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6 Optimized organometal halide perovskite solar cell fabrication 7 through control of nanoparticle crystal patterning

8 D. K. Mohamad^a, B. G. Freestone^a, R. Masters^b, M. Reinhardt^c, S. Canning^d, C. Rodenburg^b and D.
9 G. Lidzey^{1*}

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10 The addition of Hydrogen Iodide to organometal halide perovskite precursor solution at 1% by volume leads to a
11 significant enhancement in average power conversion efficiency (PCE) in inverted solar cell devices, increasing from 7.7%
12 to 11.9% and 6.1% to 10.0% in spin-cast and spray-cast devices respectively. We directly attribute this improved device
13 performance to increased thin-film surface coverage coupled with higher optical density. X-ray diffraction studies also
14 reveal that the HI additive facilitates full conversion of the precursor material to the crystalline perovskite phase. From
15 solution studies, we relate these changes in device performance to the presence and distribution of precursor aggregates
16 that effectively pattern the formation of perovskite crystals during film formation.

17 Introduction

18 Organometal halide perovskites are fascinating materials with
19 great implications for optoelectronics. Their combination of
20 high charge-carrier mobility, efficient light absorption and
21 compatibility with low-temperature solution-based processes
22 makes them particularly suited to photovoltaic applications in
23 perovskite solar cells (PSCs). Since the early work of Kojima et
24 al.¹, recent research efforts have seen their power conversion
25 efficiencies (PCEs) rise from 3.8% to 22.1%² in state-of-the-art
26 devices.

27 Conventionally, PSC active layers are deposited from a
28 precursor solution of that is most commonly composed of a
29 blend of lead halides and methyl ammonium halides. After
30 casting the precursor solution to create a thin-film, thermal
31 annealing results in the formation of a polycrystalline
32 perovskite crystal film. Managing this process is key to
33 producing high-efficiency PSCs as their performance is very
34 sensitive to active layer microstructure and crystal purity. To
35 address this issue, solution additives including water³,
36 Hydrogen Iodide (HI)⁵⁻⁷, alkyl halides^{8, 9} and
37 chloronaphthalene¹⁰ have all been shown (when added in the
38 correct concentration), to enhance PSC device efficiency by
39 controlling the perovskite crystallisation kinetics through
40 modulation of lead salt solubility and solvent drying rate.

41 In this study, we focus on the well characterised PbCl₂:MAI

42 precursor ink formulation which is used in the single-step
43 deposition of MAPbI_{3-x}Cl_x perovskite thin-films in planar PSC
44 device architectures^{11, 12}. Critically, we explore two different
45 techniques to deposit the PbCl₂:MAI precursor; spin-coating
46 and spray-coating. While spin-coating has been the method of
47 choice to fabricate PSCs, there is growing interest in the use of
48 spray-coating¹³⁻¹⁶ as it presents a ready means for possible
49 manufacture scale-up¹⁷. Through careful optimisation of PSC
50 fabrication conditions, we show addition of 1% by volume
51 (v%) of HI to the perovskite precursor solution has a marked
52 positive effect on device behaviour; an observation that applies
53 to PSCs prepared both by spin-casting and spray-casting.
54 Previous work by Heo et al.⁶ demonstrated that by adding HI at
55 9.1 v% to a 1:1 PbI₂:MAI precursor ink facilitates single-step
56 deposition of a continuous MAPbI₃ film without pinholes or
57 impurities, leading to devices having a remarkably high PCE
58 (17.2% average). These authors attributed such effects to the
59 enhanced solubility of MAPbI₃ that favours the growth of a
60 continuous perovskite crystal during the film formation process.
61 Furthermore, it was suggested that the HI facilitated a recovery
62 of decomposed MAI, resulting in the complete consumption of
63 PbI₂ and thus the formation of a pure perovskite crystal.

64 Rather than the rapid perovskite crystal formation during
65 film casting typical of single halide systems, mixed halide ink
66 systems rely on extended thermal treatments to convert the
67 precursor to the final perovskite form^{18, 19}. In such systems, the
68 crystal formation dynamics are distinctly different and thus
69 require another set of processing conditions for the fabrication
70 of efficient PSCs. In order to better understand our results, we
71 employ thin-film absorption, PL emission, scanning electron
72 microscopy (SEM) and X-ray diffraction (XRD) to explore film
73 structure. From our XRD patterns, we conclude that when
74 added at 1% by volume, the HI additive facilitates full
75 conversion of precursor material leading to a pure crystalline

^a Department of Physics and Astronomy, The University of Sheffield, Hicks Building,
70 Hounsfield Road, Sheffield S3 7RH, U.K. email: d.g.lidzey@sheffield.ac.uk

^b Department of Materials Science and Engineering, The University of Sheffield,
71 Mappin Street, Sheffield S1 3JD, U.K.

^c Ossila Ltd., Kroto Innovation Centre, Broad Lane, Sheffield, S3 7HQ, U.K.

^d Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K.

