mobilities of electron and holes.[23] For this system, there is strong evidence to suggest that the microwave transients are dominated by an electron signal.[21] Mobilities relating to the planar films are shown in the circles and those relating to the mesoscopic devices are shown in the triangles. All perovskite films were formed using either the fast-crystallization method (open symbols) or a conventional spin-coating method (filled symbols). High charge-carrier mobilities ($> 1 \text{ cm}^2/\text{Vs}$) have been previously reported in both planar and mesoscopic perovskite based devices.[19, 24-26] These high charge-carrier mobilities are similarly reflected in our TRMC measurements.

The TRMC results indicate that the sum of charge mobilities in the planar devices ($7 \pm 1 \text{ cm}^2/\text{Vs}$) are consistently higher than those measured in the mesoscopic assemblies ($3 \pm 1 \text{ cm}^2/\text{Vs}$). This was shown true for films produced through both fast-crystallization and conventional spin-coating fabrication techniques. The significantly faster mobilities in the planar assemblies reveal a correlation between the perovskite morphology and the charge transport rates, implying that grain boundaries pose an adverse effect. The inhibiting effect of grain boundaries on charge transport is well established in other photovoltaic technologies,[27] and previous studies of perovskite-based technologies have equally highlighted the correlation between crystal domain size and charge transport rates.[28, 29] Given that the compact planar samples are characterised by perovskite grains spanning the

thickness of the film, it is not surprising that both local and long-range mobility measurements of dense planar films have produced similar mobility results.[26, 30] In the case of the mesoscopic sample, however, charges are more likely to be scattered or trapped at the numerous perovskite grain boundaries. We anticipate that the relative density of perovskite grain boundaries is a dominant factor affecting the charge mobilities, however, there may also be other factors that influence the movement of charges. The slower transport rates measured for the mesoscopic devices may also be related to the insulating Al_2O_3 nanoparticles impeding the movement of charges within the perovskite layer. Alternatively, it is likely that an insufficient pore-filling of perovskite material within the mesoporous scaffold may obstruct the diffusion of carriers.

Figure 3. The $\phi\Sigma\mu$ product (see Equation (1)) determined by TRMC for planar perovskite layers (circles) and mesoscopic Al_2O_3 /perovskite layers (triangles) deposited on quartz substrates. Perovskite films fabricated through the fast-crystallization method are shown in the open symbols while those fabricated using a conventional spin-coat are shown in the filled symbols. The wavelength of the 5 ns excitation pulse was 500 nm.

One interesting point of note observed from the TRMC mobility measurements is the relatively high mobilities presented by the conventional spin-coated perovskite films. This fabrication method has been shown to produce needle-like perovskite structures that offer a very poor coverage of the underlying substrate.[7, 16] However, the charge mobilities within this structure appear to be on par with those measured in the fast-crystallised perovskite films. This result implies that the low efficiencies seen in the conventional spin-coated perovskite cells cannot be attributed in any way to limitations in the transport of charges within the perovskite layer.

3.3 Charge-Carrier Recombination

The charge-carrier mobility represents a very important part of how efficiently charges are extracted out of the perovskite layer. However, equally important is the rate at which these charges recombine. The combined consideration of how ‘fast’ mobile carriers are moving, as well as how ‘long’ they are travelling for, largely defines a solar cell’s ability to effectively harvest absorbed photons. One suitable way of assessing the charge recombination rate is through the use of TRPL, which directly correlates the rate of fluorescence with the rate of radiative charge recombination. Photoluminescence transients for planar perovskite films produced using the conventional spin-coating method (green trace), the fast crystallization method (orange trace) and a mesoscopic Al_2O_3 /perovskite film (blue trace) are depicted in Figure 4. The dotted grey lines represent the fitted response for each luminescence decay. TRPL decays for all planar and mesoscopic devices used in the present study are shown in Figure S5 (Supporting Information). Figure 4 reveals that the planar devices, produced through both fast-crystallization and conventional spin-coating methods, present significantly longer decays than the mesoscopic device. The coefficient-weighted time constants for the three decays were calculated to be 50 ± 1 , 17.1 ± 0.6 and 6.3 ± 0.2 ns for the conventional spin-coated film, the fast-crystallised planar film and the mesoscopic

