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Advances in Spray-Cast Perovskite Solar Cells

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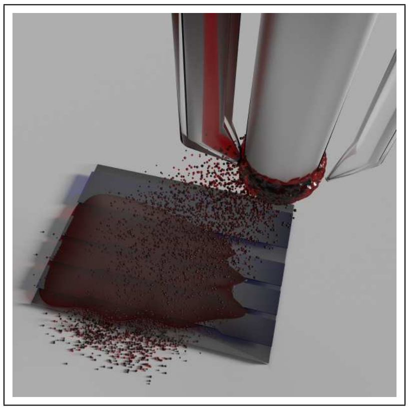
Abstract

Spray-coating is deposition technique that is widely used in industry, and could in principle be used to fabricate perovskite photovoltaic (PV) devices at low cost and at high volume. As with any deposition technique, the fabrication of thin-films requires the optimisation of a range of parameter space in order to control film uniformity and homogeneity. This is particularly important in PV fabrication, as the quality of the thin film has an important effect on device efficiency. This perspective summarises the developments in spray-cast perovskite solar cells made over the past few years, with particular attention paid to strategies employed to control the crystallisation of the perovskite. Steady progress has now been made with spray-cast perovskite PV devices recently demonstrated having a power conversion efficiency of 18.3%. We highlight trends within the research field, and discuss challenges that will be necessary to drive such techniques towards practical application.

Graphical TOC Entry



Keywords

Perovskite Solar Cell, Spray-deposition, Spray-coating, Ultrasonic, Thin Film, Multilayer

Over the past 8 years, perovskites have emerged as a promising third generation photovoltaic (PV) technology with power conversion efficiency (PCE) rising from an initial 3.8%[1] to 22.1%.[2] Perovskites are particularly interesting materials as they combine the properties of inorganic semiconductors (efficient light absorption, tunable bandgap, high charge-carrier mobility and low recombination rates) with the ease of processing from solution - a property that is typically associated with organic semiconductors.[3–5]

The ability to process such materials from solution opens the possibility of manufacturing extremely low-cost PV devices at high volume. Indeed, it has been predicted that PV modules fabricated in this manner would have an energy payback time of less than half a year; a value that compares very favourably with silicon based modules that have energy payback times of up to two and a half years dependent on their location.[6] However in order perovskite PV devices to be produced at high volume, it will be necessary to develop scalable deposition methods that can be used to produce high efficiency devices.

Currently most perovskite devices explored at lab-scale are fabricated by depositing a perovskite light absorber via spin-coating. Whilst this method is capable of producing devices having high performance, spin-coating is generally wasteful and not scalable for large scale (roll-to-roll) manufacturing. To address this issue, attention is now turning towards processing perovskite PV devices using scalable techniques such as slot-die coating,[7] blade coating,[8] ink-jet printing[9] and spray-coating,[10] with a general aim being to produce devices having an efficiency comparable to those prepared via spin coating.

In this perspective, we discuss the application of spray-deposition to fabricate perovskite PV. The attractiveness of this process comes from the fact that it is already used in industry such as automotive painting, and combines the advantages of fast throughput and high material utilisation. Importantly, spray-coating is compatible with non-planar surfaces; a feature that may lend it particular advantages as we discuss in the concluding sections. However the use of spray-coating is not without its challenges; in general, the fabrication of thin films by spray-coating generally relies on the use of "inks" that are formulated at relatively low solution concentrations, with the drying of the ink via solvent evaporation producing a film of the desired thickness. This is in contrast to inks formulated for spin-coating in which a much higher concentration is required to maintain high viscosity during the shear-based coating process. As a result of the low ink concentrations required in spray-deposition, solutions can often de-wet, and thus the coating process and ink formulation must be optimised to minimise "pooling" and dewetting during film drying. Here, a range of parameters can be optimised, including the nature and composition of the solvent, the solution concentration, fluid flow rate, spray-head height/speed and substrate temperature.[11] The optimisation of such a wide parameter space can be challenging, with process recipes often not being directly transferable between different research groups.

In the following sections, we summarise progress made in the field of spray-cast perovskite solar cells as well as addressing future research challenges. However we also include a short summary of progress made in the development of spray-cast organic (polymer-based) solar cells to place work on perovskite-based PV devices into context. Note that this article presents a flavour of the most important progress in the field from the perspective of the authors, rather than being a full review of all work published on this topic. We direct any readers who wish to obtain a full description of the development of spray-cast thin-film and organic photovoltaic devices to a number of recent reviews.[12,13]

Most spray-coating processes can be broken down into four stages, namely (i) the generation of the ink-droplets, (ii) the transport of the droplets to the substrate, (iii) the coalescence of the droplets into a wet film, and (iv) thin-film drying.

The first stage in the spray-deposition process involves the break-up of an ink into a mist of micron sized droplets. One simple way to achieve this is to flow the ink through a nozzle that includes an orifice, with the ink being sheared as it is passes through the orifice. Whilst this "air-brush" type process is often used to coat conventional materials, the size of the droplets produced can vary; a limitation that has consequences for the uniformity of the resultant film.[14,15] As PV devices require close control over layer thickness, many researchers now use ultrasonic spray-coaters in which a piezoelectric crystal is used to resonate a tip at 10s of kHz. This vibration shears the ink into a mist of micron sized droplets characterised by an increased uniformity of droplet sizes as compared to an air brush.[10,14,15] Generally the mean diameter of droplets ($D_{0.5}$) produced can be approximated using the following empirical relation

$$D_{0.5} = 0.34 \left(\frac{8\pi\sigma}{\rho f^2} \right)^{1/3} \tag{1}$$

where σ is the surface tension of the ink, ρ is its density and f is the frequency of the resonating tip.[15]

After the droplets have been generated they are then directed to the substrate of interest using a gas jet. In an ideal deposition, the droplets will then wet the surface, however this process is dependent on ink-density, droplet velocity, diameter, viscosity, nature of the substrate and the ink surface tension.[12] Arguably the most important of these parameters is the ink surface tension as this will affect the contact angle that the droplets make with the surface. If the contact angle is too large, the droplets will not merge together into a wet film, but will instead dewet.[16]

A commonly employed strategy to improve surface-wetting is to heat the substrate during spray-deposition; this reduces the surface tension of the fluid and thus reduces its contact angle.[17] Indeed, the choice of substrate temperature is of key importance when optimising a spray-deposition process; if the temperature is too high the solvent will evaporate before the ink is able to spread and merge, resulting in a non-uniform film.[10,12] We note that this process is inevitable in during spray-pyrolysis as the temperature of the substrate far exceeds the solvent boiling point. This problem is generally addressed by employing a multiple pass approach in which voids in the film are filled by subsequent passes of the spray-head. However films produced by this method are often very uneven, with one step deposition processes being generally preferred.[10–12,18–20]