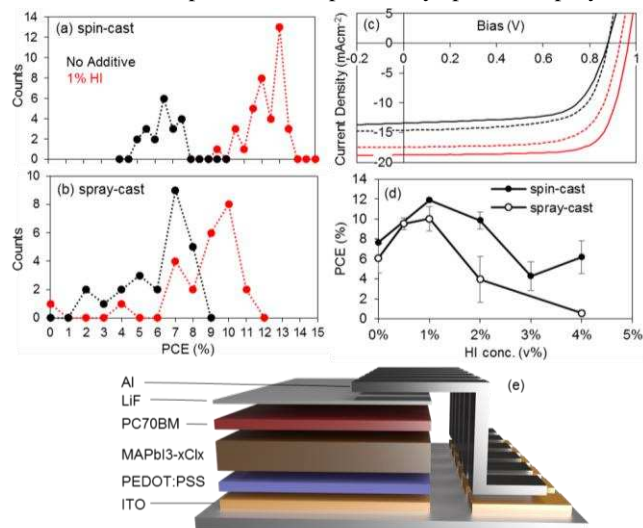
† Electronic Supplementary Information (ESI) available: See

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76 perovskite phase. In addition, our measurements also suggest an
 77 increased lattice spacing that is consistent with an observed red-
 78 shift in the onset of absorption and PL. SEM images and optical
 79 absorption spectra confirm that thin-films processed from the
 80 additive-containing precursor solutions show enhanced surface
 81 coverage which further enhances PCE. At higher HI
 82 concentrations however, we observe a reduction in device
 83 efficiency that appears correlated with the formation of large,
 84 disconnected crystallites and poor film coverage. Our
 85 measurements confirm therefore that precise control over the
 86 composition of the precursor ink is necessary to optimise the
 87 structure and performance of the final perovskite film.

88 Results and Discussion

89 We fabricated a series of devices based on the generic structure
 90 ITO/PEDOT:PSS/ MAPbI_{3-x}Cl_x/LiF/Al, where the active
 91 perovskite film was deposited from a MAI:PbCl₂ (2.9:1) \times
 92 precursor solution in DMF containing HI at 1 v%, with films
 93 being subsequently annealed at 90°C for 90 minutes. Here, both
 94 spin-coating and spray-coating were used to deposit the
 95 MAI:PbCl₂ precursor – see Experimental Methods for full
 96 formulation and device fabrication details. We summarise
 97 performance metrics of devices containing a spin-cast and
 98 spray-cast active layer in Table 1. It can be seen that by adding
 99 HI to the precursor ink, there is a marked enhancement in
 100 device performance in both spin-cast and spray-cast devices
 101 with PCE increasing from 7.7% to 11.9% and 6.1% to 10.0%
 102 respectively. This is exemplified in Fig. 1(a) and (b) where
 103 plot PCE histograms for spin-cast and spray-cast devices
 104 respectively (data recorded from devices containing the HI
 105 additive is plotted in red). For completeness, we also plot J-V
 106 traces from champion PSCs deposited by spin- and spray-



107 Fig. 1 – PSC device performance summary: PCE histograms of PSCs prepared by spin-
 108 casting (part (a)) and spray-casting (part (b)) perovskite precursor inks without (black
 109 circles) and with (red circles) the HI additive; Part (c) shows JV traces measured from
 110 spin-cast (solid lines) and spray-cast (dashed lines) champion cells with and without
 111 additive (red and black lines) under 1 Sun simulated AM1.5G irradiation. Part (d) shows
 112 the results of HI additive v% tuning experiments with spin-cast (closed circles) and
 113 spray-cast (open circles) films (Note: lines are a guide to the eye). A device structure
 114 schematic is shown in part (e).

Metric	Spin-cast		Spray-cast	
	No Additive	1 v% HI Additive	No Additive	1 v% HI Additive
PCE (%)	6.7 (7.7) ± 0.9	12.5 (13.8) ± 0.9	6.1 (8.7) ± 1.5	10.0 (11.4) ± 1.2
FF (%)	58 (66) ± 8.8	71 (77) ± 3.6	65 (68) ± 2.2	67 (70) ± 3.3
J _{sc} (mAcm ⁻²)	14.1 (17.2) ± 1.3	19.3 (22.6) ± 1.4	12.8 (14.6) ± 1.3	17.0 (17.4) ± 0.8
V _{oc} (V)	0.82 (0.88) ± 0.07	0.91 (0.97) ± 0.03	0.73 (0.88) ± 0.10	0.88 (0.93) ± 0.06

Table 1 – Performance metrics of PSC devices measured under 1 Sun simulated AM1.5G irradiation after 10 mins light soaking. Average values are expressed in bold, champion metrics in parenthesis and the spread in metrics is represented by the standard deviation.

casting in Fig. 1(c). Our analysis clearly demonstrates that the observed improvement in device performance is statistically significant.