Al_2O_3 /perovskite film, respectively. These time constants are in general agreement with previously reported values for neat perovskite films.[31, 32] Previous characterization work on planar perovskite films, formed through the two-step sequential deposition method, has also identified the link between photoluminescence lifetimes and crystallite size.[33]

Figure 4: Time-resolved photoluminescence (TRPL) measurements for planar perovskite films prepared using a conventional, un-assisted spin-coating (green trace) and the fast-crystallization method (orange trace), as well as a mesoscopic Al_2O_3 /perovskite layer prepared using the fast-crystallization method (blue trace). TRPL measurements were performed using a $\sim 50 \text{ nJ/cm}^2$ excitation pulse at a wavelength of 500 nm, and the fluorescence was collected at 770 nm. Dotted lines represent fits based on a double-exponential decay model. TRPL time constants were determined through the weighted mean of the fits.

Comparison of transient decays from TRPL and TRMC techniques provides a unique check on any mechanistic process proposed. Where TRMC transients (Figure 5) exhibit a very long-lived tail these are not observed in the TRPL measurements. To a first approximation, the fast component of the TRMC decay correlates with the average TRPL decay (see Tables 1 and 2). Our interpretation of these data is as follows. The fast and slow components of the TRPL transients may be viewed as recombination between the electrons

and holes dominated by the surface and bulk, respectively. TRMC is less sensitive to surface effects, with the majority of its signal stemming from electron intra-grain mobility. This average (bulk) decay likely corresponds to the same decay as observed in the TRPL measurement. The slow decay component of the TRMC transient could then correspond to a long-lived electron population that ultimately recombines with trapped holes. This slower, longer wavelength recombination process is unlikely to be observed in the TRPL measurement due to the fact that we only were sampling in a narrow spectral window around 770 nm. Qualitatively, the average TRPL decay times correspond to the fast decay times of the TRMC transients. We recognize that the sub-picosecond pulses from the TRPL experiments and the nanosecond pulses from the TRMC experiments are significantly different. Therefore, a direct comparison of injection levels is difficult, which may explain the observed differences (Tables 1 and 2).

Figure 5. Time-resolved microwave conductivity (TRMC) measurements for planar perovskite films prepared using a conventional, un-assisted spin-coating (green trace) and the fast-crystallization method (orange trace), as well as a mesoscopic Al_2O_3 /perovskite layer prepared using the fast-crystallization method (blue trace) and the conventional spin-coating method (red trace). TRMC transients were performed using an excitation intensity of $F_A I_0 = 1 \times 10^{12} \text{ cm}^{-2}$.

The dotted grey traces represent double-exponential fits of the TRMC decays (see Supporting Information). The displayed time constants were determined through the weighted average decay time from the fits.

Table 1: Constants and lifetimes obtained from the TRPL decay fits.

Film	C_1	τ_1 (ns)	C_2	τ_2 (ns)	$\langle\tau\rangle$ (ns)
Al ₂ O ₃ (conventional spin)	0.692	5.6	0.086	23.2	7.5 ± 0.2
Al ₂ O ₃ (gas-assisted)	0.691	4.7	0.100	17.2	6.3 ± 0.2
Al ₂ O ₃ (anti-solvent)	0.648	5.6	0.090	22.7	7.7 ± 0.2
Planar (conventional spin)	0.640	35.4	0.130	121.4	50 ± 1
Planar (gas-assisted)	0.414	10.2	0.517	22.6	17.1 ± 0.6
Planar (anti-solvent)	0.400	11.2	0.549	21.6	17.3 ± 0.9