One straight-forward way to reduce solvent contact angle is to use a solvent having a reduced surface tension, although this is often not possible as such solvents may not be able to properly dissolve the solute. A solution to this is to mix a secondary solvent into the ink that has a lower boiling point and reduced surface tension than the primary carrier solvent, with both primary and secondary solvents being mutually miscible (e.g. IPA and water). This approach can be used to enhance droplet spreading and merger into a wet film due to the solutal Marangoni effect.[16,21] On evaporation of the secondary solvent, the ink is able to flow over uncovered areas of the substrate via localised surface tension gradients. The Marangoni flow velocity (v_c) is given by

$$v_c^2(x) = \frac{1}{2\eta(x)}\frac{d\sigma}{dx}x(1-x)(-A_l\alpha_l + A_h\alpha_h) \tag{2}$$

in which η is the viscosity of the ink, σ is its surface tension, x is the volume fraction of the lower surface tension solvent, A_l and A_h are the evaporation rates of the low and high surface tension solvents respectively, and α_l and α_h are activity coefficients for the two solvents.[16]

Once a continuous wet film has been created over a substrate, the carrier solvent(s) ideally evaporate and leave a uniform film. However if a high boiling point solvent is used, the prolonged drying times that result can lead to shrinkage or dewetting, creating a film that is characterised by large-area thickness variations. This effect can be avoided by accelerating the drying time by increasing the substrate temperature, however it is necessary to take into account the effect this will have on initial droplet wetting as too high a temperature may vaporise the solvent on contact.

Before the advent of perovskite solar cells, most PV spray-coating work focused on the development of organic photovoltaic solar-cells (OPVs). The first example of the use of spray-coated to produce an OPV was in 2007, where Vak et al were able to fabricate the active layer of a P3HT:PCBM based device by spray-coating, with the device created having a PCE of 2.83%.[22] Clearly, a practical PV manufacture process based on spray-coating would ideally use similar spray-based techniques to deposit all layers in a PV device (i.e. active layer and charge extraction layers). The first example of a "multilayer" spray-cast OPV was demonstrated in 2009 when Hoth et al spray-cast the hole transporting polymer PEDOT:PSS and a blend of P3HT:PCBM, achieving a PCE of 2.7%.[23] Importantly, this study highlighted the impact of the choice of solvent on the topography of spray-cast layers.

In 2010 Girotto et al built upon this work and used a mixed solvent system to enhance the surface coverage of the films, with the efficiency of the resultant devices increasing to 3.75%.[16] The use of mixed solvent systems has subsequently become fairly common technique within the field.[11,16,24–26]

Further work addressed the development of multilayer spray-cast OPV, where both electron and hole-transporting layers (zinc oxide and PEDOT:PSS) were deposited by spray-coating in addition to the P3HT-PCBM active layer.[27] Here, device scale-up was also explored, with efficiencies of 3.17% and 1.33% achieved for devices having an active area of 0.36cm^2 and 15.25cm^2 respectively.

Further gains in efficiency were demonstrated in 2013, when Wang et al fabricated a 5% efficient OPV device incorporating a spray-cast active layer.[28] Here, devices were based on the carbazole co-polymer PCDTBT rather than P3HT. Further efficiency gains were made in 2015 when multilayer OPVs were fabricated using PEDOT:PSS hole transport layer and an PFFBT4T-2OD:PC71BM active layer blend, with devices fabricated having a PCE of 8.06%.[26] Figure 1 shows the peak efficiency of spray-cast OPV and perovskite devices discussed in this article against time.

With the emergence of perovskite solar cells, a growing number of researchers have explored the fabrication of such materials via spray-deposition, with work building upon the techniques first developed for OPV fabrication. Here, initial work was undertaken by Barrows et al at the University of Sheffield who utilised an ultrasonic spray coater to deposit a $CH_3NH_3PbI_{3-x}Cl_x$ perovskite solution, forming the active layer in an inverted architecture PV device. The devices constructed were based on a layer structure of ITO/PEDOT:PSS/Perovskite/PCBM and achieved a peak PCE of 11% efficiency.[10] Barrows et al developed a simple process in

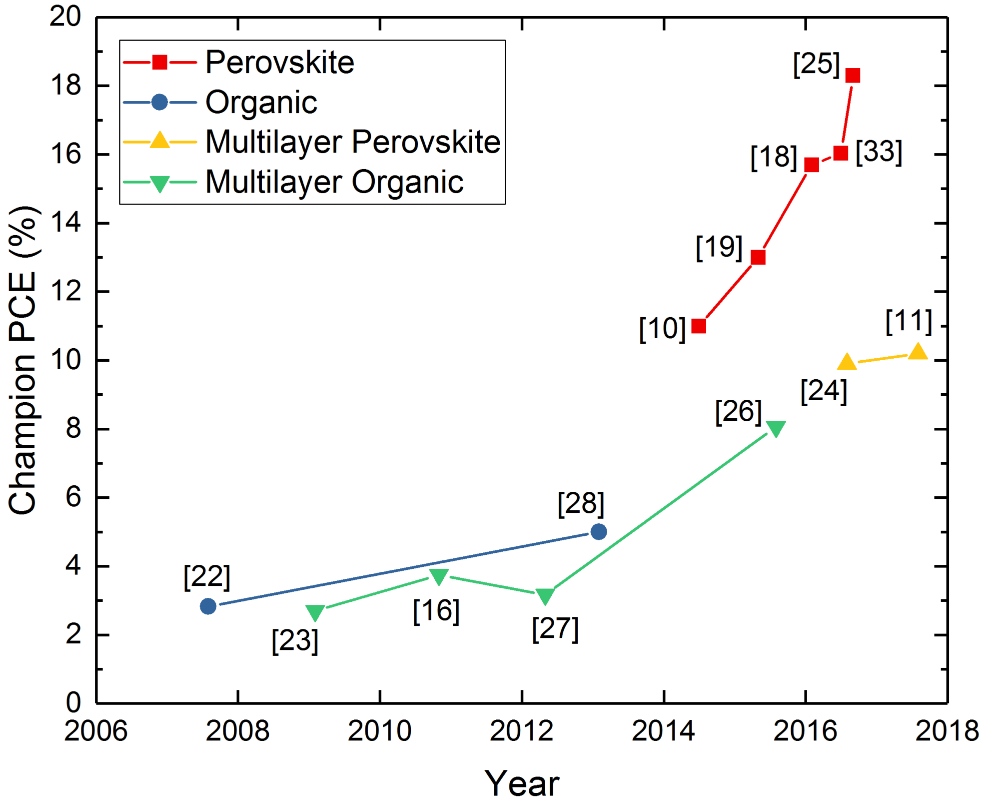


Figure 1: *Device efficiency improvements over time for spray-cast Organic (blue line) and Perovskite solar cells (red line) cited in this perspective. Organic and perovskite devices utilising more than one spray-cast layer (termed "multilayer" devices) are indicated using green and yellow symbols respectively.*

which MAI and $PbCl_2$ powder were dissolved together in a DMF solvent at a molar ratio of 3:1 at a total concentration of 100 mg/ml and then deposited in a single spray pass using an ultra-sonic system onto a heated substrate under ambient conditions. The resultant dry film was then annealed in air to facilitate the crystallisation of the perovskite film.

