Review
Scalable solution coating of the absorber for perovskite solar cells

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Abstract

Perovskite-based solar cell technology has advanced significantly and the power conversion efficiencies are nowadays on par with commercialized photovoltaic technologies. To realize the potential of perovskite solar cells, the focus is now shifting to scalable fabrication technologies that will enable low-cost solution processing of perovskite solar cells over large areas and with high yields. This review article discusses the fundamental concerns that arise when transitioning from laboratory to large area solution coating, available scalable coating technologies, and their applicability to the fabrication of high-performance perovskite solar cells. We find that a significant amount of work has been done to test scalable coating technologies, but also that often the methods that led to highest-performing cells in the laboratory (e.g. antisolvent processing) show limited compatibility with scalable coating methods. To achieve a high-yield and low-cost process, development must emphasize a high degree of control provided by sequential conversion of perovskite films and engineering of additives that fine-tune coating properties of perovskite precursor inks.

Keywords: Perovskite solar cell; Coating; Solution; Scalable

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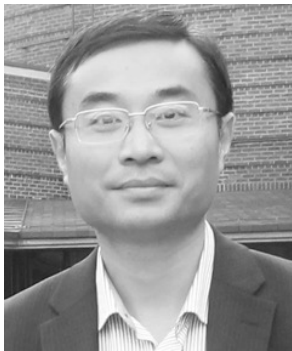
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1. Introduction

1.1. Motivation to develop scalable fabrication technology

Direct conversion of solar radiation to electricity is a major part of the push to reduce humanity's dependence on fossil fuels and minimize negative impact of human activity. In recent years great advances have been accomplished in developing high-performance solar cells based on perovskite absorber layer. As laboratory cell efficiencies (22.1% [1]) reach levels on par with established commercial photovoltaic technologies such as silicon, CIGS (22.6% [1]) and CdTe (22.1% [1]), focus is shifting to processing that would allow production of commercially practical cell sizes and yields. To achieve commercial viability and live up to the idea of minimizing environmental damage, fabrication methods must be developed that are both low cost and low waste. For example, due to very low cost of perovskite precursor materials, spin coating is not ruled out by cost concerns, but inherently high waste of material (> 90%) is unacceptable from the stand point of low impact on the environment.

Fabrication of the absorber layer by solution coating without vacuum or high temperature processes promises to lead to ultra-low cost perovskite solar cells. The concept of large area solution coating is highly developed in painting and printing industries. Many of the methods originally developed for passive coatings are now being tested for fabrication of functional films in perovskite solar cells. Examples include airbrush coating [2-7], ultrasonic spray coating [8-14], ink-jet printing [15-17], slot-die coating [18-24], doctor blade coating [25-27], screen printing [28, 29], electrospray coating [30], and so on.

This review discusses the challenges inherent in scaling up a solution coating process from laboratory to industrial scale. We review the most promising methods of scaling perovskite absorber fabrication to large area and their relative advantages. Finally, we consider compatibility between laboratory-scale methods that achieve high-performing perovskite absorber layers and scalable fabrication technologies.

1.2. Challenges of solution coating non-polymer inks

Transition from small area solution processing in the laboratory to commercially viable large area coating makes it necessary to consider the effects that are negligible when scale of fabrication is small. To realize low cost, rapid production of thin films from liquid inks, a high degree of reproducibility over large areas needs to be achieved. This section discusses some of the considerations that need to be taken into account when designing a large area solution coating process.

In the following discussion, three stages of film coating are discussed: (i) un-equilibrated wet film–wet ink on the surface of the substrate, immediately after application; (ii) equilibrated wet film–wet film after liquid motion on the surface has ceased and film thickness is changing only due to solvent evaporation. The time between ink application and equilibrated state is referred to as the equilibration time, τ_e; (iii) dry film–precipitated material after the solvent has evaporated. Dry film stage does not imply complete removal of solvent, but simply a solid state. Solvent may still be present in the film, but

convection and surface flow are no longer possible. Time between ink application and the dry film stage is referred to as the precipitation time, τ_p.