Table 2: Constants and lifetimes obtained from the TRMC decay fits

Film	C_1 (cm ² V ⁻¹ s ⁻¹)	τ_1 (ns)	C_2 (cm ² V ⁻¹ s ⁻¹)	τ_2 (ns)	$\langle\tau\rangle$ (ns)
Al ₂ O ₃ (conventional spin)	0.887	30.8	0.491	307.8	128 ± 2
Al ₂ O ₃ (gas-assisted)	1.183	31.4	0.305	395.6	106 ± 1
Planar (conventional spin)	4.231	46.2	0.714	618.3	129 ± 1
Planar (gas-assisted)	4.087	38.5	0.520	333.5	71 ± 1

The fast components of the TRMC decays for the gas-assisted planar and mesoscopic samples, characteristic of surface/grain-boundary mediated recombination,[34] are described by decay constants of $\tau_1 = 38.5$ and $\tau_1 = 31.4$, respectively (Table). The fast components of the TRPL decays similarly reflect the longer surface/grain-boundary recombination lifetimes of the planar films (Table). In this regard, both TRMC and TRPL measurements reveal that

trap-mediated recombination is higher in the relatively small-grain mesoscopic versus the large-grain planar films. Previous studies on hybrid organic-inorganic perovskites have proposed that the abundance of shallow surface-states present at the grain boundaries in mesoscopic perovskite films facilitate the trap-mediated recombination of charges.[26] Smaller-grain perovskite films are typically dominated by monomolecular recombination kinetics, while larger-grain films exhibit higher relative bimolecular recombination rates;[35] ultimately culminating in slow PL decays for bulk recombination and fast PL decays for recombination at surfaces/grain-boundaries.[34] Recent results obtained through confocal fluorescence microscopy have equally noted the deleterious effects of grain boundaries on free-carrier lifetimes.[36] The higher measured mobilities and slower monomolecular recombination dynamics apparent from our characterization of the planar devices mean that they possess a clear advantage over mesoscopic devices. However, it is worth noting that these results solely consider the transport and recombination of carriers within the perovskite material, and do not consider interfacial recombination. It is commonly accepted that a mesoporous TiO_2 layer operates as an effective heterojunction that is capable of suppressing charge recombination dynamics.[18]

An interesting result from the TRPL decay measurements is that the conventional spin-coated perovskite film presented longer charge-carrier lifetimes than both planar and mesoscopic devices prepared using the fast-crystallization technique. TRMC decays also revealed the comparatively longer decay components (τ_2) of the needle-like perovskite films for both planar (618 ns) and mesoscopic (308 ns) architectures. This indicates that the beneficial photo-electric properties of the needle-structured perovskite film extend beyond those of the homogenous films produced through the fast-crystallization method. The latter method essentially entails the forced nucleation and crystal growth of the perovskite material, and it is highly likely that this accelerated crystal growth leads to a higher concentration of

crystallographic defects compared to the relatively slow crystallization of the conventional spin-coating method. These defects formed through the fast-crystallization method readily serve as Shockley-Read-Hall (SRH) recombination sites,[37] which can reduce carrier lifetimes and overall charge collection efficiencies. It is expected that the relatively slower crystallization of the conventional spin-coating method successfully avoids this high concentration of defects, which accounts for the longer lifetimes seen in Figure 4 and Figure 5. However, as previously noted, the poor surface coverage of the perovskite needles[16] severely hampers the absorption of incident light, which leads to the poor power conversion efficiencies.

3.4 Charge-Carrier Quenching Measurements

The use of a quenching layer in electrical contact with the perovskite film is an effective way to assess the charge-carrier injection rate, the charge-carrier diffusion rates and/or the relative electron/hole mobilities within the perovskite layer.[31, 32] Both photoluminescence and microwave conductivity measurements are capable of measuring these parameters in conjunction with an effective quenching layer. Figure 6 displays both PL and TRMC measurements for perovskite films with a quenching compact TiO₂, mesoporous TiO₂ or a spiro-OMeTAD layer. The steady-state and transient PL responses are shown in Figure 6(a) and (b), respectively, while the TRMC $\phi\sum\mu$ products are shown in Figure 6(c). In the case of a planar perovskite device, there was relatively poor quenching of the PL signal by both the compact TiO₂ layer (blue line) and the spiro-OMeTAD layer (pink line), as shown in Figure 6(a). The TRPL quenching measurements, shown in Figure 6(b), reveal that the luminescence decay of the perovskite + spiro-OMeTAD film (pink trace) mirrors the decay of the neat perovskite for the first ~ 25 ns after the excitation pulse. After this point, positive charges freely inject into the spiro-OMeTAD layer. This injection results in a depleted concentration of holes within the perovskite layer, ultimately slowing the rate of

bimolecular recombination, and producing the prolonged luminescence tail seen in the TRPL decays of Figure 6(b).