It was found that it was necessary to control the precursor film drying-rate to maximise the quality of the resultant film (uniformity and lack of pinholes). For example, if the drying rate was too fast, the ink droplets dried before merging, with significant heterogeneities identified in the final film. Conversely, if the drying rate was too slow, the wet film underwent shrinkage or dewetting, resulting in a film having large-area thickness variations. By using a heated substrate, it was possible to use high boiling point solvents such as DMF without the necessity for prolonged drying times, with the films produced being of reasonably good quality.

An additional challenge encountered when spray-coating perovskite films is the necessity to control the crystallisation of the perovskite itself. Here, this process has been addressed extensively in spin-coating studies,[29,30] and it was noted that by changing the temperature of the device substrate during spray-deposition, it was possible to modify the morphology of the perovskite thin-film dramatically.[10] This is shown in Figure 2, where it can be seen that control of the deposition temperature can change the resultant size of the crystallites and the effective surface coverage of the perovskite film.

Following such progress, Das et al used ultrasonic spray-deposition to fabricate a 13% efficient perovskite solar cell having a normal architecture (FTO/compact TiO_2/Perovskite/Spiro-OMeTAD/Au).[19] Again, an ultrasonic spray-coater was used to deposit a $CH_3NH_3PbI_{3-x}Cl_x$ film in a manner very similar to that used by Barrows et al, with flexible devices fabricated onto ITO covered PET substrates having a PCE of 8.1%. It is generally difficult to deposit TiO_2 on ITO coated PET, as the TiO_2 hole-blocking contact requires sintering at 450°C to become conductive; a temperature at which both ITO and PET undergo degradation. To address this issue, an infra-red lamp was used to sinter the TiO_2 layer whilst protecting the substrate. This process has already been applied to a perovskite precursor layer to speed up its conversion into a perovskite (a process that often requires an extended annealing time).[31]

In 2016 Tait et al further increased the efficiency of spray-cast perovskite devices by fabricating a device fabricated from a lead acetate perovskite precursor ($Pb(C_2H_3O_2)_2$ or PbAc) having a PCE of 15.7%.[18] This device was scaled up to an active area of $3.8cm^2$, with modules demonstrated having an efficiency of 11.7%. Again, the active layer was deposited using an ultrasonic spray-coater, with the deposition performed within a nitrogen-filled glovebox environment. This offered control over humidity and oxygen levels which have been shown to improve perovskite crystallisation.[18,19]

Importantly, it was shown that a dual feed spray-head could be used to mix different perovskite precursors. Indeed, by controlling the flow rate, the relative ratio of the precursor materials could be tuned dynamically to determine an optimal blend ratio. Using a mixture of 25% $CH_3NH_3PbI_{3-x}Cl_x$ and 75% $CH_3NH_3PbI_{3-x}Ac_x$ it was shown that optimal efficiency could be achieved. It is known that lead acetate based mixtures form ultra-smooth high quality perovskite films that can be thermally converted from the precursor to the full perovskite after 10 minutes annealing (regular $CH_3NH_3PbI_{3-x}Cl_x$ films often require anneal times in excess of one hour).[32] Such properties are likely to be valuable in any high-speed production process. Figure 3 shows a schematic of the dual-head deposition process. Note the three stages of spray-deposition: (i) droplets landing on the substrate, (ii) coalescence of droplets into a wet film, and (iii) drying of the film.[18]

A two step method to spray-coat $CH_3NH_3PbI_3$ perovskite has also been demonstrated by Huang et al, with devices demonstrating an efficiency of 16.03% on small-area cells and 13.09% on $1cm^2$ devices.[33] This approach was based on the work of Burschka et al in which a lead iodide film was deposited via spin coating, and then infiltrated with MAI via dip coating to form a perovskite.[29] Others had previously used spray-coating to infiltrate the lead iodide scaffold but Huang et al was the first to spray both layers.[33–36]

A schematic of the process developed is shown in Figure 4. Firstly a PbI_2 film was deposited from DMSO using an ultrasonic spray-coater onto a heated substrate.[33] Next MAI in IPA was spray-coated onto a dry PbI_2 layer. This mixed film was then heated at 100°C for 2 hours to ensure all of the precursor underwent reaction, forming the perovskite. Again the substrate temperature during spray-casting was shown to be of key importance. A high temperature deposition-process (90°C) effectively removed all DMSO from the film, yielding a dense PbI_2 layer. However if the PbI_2 film was too dense, it was found that its reaction with MAI was incomplete, resulting in a film that was not fully converted. If the deposition temperature was instead lowered to 60°C it was found that some of the DMSO solvent was left in the film, allowing the MAI to infiltrate and undergo diffusion more easily. Using this technique, it was found possible to create large-area high quality perovskite films and efficient PV devices.

In 2016 Heo et al reported (to the best of our knowledge) the highest performance spray-cast perovskite devices, having a PCE of 18.3%.[25] Here, a different deposition technique was employed, where a precursor fluid was continuously spray-cast onto a surface over a period of several minutes, where the outgoing flux of evaporating solvent was balanced by an incoming flux of fresh precursor ink. This method is in direct contrast to previous spray-based techniques in which the deposition process lasted for several seconds only.

In the process developed, MAI was first reacted with lead chloride in IPA to form $CH_3NH_3PbI_{3-x}Cl_x$ nanocrystals that were then washed, forming a high purity $CH_3NH_3PbI_{3-x}Cl_x$ nanocrystalline powder. This powder was then dissolved in a mixture of DMF and GBL. As GBL has a higher boiling point than DMF, the GBL extended the film drying rate despite the high temperature of the substrate during the spray-deposition (120°C); a method that allowed the perovskite crystal growth times to be extended.

It was shown that by controlling the ratio of DMF to GBL, it was possible to balance the solvent flux out of the film due to evaporation with the incoming flux of fresh solution. Indeed, if the solution simply consisted of DMF, the solvent flux out of the film was too high and the film dried rapidly forming a film characterised by small grains. However if the solution contained too much GBL, the flux into the film was much larger than the evaporation flux, resulting in solution dewetting. It was found that a solvent blend ratio of 80% DMF to 20% GBL was necessary to balance the incoming and outgoing solvent fluxes and thus reach a dynamic equilibrium. A schematic diagram of this process is shown in figure 5. This process allowed crystals that had been formed to re-dissolve and then merge into much larger grains. This created a dense film composed of micron-sized grains that resulted in the creation of high performance devices. Using this method 10 x 10cm^2 modules were created (FTO/TiO_2/Perovskite/Spiro-OMeTAD/Au) having an efficiency of 15.5%. We note however that such a long deposition times (around 2 minutes) would not be compatible with a high-speed manufacture process.