1.2.1. Coating uniformity

To achieve high reproducibility and facilitate solar cell optimization, a uniform film thickness must be achieved. Assuming that precipitation occurs uniformly, the fundamental requirement to achieve a uniform film is that equilibration time (τ_e) and precipitation time (τ_p) must follow the following relation:

$$\tau_e \ll \tau_p$$

Time it takes for the dry film to precipitate must be at least an order of magnitude higher than the time it takes for the film to reach flat equilibrium state. If precipitation occurs on the same time scale as equilibration, variations in environmental conditions will inevitably lead to occurrence of precipitation before full equilibration. Any chance of precipitation from a non-equilibrated film will lead to poor reproducibility.

Alternatively, an inverse condition is possible:

$$\tau_e \gg \tau_p$$

This describes a condition when precipitation is much faster than equilibration, therefore equilibration does not occur at all. The dry film is formed immediately on contact of ink to the substrate. This is often referred to as a dry coating condition. This regime effectively eliminates all the concerns related to liquid-phase non-uniformity described below, but coated layers are necessarily rough. Uniform coating can be achieved by overlapping many dry coated layers.

A completely unacceptable condition is:

$$\tau_e \approx \tau_p$$

If the precipitation and equilibration times are similar, a very unstable process is created. Minor changes in environmental conditions will result in precipitation from un-equilibrated wet film. A fundamental principle of stable process design, is that a single process must dominate each step. If two processes occur simultaneously and the outcome depends on both processes, it is difficult to achieve high reproducibility.

Equilibration rate most strongly depends on the viscosity and contact angle of the ink with respect to the substrate. Viscosity and contact angle can be tuned by additives, while the contact angle can also be tuned by surface preparation (discussed in later sections). Precipitation rate is most directly related to solubility of the solute and can also be controlled by the choice of solvent or additives (see later discussion).

In reality, precipitation does not always occur uniformly, even if a uniform wet film is achieved. Several sources of non-uniformity that occur during precipitation from liquid ink are well understood. Important examples are coffee stain effect and Marangoni effect. These phenomena refer to currents that occur in evaporating liquids and can cause a large fraction of precipitate to be deposited in a small area. The name "coffee stain effect" derives from ring-shaped stains that are observed after evaporated drops of coffee. The effect was explained in 1997 by Deegan et al. [31] and described as a combination of accelerated evaporation at pinned droplet edges and a flow from droplet center to replenish evaporated liquid. Pinning of droplet/wet film edges is extremely common in practice, and consequently coffee stain effect is observed frequently.

Marangoni effect refers to flow of liquid due to a gradient of surface tension. Gradient of surface tension may occur due to non-uniform mixing of two liquids, but in context of coating it typically occurs due to different evaporation rates of multiple solvents in a solution. Similarly to coffee stain effect, because droplet (or wet film) edges evaporate faster, evaporation of volatile solvent is amplified more strongly, and a composition gradient can occur. In contrast to coffee stain effect, a typical manifestation of Marangoni effect will deposit material at the center of the drop. As a consequence, the two effects can be tuned to cancel and produce uniform coating [32]. In inks where Marangoni effect is negligible, for example a single solvent ink, coffee stain effect can be avoided by careful tuning of coating parameters [33].

Mineral salt solutes (such as PbI_2, a common perovskite precursor) precipitate preferentially at sites where nucleation has already occurred. In extreme cases, dendritic crystal growth can cause dramatic inhomogeneity of precipitated coating. To achieve uniform coating of such a material, spacing between nucleation sites must be less than the desired thickness of the film. Nucleation density depends on ink temperature, solute concentration, and substrate surface condition among other factors. The same conditions also influence all the effects described above, therefore careful optimization of parameters is necessary to achieve uniform precipitation.

1.2.2. Process speed

Simple processing is desirable under research laboratory conditions because it minimizes chances for fabrication errors. In addition, longer non-interactive process steps such as annealing can be desirable, because they reduce process sensitivity to accurate timing. In industrial processing, the considerations are inverse. Highly automated processing means that defect occurrence due to process complexity is minimal. On the other hand, processing time directly affects total fabrication cost, therefore passive processing (e.g. annealing) time must be minimized.