The injection of holes into the spiro-OMeTAD layer, however, appears relatively fast compared to the injection of electrons into the compact TiO₂ layer. We have previously reported the strong quenching of the perovskite luminescence through a contacting spiro-OMeTAD layer,[38] and this result is supported by other studies.[31, 32] For this reason, it is unlikely that the perovskite/spiro-OMeTAD contact presents a serious limitation on the overall device performance. The slow charge transfer at the perovskite/c-TiO₂ interface, which has been noted in previous literature,[21] and is equally reflected in our steady-state PL measurements. This slow electron injection into the compact TiO₂ layer presents a serious limitation for the planar system, and it is expected that the limited surface area of the flat TiO₂ layer lies at the heart of this problem. Given the limited injection of carriers into the compact TiO₂ layer, the prolonged luminescence tail (seen in the perovskite/spiro-OMeTAD system) is not observed in the perovskite/c-TiO₂ system (blue line) as both electrons and holes freely undergo radiative recombination within the perovskite phase.

Figure 6. Photoluminescence spectra (a) and decays (b) for fast-crystallization planar perovskite films comprising a neat perovskite film (orange trace), a perovskite film on a compact TiO_2 layer (blue trace) and a perovskite film with a spiro-OMeTAD layer (pink trace). Films were excited using a 500 nm source with a 5 nm slit width ($\sim 800 \mu\text{W}$). (c) TRMC determined $\phi\Sigma\mu$ products for mesoscopic Al_2O_3 /perovskite layers produced through both conventional spin-coating and fast-crystallization techniques (red, dark-blue and light-blue markers) and a mesoscopic (not compact) TiO_2 /perovskite layer (yellow markers) produced via the fast-crystallization technique.

Figure 6(c) shows the TRMC determined mobilities for several mesoscopic Al_2O_3 /perovskite layers and a mesoscopic TiO_2 /perovskite layer. Summed electron and hole mobilities in the Al_2O_3 /perovskite system are $\sim 3\text{-}4 \text{ cm}^2/\text{Vs}$, while those for the TiO_2 /perovskite system are $\sim 1\text{-}2 \text{ cm}^2/\text{Vs}$. The difference between these two results is due to the rapid injection of electrons into the nanoparticle TiO_2 film, which is a comparatively lower mobility ($\ll 1 \text{ cm}^2/\text{Vs}$) material than the perovskite layer.[19] Given that the summed mobilities are derived from the peaks of the TRMC decays, this electron injection effectively occurs within $< 1 \text{ ns}$ of the excitation pulse, as there is already a clear separation between the Al_2O_3 and TiO_2 mobilities prior to the $\phi\sum\mu$ decay. In this regard, mesoscopic TiO_2 /perovskite devices present an advantage over planar devices in terms of the fast extraction of negative carriers, however, this comes at the cost of transporting electrons through a comparatively low-mobility material.

Given that electrons in the mesoscopic TiO_2 /perovskite system are rapidly injected into the low-mobility mesoporous TiO_2 layer such that there is a significant drop in $\phi\sum\mu$, there are two possible interpretations. (1) Enough of the electrons have transferred to the TiO_2 such that the hole mobility within the perovskite layer provides the dominant contribution to $\phi\sum\mu$ in the perovskite layer, or (2) consistent with previous reports,[21] the $\phi\sum\mu$ represents the residual electrons in the perovskite layer that have not migrated to the interface with the TiO_2 . In the first case, the TRMC data shows that electrons and holes present balanced microwave mobilities within the perovskite layer, in agreement with theoretical estimates.[39] There is yet to be a consensus on the relative contributions of electron and hole mobilities towards the overall conductivity of hybrid organic-inorganic perovskites, with some sources reporting balanced mobilities,[19, 31, 35] and other sources reported the converse.[25, 40] An effective quenching layer is an imperative feature required to separate

the relative contributions of electrons and holes, and it is possible that the delayed injection of charges may contribute to the present misunderstanding of charge-carrier mobilities.