In a 1 v% HI precursor film we find that the majority of this efficiency improvement results directly from an increase in the J_{sc}, although small increases in V_{oc} and FF are observed as well. We have in fact explored a range of HI concentrations as shown in Fig. 1(d). Here it is evident that 1 v% represents an optimum HI additive concentration for both device fabrication methods, although it is clear that the spin-cast devices have higher peak and average efficiency in general than the analogous spray-cast devices. This disparity arises from reduced active-layer uniformity and the fact that these films require thicker layers of PCBM to effectively planarise them²⁰. Above an optimum 1 v% HI concentration, we find a dramatic roll-off in PSC device performance that results from significant reductions in FF, J_{sc} and V_{oc} (see Fig. S3 and S4). To explore

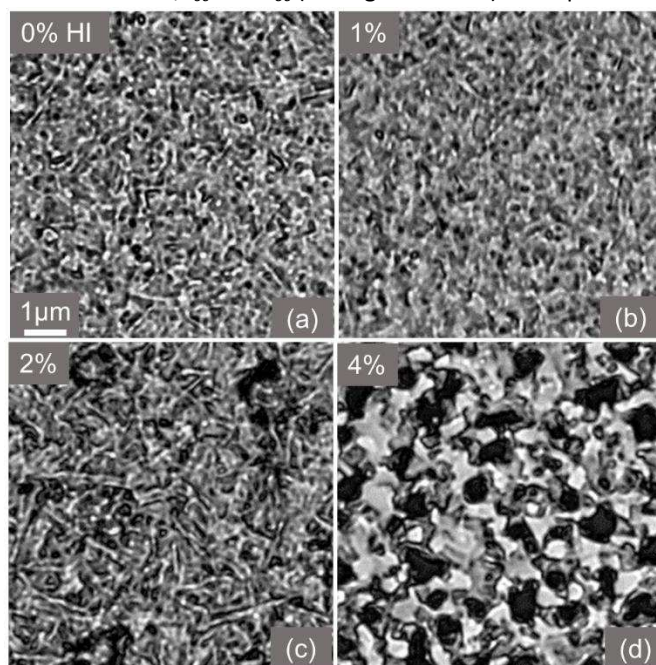
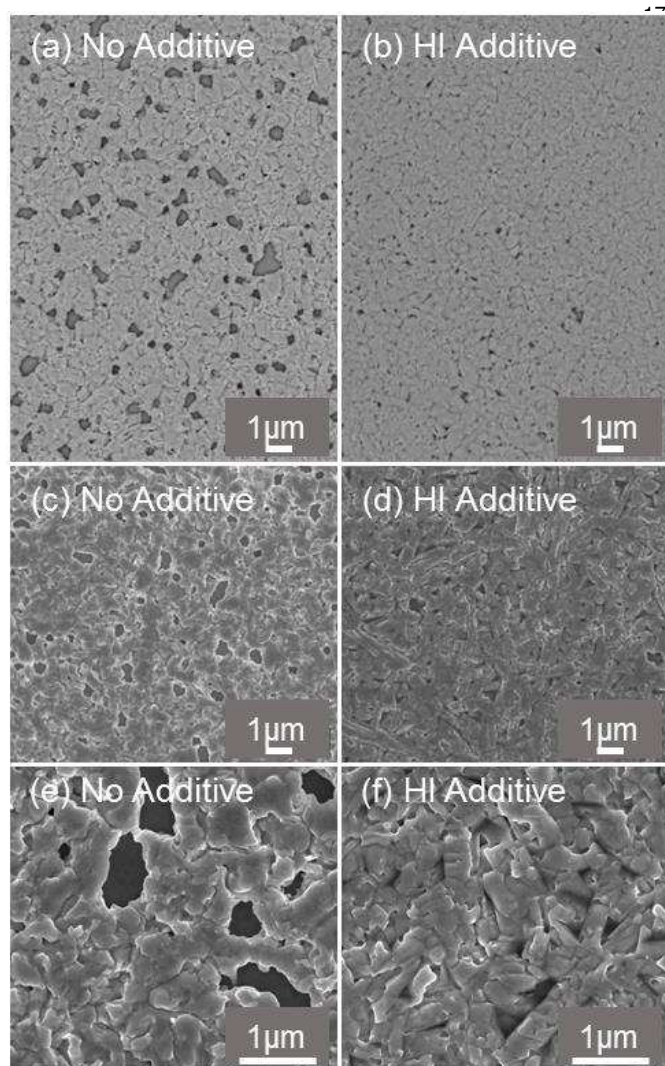


Fig. 2 – White light microscope images taken in reflection mode showing the development of PEDOT:PSS/MAPbI_{3-x}Cl_x thin-film microstructure upon increasing precursor ink HI v% from 0% (part (a)) up to 4% (part (d)). A 1 μm scale bar is shown inset.