Roll-to-roll processing introduces an additional consideration to process speed–speed matching. Processing on a continuous substrate requires that every step is accomplished with the substrate moving at the same speed. This may mean speeding up slow processes, but also slowing down processes that may perform better at high substrate speeds.

The scalable solution coating methods discussed later in this review determine the thickness of coating by applying a fixed amount of ink per area (pre-metered coating). Consequently, it is tempting to consider adjusting process speed by changing the ink application rate to match the substrate moving speed. This linear approximation is valid within the defined stability limits for each process, however these stability limits must be determined for each application. To illustrate the reasons for non-linearity, we may consider direct application methods such as slot-die coating, or blade coating (see Sections 3.1, 3.2). Due to a narrow gap between applicator blade/head and the substrate the ink experiences substantial shear that depends on the relative motion of the applicator and substrate. Most particle suspensions or polymer solutions display some non-newtonian behavior via shear-thickening or shear-thinning. The change in ink viscosity as a function of coating speed requires additional optimization to maintain coating quality. For spray coating-methods (see Sections 3.3, 3.4), the interaction between substrate and applicator nozzle is not important, however, the ink flow rate will affect the mean size of the droplets produced by the atomizer. Mean droplet size is a major factor in determining wet film equilibration time, therefore, as in the case of direct application, re-optimization may be required if the process speed is substantially changed.

1.2.3. Waste management

One of the most easily neglected costs of laboratory-based fabrication is waste management. In research laboratories waste disposal is generally handled by the parent institution, therefore the researchers are not directly aware of the cost associated with waste disposal. In industrial production, waste disposal and environmental effect mitigation can be a major part of production cost.

Solvents constitute a major source of waste in liquid ink coating processes. A vast majority of reported perovskite solution processing methods have employed one of the following solvents: N,N-dimethylformamide(DMF), dimethyl sulfoxide (DMSO), γ-Butyrolactone (GBL), or N-Methyl-2-pyrrolidone (NMP). The aforementioned solvents vary in degree of toxicity, but are all considered highly hazardous to the environment. The use of these solvents is difficult to avoid because common perovskite precursors (e.g. PbI_2) are not soluble in common environmentally benign solvents. Alternative precursors such as lead acetate ($Pb(CH_3COO)_2$) are soluble in water or alcohol. However, the works that implemented lead acetate for perovskite absorber synthesis (e.g. [34, 35]) still employed one of the four solvents listed above to achieve high performance devices. This suggests that the currently used solvents play an important role in perovskite crystal growth.

One of the pathways to avoid the use of toxic solvents during the coating process is nanoparticle-based coating (Section 1.3.1). Pre-synthesized particles may be suspended in a solvent that is optimized for a minimal environmental effect and best coating quality. Spray coating of pre-synthesized perovskite nanoparticles from and IPA solution has been demonstrated by Nejand et al. [36], which is a promising path to large scale perovskite absorber production.

Furthermore, the recent report by Chen et al. [37] described the preparation of a liquid perovskite ink entirely free of solvents. While annealing of this ink still releases hazardous vapors, it could dramatically reduce the amount of toxic waste generated in the process.

1.2.4. Ambient conditions

It is widely recognized that ambient conditions, such as humidity and temperature, strongly influence perovskite film formation. In particular, fabrication in atmosphere with a relative humidity of 50% or more requires special consideration [38, 39]. Research laboratories often address this issue by processing in dry N_2 atmosphere. In addition to equipment cost, large scale processing in non-breathable gas presents a significant safety hazard under industrial conditions, therefore it must be avoided in low-cost processing. Furthermore, it is widely recognized that some water vapor may be favorable for high-quality perovskite film fabrication. Therefore it is likely that full isolation from ambient air will not be necessary for a large-scale perovskite absorber fabrication process.