3.5 Impedance Spectroscopy (IS) Characterization

Impedance spectroscopic analysis of perovskite-based solar cells is a proven characterization technique that is capable of revealing useful information concerning the device operation.[41-44] IS is particularly useful for explaining the capacitive charging of the selective contacts,[43] as well as exploring the low-frequency ‘slow’ response of the perovskite layer.[45, 46] We have previously presented an impedance model (Figure 7(a)), based on the formative work of Bisquert and co-workers,[42, 43, 45, 46] that describes the complete impedance spectrum of a planar perovskite solar cell.[38] This model is equally applicable to a mesoscopic Al_2O_3 /perovskite based device, as the nanoparticle Al_2O_3 layer in this case is electrically inactive. In this regard, the infiltrated perovskite material within the Al_2O_3 framework, is analogous to a porous planar perovskite device. Indeed, IS measurements for both planar and mesoscopic Al_2O_3 /perovskite devices display similar impedance spectra. A representative impedance response, characteristic of the planar and mesoscopic architectures, is shown by the circles in Figure 7(a) and the fitted equivalent circuit response is shown in the solid line. As we have reported previously, the impedance spectrum for a planar perovskite solar cell comprises high-frequency and low-frequency features, which are associated with the build-up of charges at the perovskite/contact interfaces and the dielectric response of the perovskite respectively.[38] Whether this low-frequency response is derived from a slow dielectric polarization owing to fluctuations in the perovskite crystal structure,[47] or the languid drift and diffusion of mobile ions across the perovskite film,[48] is yet to be formally presented.

Figure 7. Impedance spectroscopy data measured under constant illumination with a varying applied potential. (a) A typical impedance spectrum for both planar and mesoscopic devices is shown in the circles, and the fitted response is shown in the solid red line. The inset displays the equivalent circuit used, which comprises the interfacial recombination resistance, R_{rec} , the interfacial contact capacitance, C_{con} , the dielectric relaxation resistance, R_{dr} , and the dielectric response capacitance, C_{dr} . The magnitudes of the resistive and capacitive elements is shown in plots (b) and (c) respectively.

Figure 7(b) shows the interfacial recombination resistance (filled markers), R_{rec} , and the dielectric relaxation resistance (empty markers), R_{dr} , for the mesoscopic Al_2O_3 /perovskite (blue triangles) and planar perovskite (red circles) based cells. In both cell structures, as the applied potential approaches the open-circuit voltage, there is a decrease in the recombination resistance due to the increase in the recombination dynamics. The drop in the recombination resistance is expected, as recombination dynamics are more prevalent around the open-circuit potential. The interfacial recombination resistance appears to be higher in the case of the mesoscopic device. This is largely due to the contact area between the perovskite and the compact TiO_2 layer being smaller in the mesoscopic assembly. The reduced contact area leads to a reduced recombination rate at the c- TiO_2 /perovskite interface. The smaller

interfacial contact area is also apparent from the capacitance values shown in Figure 7(c). This graph displays the interfacial contact capacitance (filled markers), C_{con} , and the dielectric response capacitance (empty markers), C_{dr} , for the mesoscopic Al_2O_3 /perovskite (blue triangles) and planar perovskite (red circles) based cells. The high-frequency feature of the impedance spectrum is dominated by C_{con} , and the low-frequency feature by C_{dr} . In the case of the mesoscopic device, the reduced interfacial area between the perovskite and the compact TiO_2 layer leads to a significantly higher contact capacitance compared to the planar device. Although it is shown in Figure 7(c) that the lower contact area impedes the interfacial recombination, it is also likely that the limited contact area in the mesoscopic Al_2O_3 /perovskite device frustrates the injection of electrons into the c- TiO_2 layer.