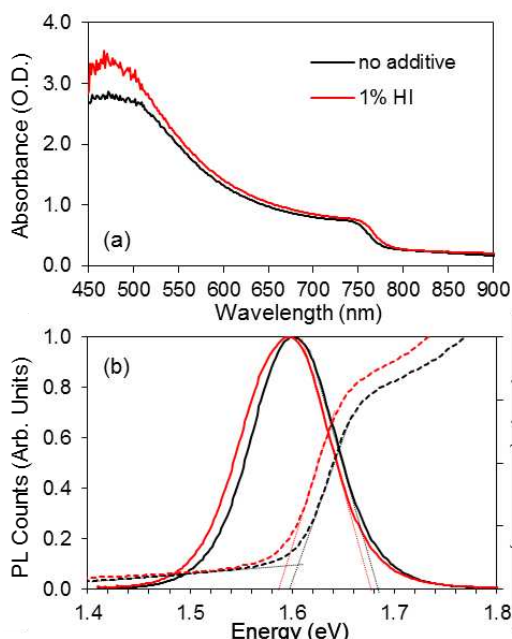
140 the origin of this reduction, we used white light reflectance
 141 microscopy to characterise PEDOT:PSS/MAPbI_{3-x}Cl_x thin-
 142 films (post anneal) that were cast using different initial
 143 concentrations of HI (see Fig. 2(a) to (d)). Here, it can be seen
 144 that films containing 0 v% and 1 v% of HI appear relatively
 145 compact, however as the HI concentration is increased, the film
 146 is increasingly characterised by large, disconnected crystallites
 147 having poor surface coverage. This reduction in surface
 148 coverage is correlated with a progressive reduction in thin-film
 149 optical density as shown in Fig. S5(a) and (b), suggesting that
 150 reduced light harvesting ability plays a role in reducing device
 151 efficiency. It is apparent however that the addition of 1 v% HI
 152 to the precursor solution enhances the performance of devices
 153 fabricated by spin- and spray-casting, and underlines the
 154 importance of this finding as a transferrable method for
 155 controlling perovskite crystallisation dynamics and promoting
 156 high PCE.



157 Fig. 3 – SEM images of ITO/PEDOT:PSS/MAPbI_{3-x}Cl_x thin-films spin-cast from additive-
 158 free (parts (a), (c), (e)) and additive-containing (parts (b), (d), (f)) precursor solutions
 159 imaged with different detectors and at different magnifications, respectively: (a) and
 160 (b) are backscattered electron (BSE) images, with (c) to (f) being secondary electron
 161 (SE) images. A 1 μm scale-bar is shown inset.

To further explore the role of the HI precursor additive on modifying perovskite film-structure, we have used scanning electron microscopy (SEM) to explore MAPbI_{3-x}Cl_x/PEDOT:PSS films at higher resolution as shown in Fig. 3. Here, we compare films cast from solutions without (Fig. 3 (a), (c), (e)) and with a 1% HI additive (Fig. 3 (b), (d), (f)) at comparable thickness (see Table S1). In all figures, the darkest areas correspond to gaps in the film that are most clearly identified in the back-scattered electron (BSE) images as shown in Fig. 3 (a) and (b). From the latter it is immediately clear that the film cast from the precursor containing the 1 v% HI additive forms a more continuous layer and has a significantly increased surface coverage, being 93.8% (no additive) and 99.7% with 1 v% HI additive. We believe this increase in film coverage is partially responsible for the observed increase in PSC photocurrent due to the enhanced optical absorption in these films. However it is also likely that in devices processed without the HI additive, uncovered regions of PEDOT:PSS form a Schottky junction with the overlying PCBM with a V_{OC} ~ 0.5V leading to an overall reduction in cell V_{OC}²¹. The SE images (see Fig. 3(c) to (f), reveal the individual grains from which we determine the average size of the crystallites in films cast from additive-free precursor inks is 36% smaller than films cast without the HI additive (527 ± 20 and 385 ± 19 nm respectively). These findings are in agreement with morphological studies of such samples²²⁻²⁴. From the lower magnification images (Fig. 3(c) and (d)) it is apparent that films cast from the precursor containing the HI additive show strong local morphology variations and contain two distinctly different morphologies: (1) rounded and (2) elongated crystallites. The latter is absent in the film cast from the precursor without the HI additive. In the higher magnification images of both materials (Fig. 3 (e) and (f)) it becomes clear that smaller grains are located on top of rather larger grains. All of the above observations are consistent with a model proposed by Williams et al.²⁵, that explains the morphological variations in MAPbI_{3-x}Cl_x films as a result of templated topotactic self-assembly in the presence of chloride. In this model the larger rectangular structures in Fig. 3(d) and 3(f) are suggested to result from the rapid growth of MAPbCl₃ present only in films cast from fresh solutions containing PbCl₂, linked to subtle variations in chloride concentration due to aggregation in the solution²⁵. We note the absence of such rectangular features in films cast from solutions without the HI additive (Fig. 3(c) and 3(e)) and speculate that it is related to the nature of aggregates in the additive-free solutions as discussed further below. Thus, the addition of HI to the precursor solution has a strong influence on the perovskite crystallisation dynamics and thus the resultant morphology of the converted perovskite thin-film.