Regardless of what values of ambient temperature and humidity are eventually accepted as optimal, it is imperative that the processing conditions are controlled and stabilized. High reproducibility can only be achieved if the environmental conditions are consistent with the fabrication batches. Furthermore, attention must be paid to conditions that are not as straightforward to measure as humidity and temperature. Ambient gas flow rate on the surface of wet ink (e.g. due to the exhaust system) will strongly affect the solvent evaporation rate. Remeika et al. [14] considered quantitative characterization of ambient conditions in a spray coating system process chamber. Direct measurement of solvent evaporation rate and modeling to adjust for varying sample geometry are proposed as a way to compare relevant environmental conditions between production sites. Further research will likely reveal that even more detailed characterization of ambient conditions is required.

It is extremely difficult to foresee all the environmental factors that will affect the film quality. High-end electronics industry has famously gone to extremes by reproducing even factory layouts between development and production sites. For low-cost fabrication of solar cells, cost constraints will not allow such extreme measures, but inevitably control of ambient conditions will be an important part of the total production cost.

1.3. Types of scalable solution coating

1.3.1. Nanoparticle / inert material

It is important to distinguish two approaches to solution processing of functional thin films. An approach that is frequently taken in industry, is to coat a suspension of micro/nano- particles or non-reactive precursors by solution processing and apply post-processing to functionalize the film or optimize performance.

The key to this approach, is that no chemical reaction takes place during coating. Micro/nano-particles with desired functional properties are prepared, suspended in solution, and the solution is coated on the surface. Alternatively, non-reactive precursors may be chemically dissolved and coated to form a precursor film. Following the coating, nanoparticle film is generally post-processed by the application of heat, photo-excitation or reactive gas to remove the surface coatings from nanoparticles and form electrical contact (sinter) between nanoparticles and substrate. The precursor thin film is also post-processed in a similar fashion, to form the desired functional film.

The advantage of this process is the separation of coating process and film formation. Achieving uniform solution coating on a desired surface is typically challenging, therefore optimizing all the conditions for uniformity without regard for functional film formation reduces cost and improves reproducibility of the process. A potential disadvantage is that to implement coating of a particle

suspension, it may be necessary to coat the particles with additional materials to prevent particle aggregation and improve stability of the suspension. These coatings require post-processing to remove, which may damage functional nanoparticles. Precursor coating may also require additives to form a uniform film. If a precursor solution consists of multiple components, mobility of atoms in the dry film is much more limited than that in wet film, so post-processing of the dry film may not be able to achieve the same quality as achievable by direct crystallization from a wet film.

A good illustration of the absorber formation from a nanoparticle suspension is presented by Miskin et al. [40]. CZTS nanoparticles are synthesized, suspended in the solution and doctor blade-coated on a Mo-Glass substrate. To optimize performance, the films are annealed in Se vapor atmosphere. The resulting device yields 9.0% efficiency, which compares well with the current world record for CZTS devices (12.6% [41]) Similarly, perovskite nanoparticle spray coating followed by mechanical compression has been demonstrated as a means of eliminating environmentally hazardous solvents from the process [36].

1.3.2. Precursor

An approach that is more common in academic laboratories, is coating of dissolved precursors that immediately react to form a functional film during solvent evaporation. In contrast to nanoparticle pre-fabrication, this process combines materials synthesis with film coating, resulting in fewer process steps. It also results in monolithic films, generally leading to superior performance compared with nanoparticle based films.

The main drawback of this process is the necessity to simultaneously optimize functional film formation and coating uniformity. As described in Section 1.2.1, achieving a uniform coating over large areas entails considerable challenges. Steps taken to optimize film uniformity, may be unfavorable for high quality functional material formation.

Despite inherent challenges, precursor solution coating has been implemented in large scale fabrication of photovoltaic devices. A prominent example is the implementation of large scale production of polymer photovoltaic cells by slot-die coating [42].

2. Pre-processing

Pre-processing encompasses a wide range of processes that are performed before absorber deposition. The goal is to achieve a uniform surface condition, improve absorber adhesion, and achieve high quality interface between absorber and underlying layer.