In an ideal commercial perovskite PV manufacture process, all solution-processed layers would be deposited via spray-deposition under ambient conditions. This was demonstrated in 2016 by Mohamad et al, who reported an inverted device architecture based on spray-cast PEDOT:PSS, $CH_3NH_3PbI_{3-x}Cl_x$, and PCBM, with devices achieving an average efficiency of 7.1±1.7% (peak 9.9%) relative to a spin-cast reference of 12.1±0.9%.[24] To the best of our knowledge this is the first example of an spray-cast perovskite device in which all the layers were sequentially deposited under ambient conditions, with a single spray pass used to deposit each layer; a technique that would be compatible with a production line.[11,24,37–39]

Later work by Bishop et al built upon this work by switching to a normal architecture (FTO/compact TiO_2/Mesoporous TiO_2/Perovskite/Spiro-OMeTAD/Au).[11] Here, a spray-based process was developed to sequentially deposit compact TiO_2, mesoporous TiO_2, $CH_3NH_3PbI_{3-x}Cl_x$, and spiro-OMeTAD. Again each layer was deposited in a single spray pass under ambient conditions. The devices created had an average efficiency of 9.2±0.6% (peak 10.2%) relative to a spin-cast reference of 11.4±1.0% on small-area devices. Significantly, it was found that compared to a spin-cast reference, there was some reduction in device efficiency observed which was mainly attributed to the quality of the spray-cast spiro-OMeTAD film that tended to de-wet. Some scale-up of the process was explored, with devices having an active area of $1.5cm^2$ demonstrated to have an efficiency of 6.9%. Here the efficiency reduction on scale-up was attributed to a reduction in PV fill factor resulting from a higher series resistance of the FTO channel-lengths used. Improved patterning of this device would have likely improved its performance. One limitation identified by Mohamad et al and Bishop et al is the quality of the perovskite layer that can be spray-cast under ambient conditions. It is likely that better control over perovskite crystallisation will further enhance the efficiencies of multilayer all spray-cast devices.

It is important to develop a spray-based process that will allow devices to have an efficiency that approaches the most efficient devices fabricated by spin-casting, which currently have a PCE in excess of 22.1%.[2] At present, the most efficient spray-cast devices have an efficiency of around 18% and thus there is still significant work to be done in order to optimise this process.[25] Until now almost all spray-cast devices rely on methylammonium lead triiodide as the perovskite absorber. However state-of-the-art perovskite devices are now increasingly based on mixed cation formulations that generally incorporate caesium and formamidinium in addition to methylammonium at the A site position.[2,40] Such perovskites have enhanced efficiency and stability and are more likely to be the absorber of choice in a commercial device.[40]

In addition to the use of more complex perovskite formulations, it will also be necessary to integrate them with the highest performance hole and electron transport layers, with all such layers ideally deposited using spray-based processes.[41] Recent progress has been made into the use of copper thiocyanate (CuSCN) as an efficient hole-transporting material.[39,42] Significantly, this material has recently been deposited by spray-coating in a perovskite device (where only the CuSCN layer was spray-cast) with an efficiency of 17.1% demonstrated.[39] Notably however, attempts to spray-cast a spiro-OMeTAD hole-transporting layer have been frustrated by a tendency of the film to undergo dewetting from the perovskite surface.[11] This effect appeared to be promoted by the addition of dopant molecules to the spiro-OMeTAD to improve its conductivity, however it was found that dewetting could be largely suppressed by the use of viscosity modifiers.[11] Such additives have also been used to suppress dewetting of PEDOT:PSS films, and thus this approach could be applied more generally when formulating semiconductor inks for spray-coating applications.[43] Note however it will be important to explore the extent to which such materials can be used (even within the perovskite active layer) to improve processing and film morphology without compromising electronic functionality.

The use of spray-coating also offers an opportunity to dispense entirely with the use of hole-transport materials. Here, the development of graded perovskite heterostructures created through vertical control of halide concentration within a device can be used to manipulate the electric field distribution and thereby enhance electron-hole splitting and hole extraction without the use of a hole-transporting semiconductor.[44] We believe, the ability to spray-cast perovskite semiconductors opens an interesting opportunity to develop such concepts by fabricating nanoscale structures within the perovskite absorber layer that cannot easily be formed through a regular solution-based deposition route. For example, by utilising a perovskite precursor ink that rapidly dries and crystallises during the spray-mist phase, it should be possible to deposit perovskite nanoparticles as a “dry” film onto other perovskite layers. This may allow a series of different perovskite materials to be deposited using a multiple-pass spray-process, with graded heterojunctions formed that offer a tailored control over electric-field and band offsets within a device.

Up to now, most work on the development of spray-cast PV devices has concentrated on the fabrication of relatively small devices or simple modules. The scale-up of this technology however will require individual devices to be patterned, allowing them to be connected together forming a device module. While thin-films can be patterned by spray-casting through a mask or stencil, this is not practical for high volume roll-to-roll manufacture. For this reason, it will be necessary to use a laser-based ablation technique to pattern the various layers within a spray-cast device. Laser machining of semiconductor films is already at an advanced stage and routinely used in manufacture, and thus such techniques could be readily adapted.[45]

It is important to acknowledge that whilst it is likely a process to fabricate high efficiency multilayer spray-cast PSCs will be developed, this does not necessarily mean that it will successfully transition into the commercial market. Silicon based devices, traditionally held back by high cost, have in recent years dramatically reduced in price and continue to do so. Decades of research and development have brought module costs down to the point where they are equal to if not exceeded by those of the balance of systems.[46] Open questions remain as to whether a commercial perovskite module will ever reach a cost low enough to give it a significant edge over industrially mature silicon. Therefore we must look for new ways the technology can be applied to disrupt silicon's near monopoly of the market. This may involve creating perovskite-silicon tandem cells,[47] or to look for new opportunities to use perovskite cells in areas in which silicon based devices are unsuitable.

As spray-coating does not involve the close proximity of a coating head to a surface, it will in principle be possible to use it to fabricate PV devices over non-planar surfaces. This opens up the opportunity to coat PV devices over a range of different structural materials and thereby integrate PV onto complex, structured surfaces in a seamless and "invisible" fashion. This offers the potential to integrate PV with the built environment, the surface of airplane wings, autonomous aerial vehicles and automobiles etc. Here, distinct challenges remain; firstly, such surfaces may be much rougher than the well-controlled transparent conductive oxide materials that are often used to prototype devices. This will require the use of planarization layers to control the roughness of the surface of interest. Secondly, problems with inks dewetting and "running" are likely to be more severe when depositing over a three-dimensional surface, and thus various techniques will be necessary to control the motion of the ink, such as the use of viscosity modifiers and air-knives. It will also be necessary to develop high-performance encapsulation systems that are compatible with deposition over non-planar surfaces.

Looking further forward, it will be possible to use spray-coating to fabricate a range of other thin-film devices including perovskite light-emitting diodes. Here, such devices could be integrated over a variety of non-planar surfaces, creating an attractive media for lighting and signage etc.

In conclusion, significant progress has been made in the fabrication of perovksite PV via spray-coating. Such techniques however present a series of challenges through the development of ink formulation and optimisation of parameter-space to create uniform thin films. However, the deposition of solution processable semiconductor materials via spray-coating offers a ready method to fabricate a range of electronic thin-film devices at high speed with low wastage. The coming years will determine whether this technology makes the transition from lab-based demonstrations to a practical manufacture environment.

Author Information

James Bishop was born and raised in the Black Country west of Birmingham (UK). In 2015 he graduated with an M.Phys from the University of Sheffield. He is currently studying for a Ph.D in Spray-Cast Perovskite Solar Cells as a member of the Electronic and Photonic Molecular Materials group (EPMM) under the supervision of Prof David Lidzey.