In Fig. 4(a) we plot the optical absorption spectra of spin-cast perovskite films cast with and without the HI additive (1%) deposited onto an ITO/PEDOT:PSS substrate. It is found that there is a clear increase in optical density (by 6%) across the entire spectrum resulting from the addition of HI to the precursor solution. Given that these films are of comparable thicknesses, this increase in absorption may be accounted for

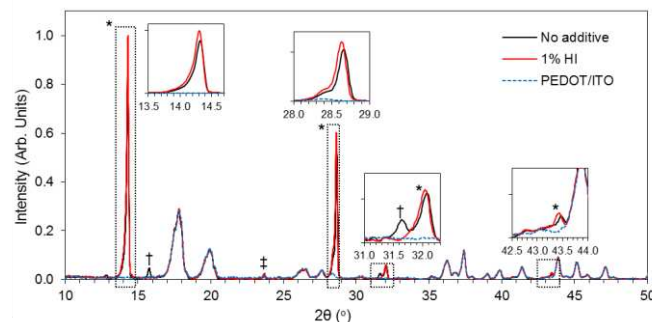


218 Fig. 4 – Optical spectroscopy of spin-cast ITO/PEDOT:PSS/MAPbI_{3-x}Cl_x thin-film
 219 prepared from precursor solutions without (black line) and with (red line) a 1
 220 HI-additive. Part (a) plots steady-state optical absorption spectra. Part (b) shows
 221 steady-state PL spectra (left-axis) with a Tauc plot (right-axis) showing absorption
 222 data.

223 by an increase in surface coverage across the active layer.
 224 fact that is supported by SEM images shown in Fig. 3(a) and
 225 (b). However, since this disparity lies within the error of our
 226 profilometry measurement, we cannot rule out a simple change
 227 in thickness between samples being responsible for the
 228 observed increase in optical density. Interestingly, the
 229 absorption onset is also red-shifted by 13 meV in the 1%
 230 additive-containing films as can be seen in the Tauc plot shown
 231 in Fig. 4(b). This red-shift in absorption onset is accompanied
 232 by a similar red-shift in PL emission as is also shown in Fig. 4(b)
 233 which is believed to result from enhanced perovskite crystal
 234 growth¹⁰.

235 In Fig. 5, we present XRD patterns recorded from films cast
 236 from precursor solutions both with and without a 1 v% HI
 237 additive onto an ITO/PEDOT:PSS surface. An uncoated ITO/
 238 PEDOT:PSS control sample is also shown for reference. It
 239 appears that many features in the XRD patterns arise from
 240 this substrate. We see a small feature at 23.8° (‡) which has
 241 been assigned to the mixed halide MAPbI_{3-x}Cl_x perovskite
 242 cubic phase²⁶. Peaks associated with the MAPbI₃ perovskite
 243 marked using an asterisk (*) and are located at 14.3, 28.6, 32.0,
 244 43.4° (tetragonal I4/mcm (β) phase)²⁷. All of these peaks are
 245 more intense and shifted to smaller angles in films cast using
 246 the HI additive. This result suggests that the perovskite lattice
 247 spacing increases from 6.18 to 6.19 Å in response to the
 248 addition of HI to the precursor ink; a result also consistent with
 249 red-shifted absorption and PL onsets shown in Fig. 4(b).
 250 change in composition, possibly due to differences in chlorine
 251 concentration may explain this effect in terms of lattice
 252 distortion²⁸. Furthermore, we find an absence of peaks
 253 associated with the intermediate perovskite reaction products

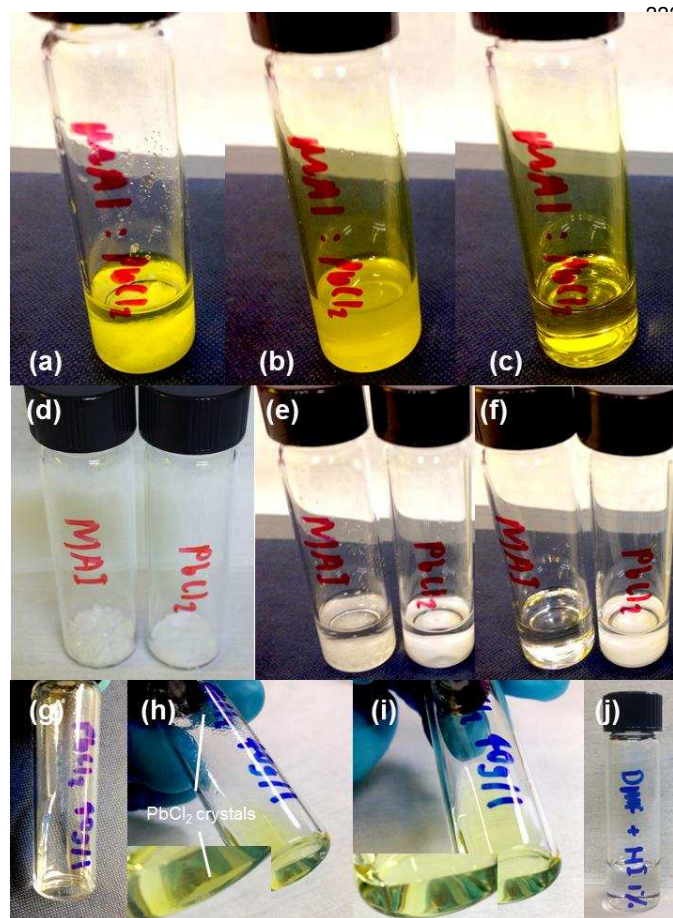
254 marked with a dagger (†) at 15.7 and 31.7°²⁸ and PbI₂ at 12.8°²⁷
 255 suggesting that the addition of HI to the precursor solution
 256 facilitates full conversion of the precursor to perovskite crystal
 257 phase.