The low-frequency feature obtained from IS measurements has been linked with the dielectric behavior of the perovskite layer,[45] however, it is likely that the low-frequency feature may also relate to other polarization mechanisms occurring in perovskite-based devices. This ‘slow’ behavior is described by the R_{dr} and C_{dr} elements of the equivalent circuit, shown in Figure 7(a). The dielectric relaxation resistances of the mesoscopic and planar devices exhibit similar magnitudes, despite their shape as a function of the applied potential. In the mesoscopic device, R_{dr} increases as the potential approaches V_{OC} , while in the planar architecture the magnitude of R_{dr} decreases. Similarly, the dielectric response capacitance is relatively constant for the mesoscopic device, while C_{dr} increases with the applied potential in the case of the planar device. We have previously shown that for a planar device, an increase in the charge-carrier concentration prompts a decrease in the dielectric relaxation resistance, and an increase in the dielectric response capacitance.[38] The C_{dr} of the mesoscopic device does not seem to hold the same dependence on the charge-carrier concentration. We speculate that the perovskite dielectric domains constrained within the pores of the Al_2O_3 scaffold are not free to polarize in the same fashion as the planar device,

leading to the constant C_{dr} as a function of the varying potential. However, it is yet to be shown how the polarization of the perovskite layer affects the overall device performance. So whether this limited polarizability is a hindrance or a help is yet to be established.

3.6 Device Optimization

The key lessons learnt from the characterization measurements were as follows:

- A. Charge-carrier mobilities in the large-grain, planar perovskite architecture are faster than mobilities in the small-grain, mesoscopic perovskite system.
- B. Trap-mediated recombination rates within the perovskite layer are significantly slower in the planar devices compared to the mesoscopic devices. The needle-like structures produced from the conventional spin-coat method presented even slower recombination rates, most likely due to the lower concentration of defects produced during the slow crystallization process.
- C. Electron injection rates into the compact TiO_2 layer are generally slow, and could present a limit on charge separation. Electron injection rates into a mesoporous TiO_2 scaffold proved significantly faster.
- D. A mesoporous scaffold is capable of successfully reducing the parasitic recombination of charges across the FTO/c- TiO_2 /perovskite interfaces.

With these lessons in mind, cells were optimized in an attempt to utilize the best aspects of both planar and mesoscopic perovskite morphologies. The first two lessons indicate that planar architectures are far more suitable to faster charge transport and longer charge lifetimes, compared to mesoscopic architectures. However, the third lesson highlighted the relatively slow electron injection into the compact TiO_2 layer apparent in a planar architecture. Therefore, an optimized device architecture should ideally comprise large,

planar perovskite grains with a thin, mesoporous TiO_2 contact to aid charge injection, and reduce recombination at the perovskite/substrate interface. To this effect, optimized cells were formed using a hybrid planar/mesoscopic architecture, consisting of a 200 – 250 nm planar perovskite film on top of a 50 – 60 nm thick mesoscopic TiO_2 /perovskite layer. The inclusion of a thin mesoscopic layer allows for the fast extraction of negative charges, without sacrificing the beneficial charge transport and recombination dynamics of the planar perovskite morphology.

A further outcome of the characterization measurements was the relatively fast charge transport and slow recombination exhibited by the needle-like perovskite morphology of the conventional spin-coating method. This morphology, however, is not effective to use in an optimized device as the surface coverage and optical absorption of the needle-like perovskite film is poor. The long carrier lifetimes displayed by the needle-like structures are likely caused by the lower concentration of trapping defects formed during the slow crystallization process. An indirect way of observing the decrease in trap-mediated recombination is through studying the relative intensity of radiative recombination processes. As seen in Figure 8, wide-field fluorescence maps of both conventional spin-coated (Figure 8(a)) and gas-assisted (Figure 8(b)) films reveal a higher relative PL intensity in the needle-like perovskite morphologies versus the dense planar film. This high PL yield implies a successful reduction of defect states in the needle-like structures, whereas the low PL yield shown by the gas-assisted film denotes a higher degree of defect-mediated SRH recombination. It is worth noting that the spatially resolved PL maps exhibit the same grain-to-grain fluorescence discrepancies recently reported by de Quilettes *et al.*[36] Although a degree of fluorescent blinking[49] was observed in both needle-like and planar perovskite films, super-resolution stochastic optical reconstruction microscopy was not possible due to the relatively uniform nature of the planar perovskite samples.