Thomas Routledge, originally from Solihull, Birmingham (UK), has been in Sheffield since 2010. In 2014 he received his M.Phys from the University of Sheffield. He is currently studying for a Ph.D in Spray-Cast Organic Light-Emitting Diodes under the supervision of Dr Alastair Buckley as a member of the EPMM group.

David Lidzey is originally from London, and studied for his B.Sc (1985-88) and Ph.D (1990-95) degrees in Physics at the University of Birmingham. Between degrees, he worked for Kodak Ltd (Harrow), undertaking research into new photographic products. In 1995, he moved to the University of Sheffield to undertake postdoctoral research in polymer LEDs. He was promoted to a personal Chair in Physics in 2007, and has held Fellowships from Lloyds of London and the EPSRC. He has an interest in the commercialisation of research, and is the Chairman and co-founder of the materials science company Ossila. His research interests are broad, and include the development of photovoltaic devices based on molecular materials and perovskites, spectroscopy of organic thin films, and photonic and polaritonic structures and devices based on organic and hybrid semiconductors.

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References

(1) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society* **2009**, *131*, 6050–6051.

(2) Yang, W. S.; Park, B.-W.; Jung, E. H.; Jeon, N. J.; Kim, Y. C.; Lee, D. U.; Shin, S. S.; Seo, J.; Kim, E. K.; Noh, J. H. et al. Iodide management in formamidinium-lead-halide–based perovskite layers for efficient solar cells. *Science* **2017**, *356*, 1376–1379.

(3) Green, M. A.; Ho-Baillie, A.; Snaith, H. J. The emergence of perovskite solar cells. *Nature Photonics* **2014**, *8*, 506–514.

(4) Eperon, G. E.; Stranks, S. D.; Menelaou, C.; Johnston, M. B.; Herz, L. M.; Snaith, H. J. Formamidinium lead trihalide: a broadly tunable perovskite for efficient planar heterojunction solar cells. *Energy & Environmental Science* **2014**, *7*, 982–988.

(5) Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. *Science* **2013**, *342*, 341–344.

(6) Gong, J.; Darling, S. B.; You, F. Perovskite photovoltaics: life-cycle assessment of energy and environmental impacts. *Energy & Environmental Science* **2015**, *8*, 1953–1968.

(7) Schmidt, T. M.; Larsen-Olsen, T. T.; Carlé, J. E.; Angmo, D.; Krebs, F. C. Upscaling of perovskite solar cells: fully ambient roll processing of flexible perovskite solar cells with printed back electrodes. *Advanced Energy Materials* **2015**, *5*.

(8) Deng, Y.; Peng, E.; Shao, Y.; Xiao, Z.; Dong, Q.; Huang, J. Scalable fabrication of efficient organolead trihalide perovskite solar cells with doctor-bladed active layers. *Energy & Environmental Science* **2015**, *8*, 1544–1550.

(9) Li, S.-G.; Jiang, K.-J.; Su, M.-J.; Cui, X.-P.; Huang, J.-H.; Zhang, Q.-Q.; Zhou, X.-Q.; Yang, L.-M.; Song, Y.-L. Inkjet printing of CH 3 NH 3 PbI 3 on a mesoscopic TiO 2 film for highly efficient perovskite solar cells. *Journal of Materials Chemistry A* **2015**, *3*, 9092–9097.

(10) Barrows, A. T.; Pearson, A. J.; Kwak, C. K.; Dunbar, A. D.; Buckley, A. R.; Lidzey, D. G. Efficient planar heterojunction mixed-halide perovskite solar cells deposited via spray-deposition. *Energy & Environmental Science* **2014**, *7*, 2944–2950.

(11) Bishop, J. E.; Mohamad, D. K.; Wong-Stringer, M.; Smith, A.; Lidzey, D. G. Spray-cast multilayer perovskite solar cells with an active-area of 1.5 cm 2. *Scientific reports* **2017**, *7*, 7962.

(12) Eslamian, M. Spray-on thin film PV solar cells: advances, potentials and challenges. *Coatings* **2014**, *4*, 60–84.

(13) Reale, A.; La Notte, L.; Salamandra, L.; Polino, G.; Susanna, G.; Brown, T. M.; Brunetti, F.; Di Carlo, A. Spray Coating for Polymer Solar Cells: An Up-to-Date Overview. *Energy Technology* **2015**, *3*, 385–406.

(14) Bose, S.; Keller, S. S.; Alstrøm, T. S.; Boisen, A.; Almdal, K. Process optimization of ultrasonic spray coating of polymer films. *Langmuir* **2013**, *29*, 6911–6919.

(15) Majumder, M.; Rendall, C.; Li, M.; Behabtu, N.; Eukel, J. A.; Hauge, R. H.; Schmidt, H. K.; Pasquali, M. Insights into the physics of spray coating of SWNT films. *Chemical Engineering Science* **2010**, *65*, 2000–2008.

(16) Girotto, C.; Moia, D.; Rand, B. P.; Heremans, P. High-performance organic solar cells with spray-coated hole-transport and active layers. *Advanced Functional Materials* **2011**, *21*, 64–72.

(17) Gittens, G. Variation of surface tension of water with temperature. *Journal of Colloid and Interface Science* **1969**, *30*, 406–412.

(18) Tait, J.; Manghooli, S.; Qiu, W.; Rakocevic, L.; Kootstra, L.; Jaysankar, M.; de la Huerta, C. M.; Paetzold, U. W.; Gehlhaar, R.; Cheyns, D. et al. Rapid composition screening for perovskite photovoltaics via concurrently pumped ultrasonic spray coating. *Journal of Materials Chemistry A* **2016**, *4*, 3792–3797.

(19) Das, S.; Yang, B.; Gu, G.; Joshi, P. C.; Ivanov, I. N.; Rouleau, C. M.; Aytug, T.; Geohegan, D. B.; Xiao, K. High-performance flexible perovskite solar cells by using a combination of ultrasonic spray-coating and low thermal budget photonic curing. *Acs Photonics* **2015**, *2*, 680–686.

(20) Yao, J.; Yang, L.; Cai, F.; Yan, Y.; Gurney, R. S.; Liu, D.; Wang, T. The impacts of PbI 2 purity on the morphology and device performance of one-step spray-coated planar heterojunction perovskite solar cells. *Sustainable Energy & Fuels* **2018**,

(21) Fanton, X.; Cazabat, A. Spreading and instabilities induced by a solutal Marangoni effect. *Langmuir* **1998**, *14*, 2554–2561.

(22) Vak, D.; Kim, S.-S.; Jo, J.; Oh, S.-H.; Na, S.-I.; Kim, J.; Kim, D.-Y. Fabrication of organic bulk heterojunction solar cells by a spray deposition method for low-cost power generation. *Applied Physics Letters* **2007**, *91*, 081102.

(23) Hoth, C. N.; Steim, R.; Schilinsky, P.; Choulis, S. A.; Tedde, S. F.; Hayden, O.; Brabec, C. J. Topographical and morphological aspects of spray coated organic photovoltaics. *Organic Electronics* **2009**, *10*, 587–593.