258 Fig. 5 – X-ray diffractograms of representative ITO/PEDOT:PSS/MAPbI_{3-x}Cl_x thin-films
 259 spin-cast from a precursor solution without (black lines) and with a 1v% HI-additive (red
 260 lines) precursor solutions. Data recorded on an uncoated ITO/PEDOT:PSS substrate is
 261 shown for comparison using a dashed blue line. Regions marked with boxes are shown
 262 expanded in the insets. Features assigned to the perovskite crystal and intermediate
 263 phase are marked with * and † respectively. ‡ refers to the mixed halide cubic phase.

264 Finally, we turn our attention to the effect of HI in the
 265 context of solution engineering and present the results of these
 266 studies in Fig. 6. After ink preparation, we find that perovskite
 267 precursor inks appear turbid indicating the presence of
 268 unsolvated precursor materials. In Figure 6(a) to (c) we
 269 demonstrate that by adding small quantities of HI, we
 270 effectively eliminate these suspended particles leading to the
 271 formation of a clear solution. This observation is supported by
 272 the dramatic reduction in dynamic light scattering (DLS) count
 273 rate after HI addition. This measurement confirms that on
 274 addition of HI, there is (i) a large reduction in solution
 275 turbidity, and (ii) a change in the average particle size. Indeed,
 276 without the presence of HI, the solution contains a significant
 277 population of micron-sized crystallites (1370 ± 480 nm). On
 278 addition of 1 v% HI, these are apparently absent, and are
 279 replaced by a population of nanoparticles having a diameter of
 280 1.7 ± 0.4 nm (see Fig S6(a) and (b)). We note that Williams et
 281 al.²⁵ have also detected the presence of 40 nm diameter
 282 aggregates in this precursor ink formulation. Note that owing to
 283 difficulties associated with effectively separating the aggregates
 284 from their parent solutions without significantly altering them,
 285 we restrict our investigation to comparative studies of
 286 precursors in solution as shown in Fig. 6. Given the large
 287 disparity between MAI and PbCl₂ material solubility (see Fig.
 288 6(e) and (f)), we suspect that the suspended particles are in fact
 289 undissolved PbCl₂ microcrystals^{25, 29}. We find that mixing the
 290 precursors leads to a large increase in PbCl₂ solubility and gives
 291 the ink a yellow appearance implying the formation of a lead
 292 polyhalide-based soft coordination complex with corresponding
 293 red-shifted excitonic absorption³⁰. However, this process alone
 294 does not appear to be sufficient to fully disrupt the cohesive
 295 forces within the PbCl₂ precursor and some material remains
 296 undissolved in the ink without the presence of the HI additive.
 297 It is clear therefore that HI additive has a marked effect on the
 298 PbCl₂ solubility. This can be evidenced in Fig. 6(g) to (i),
 299 where we show that the addition of 2% HI to a PbCl₂ solution

300 just above its solubility limit in DMF (40 mg/ml) appears
 301 solvate all the previously undissolved PbCl_2 solid. We find
 302 this solvation process is accompanied by a colour change of
 303 solution from colourless to yellow, indicative of the presence
 304 a mixed lead-halide coordination compound.



305 Fig. 6 – The effect of HI addition on DMF-based perovskite precursor solutions. Part
 306 2.9:1.0 MAI: PbCl_2 precursor ink at 500 g/l before vortex mixing, (b) after 2 mins vortex
 307 mixing and (c) after 1% HI addition and further mixing. Part (d) shows the pure MAI
 308 and PbCl_2 precursors before solvent is added, (e) immediately after DMF solvent
 309 addition at 312 and 188 mg/ml respectively, and (f) after extended vortex mixing. Part
 310 (g) shows pure PbCl_2 in DMF at 40 mg/ml after extended mixing, (h) immediately after
 311 2% HI addition, and (i) after further vortex mixing. DMF containing 1% HI is shown for
 312 comparison in part (j).

313 We propose therefore that by adding HI to our mixed
 314 precursor inks, we are able to shift the dynamic solution
 315 equilibria from undissolved PbCl_2 microcrystallites towards a
 316 fully coordinated mixed halide complex that is readily solvated.
 317 The position of this equilibrium is expected to influence crystal
 318 microstructure through the templated self-assembly process
 319 directed by formation of the chloride-rich $(\text{MAPbCl}_3)_x$
 320 intermediate phase²⁵ or through the size and population
 321 PbCl_2 heterogeneous nucleation sites²⁹. Both of these species
 322 have been implicated in the dynamics of film formation which
 323 is supposed to extend as far back as the solution state upon
 324 deposition³¹. In films prepared from inks without the additive,
 325 we speculate that the presence of significant amounts of PbCl_2
 326 suspended in the solution as large microcrystals is likely to lead
 327 to a non-stoichiometric mixture of precursor materials that will

328 hamper this process. It is not clear however why device
 329 efficiency is further reduced when perovskite films are cast
 330 from precursor solutions containing more than 1 v% of the HI
 331 additive. We speculate that small changes in the size or
 332 population density of chloride-rich nanoparticles (as suggested
 333 by the intensity reduction in DLS scattering signal (see Fig.
 334 S6(c)) will disrupt structural templating in the nascent
 335 perovskite thin-film. Indeed, changes in the population of
 336 nanoparticles able to act as nucleation sites for the growth in
 337 crystallites is likely to result in a distinct change in active-layer
 338 microstructure from a dense arrangement of elongated
 339 crystallites to one which is characterised by large disconnected
 340 crystallites and poor surface coverage. We do not expect
 341 chemical reactions between HI and precursor materials,
 342 however recovery of decomposed MAI is possible by reaction
 343 between MA and HI. We anticipate that HI will be removed
 344 from the film during the extended annealing stage and is merely
 345 added to engineer the solution for favourable device processing.