Figure 8. Wide-field fluorescence maps of perovskite films prepared through the conventional spin-coating (a) and gas-assisted ((b) and (c)) methods. The perovskite materials in samples (a) and (b) were heated at 85 °C for 10 mins, while the film in (c) was heated at 85 °C for 30 mins. Equal excitation intensities and exposure times (25 ms/frame) were used for all fluorescence measurements. The resulting images comprise 2000 frames. (d) A histogram displaying the relative PL intensities of the three films described above.

A facile way of reducing the defect density in the gas-assisted films, while still maintaining a high surface coverage, is through the prolonged annealing of the perovskite film. We have previously identified the increase in grain size, typical of Ostwald ripening, as a function of the annealing duration.[8] The significant mass diffusion characteristic of Ostwald ripening, is more than sufficient to effectively passivate crystallographic defects. However, extended annealing of the perovskite film can lead to the degradation of the material,[50] so there exists a delicate balance between the optimized crystal morphology and the chemical decomposition of the perovskite layer. For this reason, the optimized devices were annealed at 85 °C for an extended period of 30 minutes in order to passivate

crystallographic defects while still preserving the chemical composition of the perovskite material. The inclusion of both the extended annealing time and the thin nanoparticle TiO_2 layer resulted in a maximum device efficiency of 16%, which was significantly higher than the best performing planar or mesoscopic devices (Figure S10, Supporting Information) for each respective architecture. The photovoltaic response of the highest performing device, as well as a schematic representation of the device structure, is shown in Figure 9.

Figure 9. (a) Schematic representation of the optimized device structure. (b) Current-voltage response of the highest-performing optimized device. The solid line presents a scan direction from forward-bias to short-circuit (FB – SC) and the dashed line presents a scan direction from short-circuit to forward-bias (SC – FB). The performance parameters are shown in the table inset.

Although the extended annealing time plays a role in lowering the concentration of monomolecular recombination sites, it is likely that the effects of this remedy on the device performance are relatively minor. Figure 8(c) illustrated the moderate abatement of monomolecular recombination (higher radiative recombination contribution) achieved after the extended annealing time, which was still well short of the strong fluorescence shown by the needle-like film. We envisage that a superior device morphology would incorporate both a planar perovskite film and a network of connected dendritic needles. This would allow for the effective coverage of the underlying substrate, as well as exploiting the beneficial

properties of the conventional spin-coated film. However, the challenge remains of how to fabricate this complex microstructure.

4. Conclusion

Planar and mesoscopic perovskite architectures, formed through fast-crystallization and conventional spin-coating methods, were characterized in order to assess the effect of the perovskite morphology on the charge transport and recombination dynamics. TRMC and TRPL measurements revealed that the large perovskite grains, typical of planar structures, exhibited longer radiative recombination lifetimes as well as faster charge mobilities. This result discloses an inherent advantage of planar perovskite morphologies over mesoscopic morphologies. However, the limited contact area between the compact TiO_2 layer and perovskite film in planar assemblies frustrates the extraction of electrons, which is not an apparent issue in mesoscopic perovskite/ TiO_2 structures. IS measurements indicated that the mesoporous scaffold is also effective at suppressing recombination across the FTO/c- TiO_2 /perovskite interfaces. With these lessons in mind, an optimized device architecture was formed, utilizing the benefits of both planar and mesoscopic architectures. This optimized perovskite morphology resulted in a maximum efficiency of 16%, surpassing the best cells produced in this study using solely planar or mesoscopic architectures. This study highlights the absolute importance of perovskite morphological control towards the maximized performance of PSC devices.

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Appendix A: Supplementary Material

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TOC Graphic

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