(24) Mohamad, D. K.; Griffin, J.; Bracher, C.; Barrows, A. T.; Lidzey, D. G. Spray-Cast Multilayer Organometal Perovskite Solar Cells Fabricated in Air. *Advanced Energy Materials* **2016**, *6*.

(25) Heo, J. H.; Lee, M. H.; Jang, M. H.; Im, S. H. Highly efficient CH 3 NH 3 PbI 3- x Cl x mixed halide perovskite solar cells prepared by re-dissolution and crystal grain growth via spray coating. *Journal of Materials Chemistry A* **2016**, *4*, 17636–17642.

(26) Zhang, Y.; Griffin, J.; Scarratt, N. W.; Wang, T.; Lidzey, D. G. High efficiency arrays of polymer solar cells fabricated by spray-coating in air. *Progress in Photovoltaics: Research and Applications* **2016**, *24*, 275–282.

(27) Kang, J.-W.; Kang, Y.-J.; Jung, S.; Song, M.; Kim, D.-G.; Kim, C. S.; Kim, S. H. Fully spray-coated inverted organic solar cells. *Solar Energy Materials and Solar Cells* **2012**, *103*, 76–79.

(28) Wang, T.; Scarratt, N. W.; Yi, H.; Dunbar, A. D.; Pearson, A. J.; Watters, D. C.; Glen, T. S.; Brook, A. C.; Kingsley, J.; Buckley, A. R. et al. Fabricating High Performance, Donor–Acceptor Copolymer Solar Cells by Spray-Coating in Air. *Advanced Energy Materials* **2013**, *3*, 505–512.

(29) Burschka, J.; Pellet, N.; Moon, S.-J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Grätzel, M. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature* **2013**, *499*, 316–319.

(30) Yang, W. S.; Noh, J. H.; Jeon, N. J.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science* **2015**, *348*, 1234–1237.

(31) Sanchez, S.; Hua, X.; Phung, N.; Steiner, U.; Abate, A. Flash Infrared Annealing for Antisolvent-Free Highly Efficient Perovskite Solar Cells. *Advanced Energy Materials* **2018**,

(32) Zhang, W.; Saliba, M.; Moore, D. T.; Pathak, S. K.; Hörantner, M. T.; Stergiopoulos, T.; Stranks, S. D.; Eperon, G. E.; Alexander-Webber, J. A.; Abate, A. et al. Ultrasmooth organic–inorganic perovskite thin-film formation and crystallization for efficient planar heterojunction solar cells. *Nature communications* **2015**, *6*.

(33) Huang, H.; Shi, J.; Zhu, L.; Li, D.; Luo, Y.; Meng, Q. Two-step ultrasonic spray deposition of CH 3 NH 3 PbI 3 for efficient and large-area perovskite solar cell. *Nano Energy* **2016**, *27*, 352–358.

(34) Li, F.; Bao, C.; Gao, H.; Zhu, W.; Yu, T.; Yang, J.; Fu, G.; Zhou, X.; Zou, Z. A facile spray-assisted fabrication of homogenous flat CH 3 NH 3 PbI 3 films for high performance mesostructure perovskite solar cells. *Materials Letters* **2015**, *157*, 38–41.

(35) Boopathi, K. M.; Ramesh, M.; Perumal, P.; Huang, Y.-C.; Tsao, C.-S.; Chen, Y.-F.; Lee, C.-H.; Chu, C.-W. Preparation of metal halide perovskite solar cells through a liquid droplet assisted method. *Journal of Materials Chemistry A* **2015**, *3*, 9257–9263.

(36) Xia, X.; Wu, W.; Li, H.; Zheng, B.; Xue, Y.; Xu, J.; Zhang, D.; Gao, C.; Liu, X. Spray reaction prepared FA 1- x Cs x PbI 3 solid solution as a light harvester for perovskite solar cells with improved humidity stability. *RSC Advances* **2016**, *6*, 14792–14798.

(37) Huang, H.; Shi, J.; Lv, S.; Li, D.; Luo, Y.; Meng, Q. Sprayed P25 scaffolds for high-efficiency mesoscopic perovskite solar cells. *Chemical Communications* **2015**, *51*, 10306–10309.

(38) Troughton, J.; Bryant, D.; Wojciechowski, K.; Carnie, M. J.; Snaith, H.; Worsley, D. A.; Watson, T. M. Highly efficient, flexible, indium-free perovskite solar cells employing metallic substrates. *Journal of Materials Chemistry A* **2015**, *3*, 9141–9145.

(39) Yang, I. S.; Sohn, M. R.; Do Sung, S.; Kim, Y. J.; Yoo, Y. J.; Kim, J.; Lee, W. I. Formation of pristine CuSCN layer by spray deposition method for efficient perovskite solar cell with extended stability. *Nano Energy* **2017**, *32*, 414–421.

(40) Saliba, M.; Matsui, T.; Seo, J.-Y.; Domanski, K.; Correa-Baena, J.-P.; Nazeeruddin, M. K.; Zakeeruddin, S. M.; Tress, W.; Abate, A.; Hagfeldt, A. et al. Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. *Energy & environmental science* **2016**, *9*, 1989–1997.

(41) Wong-Stringer, M.; Bishop, J. E.; Smith, J. A.; Mohamad, D. K.; Parnell, A. J.; Kumar, V.; Rodenburg, C.; Lidzey, D. G. Efficient perovskite photovoltaic devices using chemically doped PCDTBT as a hole-transport material. *Journal of Materials Chemistry A* **2017**, *5*, 15714–15723.

(42) Arora, N.; Dar, M. I.; Hinderhofer, A.; Pellet, N.; Schreiber, F.; Zakeeruddin, S. M.; Grätzel, M. Perovskite solar cells with CuSCN hole extraction layers yield stabilized efficiencies greater than 20%. *Science* **2017**, eaam5655.

(43) Griffin, J.; Ryan, A. J.; Lidzey, D. G. Solution modification of PEDOT: PSS inks for ultrasonic spray coating. *Organic Electronics* **2017**, *41*, 245–250.

(44) Li, B.; Zhang, Y.; Zhang, L.; Yin, L. Graded Heterojunction Engineering for Hole-Conductor-Free Perovskite Solar Cells with High Hole Extraction Efficiency and Conductivity. *Advanced Materials* **2017**, *29*.

(45) Galagan, Y.; Fledderus, H.; Gorter, H.; t Mannetje, H. H.; Shanmugam, S.; Mandamparambil, R.; Bosman, J.; Rubingh, J.-E. J.; Teunissen, J.-P.; Salem, A. et al. Roll-to-Roll Slot–Die Coated Organic Photovoltaic (OPV) Modules with High Geometrical Fill Factors. *Energy Technology* **2015**, *3*, 834–842.

(46) Carbajales-Dale, M.; Zhou, Z. Assessing the photovoltaic technology landscape: efficiency and energy return on investment. *Energy & Environmental Science* **2018**,

(47) Bush, K. A.; Palmstrom, A. F.; Zhengshan, J. Y.; Boccard, M.; Cheacharoen, R.; Mailoa, J. P.; McMeekin, D. P.; Hoye, R. L.; Bailie, C. D.; Leijtens, T. et al. 23.6%-efficient monolithic perovskite/silicon tandem solar cells with improved stability. *Nature Energy* **2017**, *2*, 17009.