346 It is worth noting that our HI additive is based on a 57wt%
 347 HI solution in water. Therefore, we cannot rule out any effects
 348 associated with increasing water concentrations in our
 349 precursor inks as we add greater amounts of HI. Large
 350 concentrations of water (>3 v%) have been shown to reduce
 351 perovskite/PEDOT surface coverage due to the differing
 352 solubilities of precursors – in particular PbCl_2 is poorly
 353 solvated by water in contrast with MAI³. Such effects may alter
 354 the precursor-perovskite reaction kinetics by facilitating rapid
 355 mass transfer of MAI and by accelerating the removal of excess
 356 MAI formation of methylamine and HCl via acid-base
 357 interactions between MAI and water^{32, 33}. Water incorporation
 358 into the perovskite lattice, as $\text{MAPb}_{3-x}\text{Cl}_x \cdot n\text{H}_2\text{O}$ hydrate, is
 359 thermodynamically favoured and therefore expected to occur
 360 spontaneously³⁴. However, the crystalline hydrate species lie
 361 beyond the detection limit of our XRD measurement (the
 362 features expected at 8.6, 11.6 and 11.7^o appear absent).
 363 Nevertheless, the emergence of an increasing hysteresis in JV
 364 sweeps in devices processed with increasing HI v% (see Fig.
 365 S1-2) suggests that water may in fact be incorporated within the
 366 perovskite lattice leading to the presence of a greater
 367 concentration of mobile ions³⁷.

368 Conclusion

369 We have fabricated $\text{MAPb}_{3-x}\text{Cl}_x$ photovoltaic devices based on
 370 an inverted architecture, and have explored the effect of the
 371 addition of a small volume of a hydrogen iodide additive to the
 372 precursor solution that is used to cast the device active layer.
 373 We fabricate a range of devices in which various quantities of
 374 HI were added to the precursor solution, and find that devices
 375 cast from a precursor containing 1 v% HI have enhanced power
 376 conversion efficiency (13.8% champion power conversion
 377 efficiency, $(12.5 \pm 0.9)\%$ average efficiency). We propose that
 378 the HI additive has a strong effect on PbCl_2 solubility and
 379 therefore regulates the size and population of aggregates which
 380 are implicated in the structural templating occurring early in the
 381 film-formation process. We find a small amount (1 v%) of HI
 382 leads to the dissolution of large PbCl_2 microcrystals and drives

383 the dynamic solution equilibria toward the formation of fully
 384 coordinated lead polyhalide coordination complexes which
 385 a marked positive effect on device efficiency; an observation
 386 that is replicated in devices that are prepared by both spin-
 387 casting and spray-casting. We have used our XRD to study the
 388 structure of the perovskite films, and conclude that the
 389 additive facilitates full conversion of precursor material leading
 390 to a pure crystalline perovskite phase. In addition, we see
 391 increased lattice spacing and corresponding red-shift in
 392 absorption and PL onsets. SEM images and optical absorption
 393 spectra confirm that thin-films processed from precursor
 394 solutions containing 1 v% HI additive have enhanced surface
 395 coverage which further enhances PCE.

396 Materials and Methods

397 Solar Cell Fabrication

398 ITO substrates ($20 \Omega \square^{-1}$) purchased from Ossila Ltd were first
 399 cleaned by sonication in Helmanex solution, deionized water
 400 then isopropyl alcohol (IPA), then dried with compressed
 401 nitrogen and ozone-plasma treated before use. To deposit
 402 PEDOT:PSS by spin-coating, Clevious PVP AI4083 was first
 403 filtered through a $0.45 \mu\text{m}$ PVDF syringe filter and then spin-
 404 cast at 5000 rpm to form a $35 \pm 2 \text{ nm}$ thick layer that was then
 405 annealed in air at $120 \text{ }^\circ\text{C}$ for 10 minutes prior to use.

406 For spray-coating (USI prism 300), the ultra-sonic tip was
 407 held at 40 mm above the substrate surface and vibrated at
 408 kHz while fluid from a coating reservoir above was fed to the
 409 tip. The ink droplets created were directed to the surface using a
 410 carrier gas whose pressure was set to 10 psi giving a wide spray
 411 pattern (ca 50 mm). At the same time, the spray head was
 412 robotically scanned a distance of 150 mm over ITO device
 413 substrates in a single pass. We also found that multiple pass
 414 spray-routines create poor quality films as they tend to re-
 415 dissolve the underlying films. Unlike airbrush techniques in
 416 which droplets contain very little solvent when they reach the
 417 surface, ultrasonic spray-cast films consist of droplets that
 418 coalesce to form a fully wet film before drying³⁸. Note that the
 419 width of the spray-pattern is significantly larger than that of the
 420 individual device pixels (each having a size $(2 \times 2) \text{ mm}^2$), and
 421 thus significant heterogeneity across the spray-mist pattern
 422 the sample surface is not anticipated. Substrates were mounted
 423 on a hotplate to ensure stable elevated temperatures in order to
 424 control the wet film drying rate.