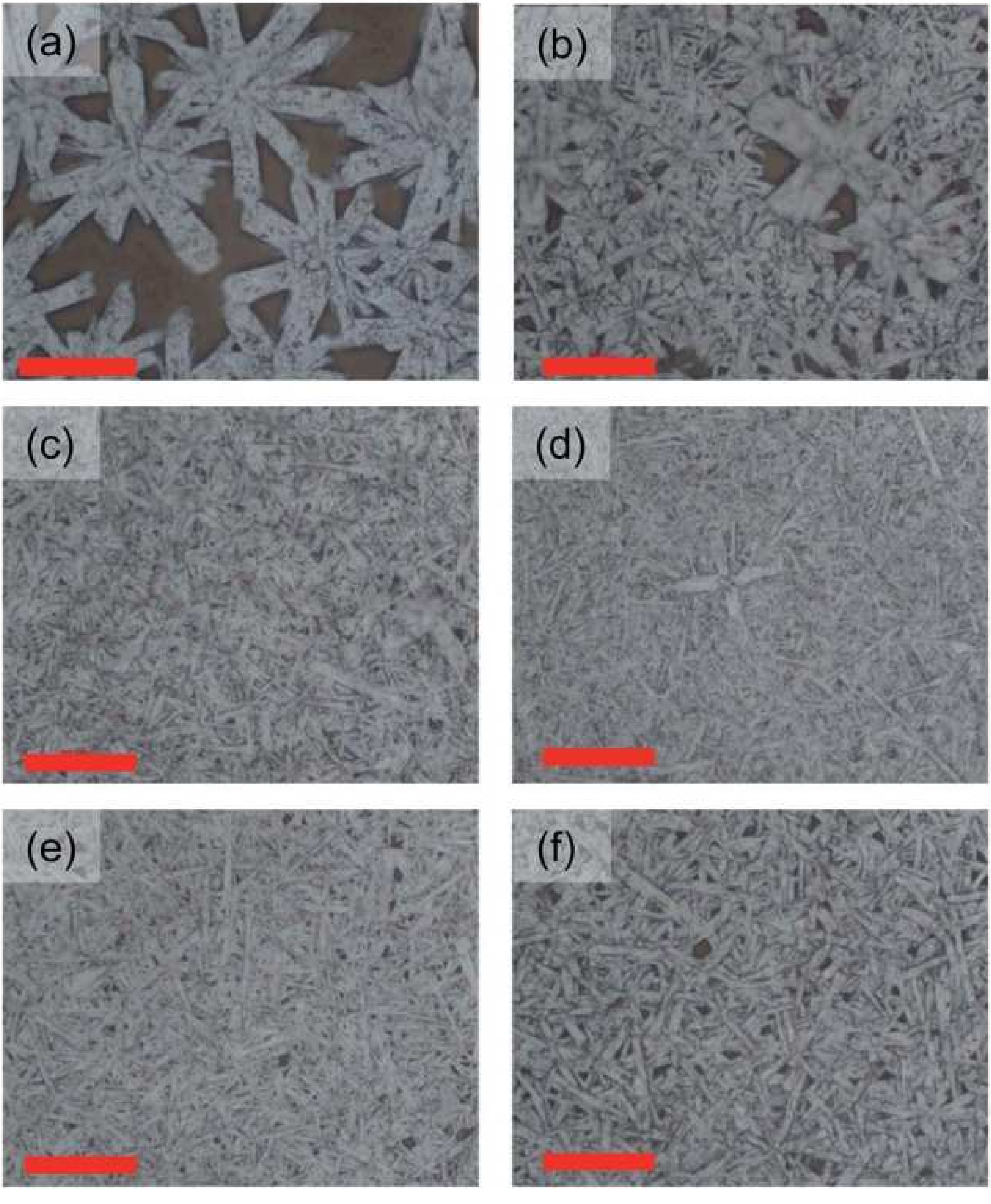

Figure 2: *Optical microscopy images of spray-deposited thin-films of methylammonium iodide and lead chloride onto substrates held at a range of elevated temperatures. (a) 28 °C, (b) 38 °C, (c) 55 °C, (d) 75 °C, (e) 80 °C, (f) 87 °C. The scale bar in each image corresponds to 20 mm. Reproduced from Ref. 10 with permission from The Royal Society of Chemistry.*

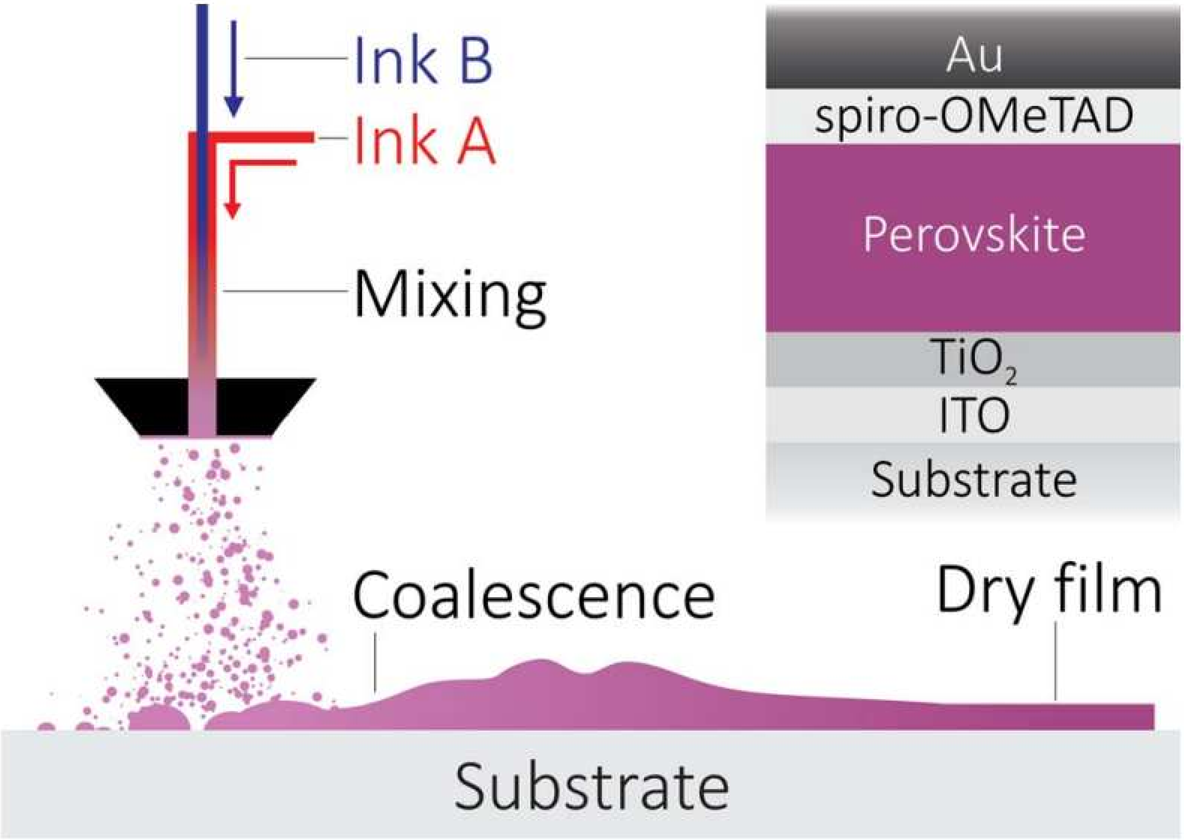

Figure 3: *Schematic of concurrently pumped ultrasonic spray coating for perovskite precursor deposition. The inks ultrasonically mix inside the nozzle, prior to aerosolization. The inset shows the basic device architecture implemented. Reproduced from Ref. 18 with permission from The Royal Society of Chemistry.*