425 Perovskite precursor solutions were prepared from methyl
 426 ammonium iodide (MAI, purchased from Ossila Ltd), hydrogen
 427 iodide (Sigma 210021) and PbCl_2 (Sigma 203572) and were
 428 used as received. Spin-coated samples were cast at a spin-speed
 429 of 4000 rpm from a 500 mg ml^{-1} 2.9:1.0 MAI: PbCl_2 solution
 430 containing 0 to 4v% HI in DMF (Sigma 227056). Prior to film
 431 deposition, both the substrate and casting solution were held at
 432 a temperature of $90 \text{ }^\circ\text{C}$ and $70 \text{ }^\circ\text{C}$ respectively to enable rapid
 433 drying of the films and to optimize device performance. Spray-
 434 cast perovskite precursor films were deposited from a 200 mg
 435 ml^{-1} 2.9:1.0 MAI: PbCl_2 solution in DMF containing 0 to 4v%
 436 HI (solution at ambient temperature) onto substrates held at
 437 $^\circ\text{C}$ with a head-speed of 220 mm s^{-1} . In all cases, film thickness

was determined from post-annealed films at five locations using
 profilometry. Spray-coated and spin-coated film thickness was
 adjusted to be within 20% of each other however the addition
 of HI was seen to modulate this (see Table S1). Lab humidity
 was controlled with an air conditioning system and a desiccant
 dehumidifier (Humidity control systems Ltd DC31 T16).

The perovskite films were spin-coated with a PC_{70}BM
 electron-extraction layer (95% purity supplied by Ossila Ltd).
 Spin-cast films were deposited in a nitrogen-filled glove-box.
 PC_{70}BM solutions for spin-casting were prepared at 50 mg ml^{-1}
 or 70 mg ml^{-1} in chlorobenzene, creating 150 and 200 nm thick
 films respectively. Prior to deposition, solutions were heated to
 $70 \text{ }^\circ\text{C}$ for 1 hour, allowed to cool and then filtered through a
 $0.45 \mu\text{m}$ PTFE syringe filter.

A cathode of LiF and aluminium was thermally evaporated
 at 2 nm at $0.1 \text{ }^\circ\text{A s}^{-1}$ and 100 nm at $1 \text{ }^\circ\text{A s}^{-1}$ respectively within a
 vacuum chamber held at ca 10^{-6} mbar. Devices were
 encapsulated using a UV-treated epoxy (supplied by Ossila Ltd)
 before testing.

Steady-state photoluminescence was performed using a
 Laser-LDCU CW 450nm diode laser rated at 1mW with a
 power density of $\sim 0.1 \text{ W/cm}^2$ on the sample. All
 photoluminescence spectroscopy was performed under vacuum
 ($<10^{-5}$ mBar). UV-vis measurements were performed under
 ambient conditions using UV-VIS-NIR light source (Ocean
 Optics – DH-2000-BAL), collection fibre optic cables (Ocean
 Optics) and spectrometer (Ocean Optics – HR2000+ES).

X-ray diffraction

Thin-film X-ray diffraction was performed on
 perovskite/PEDOT:PSS/ITO glass samples using a Bruker D8
 diffractometer using $\text{Cu-K}\alpha$ radiation in 0.05° increments over
 the Bragg angle range of $10\text{--}50^\circ$.

SEM

Samples were imaged in a FEI Nova NanoSEM 450, operating
 at a primary beam energy of 5 keV. The through-lens detector
 (TLD) was used to collect images at a working distance of 5
 mm with immersion lens active. For surface coverage
 measurements, the TLD was set to backscattered electron
 imaging mode in order to generate images that best emphasised
 any holes in the film. For crystallite size measurements the
 TLD was set to secondary electron mode in order to generate
 images that better highlighted grain boundaries.

Dynamic Light Scattering (DLS).

Perovskite precursor ink solutions were prepared under
 representative conditions and analysed using a Malvern
 Zetasizer NanoZS instrument. Data were averaged over three
 consecutive measurements of ten runs each. Measurements
 were made at 25°C .

Solar cell characterisation

Device performance was tested under ambient conditions using
 a Newport 92251A-1000 solar simulator (AM1.5). An NREL
 certified silicon reference cell was used to calibrate the
 integrated light-output from the simulator to 100 mW cm^{-2} at 25

- 491 °C. Here, an aperture mask (0.025 cm²) was placed over each
 492 solar cell to accurately define the device area and minimize
 493 absorption of stray light. PCEs were determined for a cell
 494 initially held at +1 V, swept to -1 V and back to +1V a rate of
 495 0.4 V s⁻¹. Performance metrics are quoted from the portion of
 496 V sweep as the bias is swept from +1 to -1V.
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