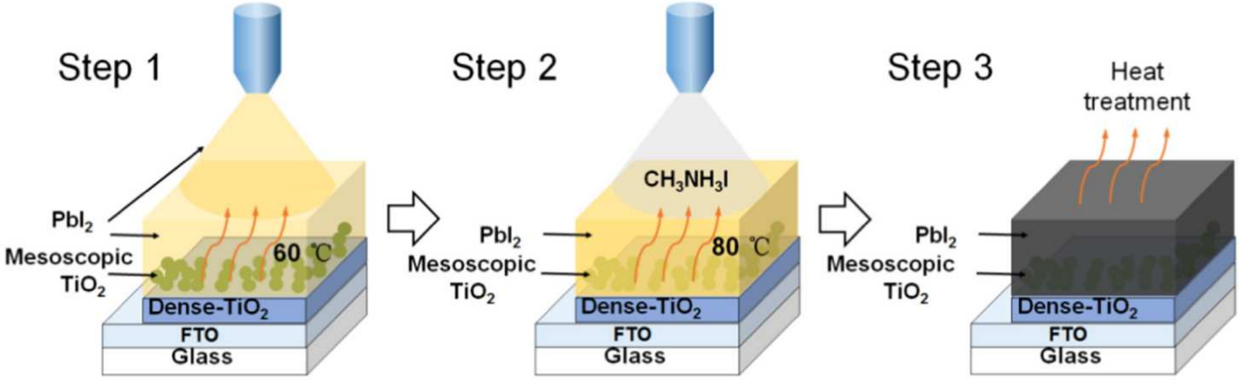

Figure 4: *Schematic diagram of the two-step spray method for the deposition of perovskite* $CH_3NH_3PbI_3$ *film. In Step one,* PbI_2 *dissolved in DMSO is ultrasonic sprayed onto the FTO/TiO2 substrate at 60° C. In step two, the* CH_3NH_3I *in isopropanol is sprayed onto the* PbI_2 *film at 80° C. In step three, the as-prepared film is heat treated to promote the interdiffusion reaction between* PbI_2 *and* CH_3NH_3I *and crystallization of* $CH_3NH_3PbI_3$*. Reproduced from Ref. 33 with permission from Elsevier.*

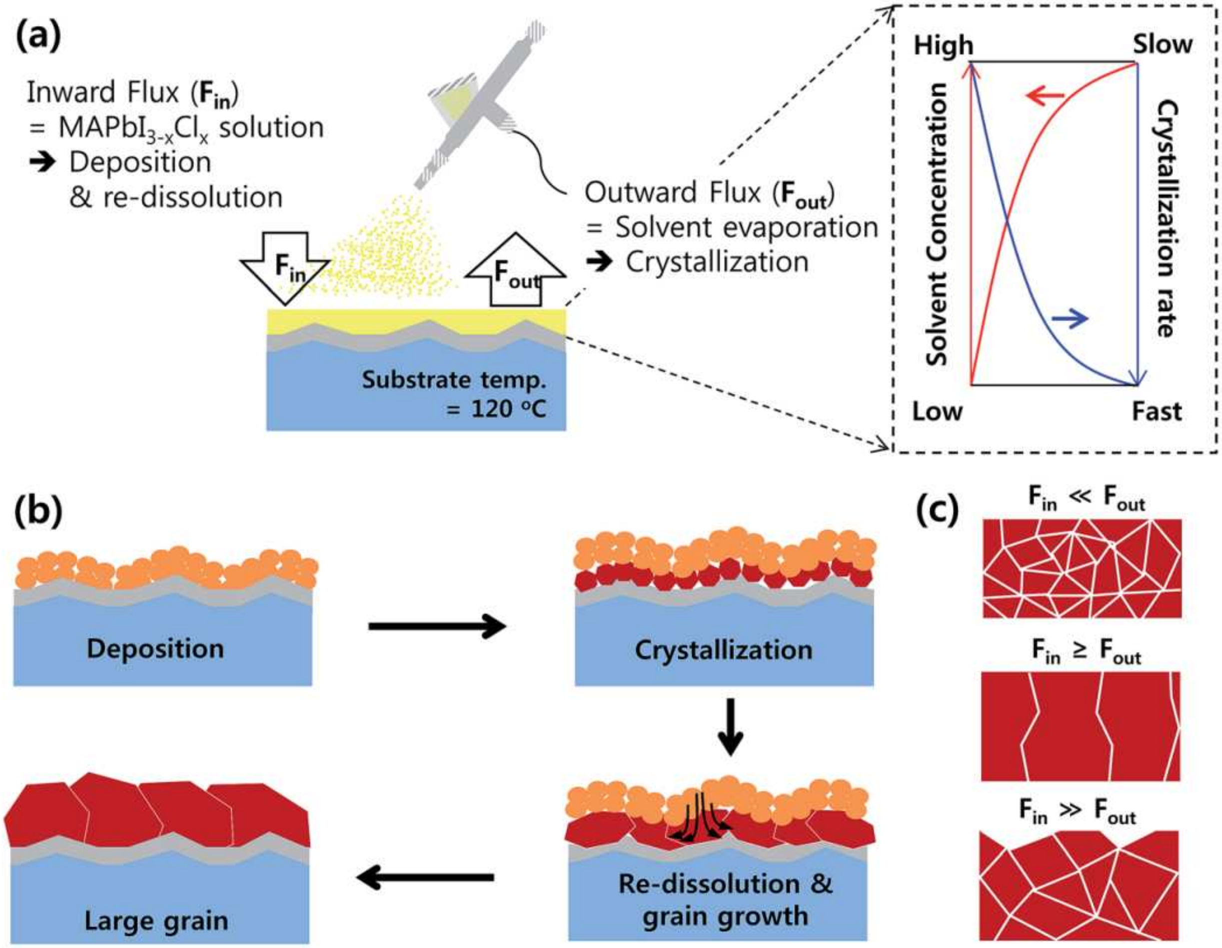

Figure 5: *Schematic illustration of (a) the proposed mechanism of the spray coating process, (b) crystalline grain growth, and (c) the morphology of the formed crystalline grains in the perovskite film with respect to the balance between* F_{in} *and* F_{out}. *Reproduced from Ref. 25 with permission from The Royal Society of Chemistry.*