The most common pre-processing step is surface decontamination. Surface impurities can be removed by water-based detergents, organic solvents, wet etching, dry etching, ultrasonic cleaning, mechanical adhesion, heating etc. For high volume fabrication, low-cost environmentally-friendly solutions are crucial. This means that water based non-toxic soap washing is preferred over organic solvents. Dry etching is preferred over wet etching as it does not generate solvent waste. In particular, non-vacuum oxygen treatment (discussed below) is crucial to achieving high-quality liquid ink coating. Adhesive cleaning for particle removal is strongly preferred over ultrasonic cleaning. High-throughput, residue-free adhesive cleaning systems are readily available [43] and are more compatible with large-area substrates than ultrasonic cleaning as they do not require immersion into a detergent bath.

A very common final decontamination step is reactive oxygen treatment. Atomic or ionized oxygen oxidizes organic impurities on the surface and allows volatile products (CO_2, H_2O) to escape from a clean surface. In addition, the surface is partially oxidized, increasing its surface energy. High surface energy means that the contact angle of liquids will be reduced (improved wetting) which is favorable for uniform coating by liquid inks.

Three most common approaches to the oxygen treatment are oxygen plasma, UV-ozone and Corona discharge treatments. Oxygen plasma is the most reactive one, but requires a low vacuum chamber, significantly increasing the process cost in a mass production environment. UV-ozone is accomplished by exposure of the substrate to UV light in ambient atmosphere, which results in the generation of ozone and atomic oxygen. It is a low cost process, but a typical exposure is around 15 min. For a roll-to-roll

system running at several m/s it would be impractical to implement a UV treatment chamber of a sufficient length. Corona discharge system uses an electrical discharge to generate atomic oxygen in ambient air. The system has been commercialized for continuous processing of substrates at industrial roll-to-roll speeds. Corona treatment is clearly preferable in terms of process cost. However, it should be kept in mind that the different treatments are not exactly equivalent. In addition to reaction with atomic oxygen, plasma treatment can include sputtering by accelerated ions and UV-Ozone exposes the substrate to UV light that is sufficient to cause cleaning in the absence of oxygen [44]. These secondary effects should be taken into account when transiting from laboratory to mass production process.

In addition to pre-processing methods discussed above, some groups have reported (e.g. [39]) the preparation of high-performance perovskite solar cells by spin coating on pre-heated substrates. Heating the substrate to de-sorb moisture and other contaminants is a potentially low-cost final pre-processing step. However, it is only compatible with high-volume processing if the substrate temperature is explicitly controlled during the next fabrication step. Several groups have reported spin-coating a pre-heated substrate before it equilibrates with ambient temperature–this is not a process that can be scaled up to large scale production. High reproducibility can only be achieved if all the process parameters are precisely controlled. When a heat source is removed, the substrate cooling rate will be determined by environmental conditions, such as ambient air temperature, humidity, exhaust flow rate, etc. If the process relies on processing the sample at an undetermined transient temperature, achieving high reproducibility over large area will be challenging.

Coating technology	Material waste	Wet film	Roll-to-roll compatible	Patterning	Ink viscosity range	Substrate
Spin coating	≈90%	very flat	no	no	wide range	flat
Blade coating	low	flat	yes	no	high viscosity	flat
Slot Die coating	very low	flat	yes	1-dimension	wide range	flat
Airbrush spray coating	medium	droplets	yes	masking	low viscosity	non-flat
Ultrasonic spray coating	low	droplets	yes	masking	low viscosity	non-flat
Ink-jet printing	none	droplets	yes	high resolution	low viscosity	flat
Screen printing	low	possible mesh trace	yes	high resolution	high viscosity	flat

Fig. 1. Comparison of scalable solution coating methods and spin coating. Red cells indicate properties that are unfavorable for large scale processing, green indicates very favorable properties, and yellow indicates that a property may present a concern, depending on the application.

3. Absorber coating processes

A wide range of large-area solution coating processes are available. Fig. 1 shows a list of common scalable solution coating methods and illustrates their respective advantages and disadvantages. This section reviews the principles of operation of technologies that are being explored for up-scaling of perovskite absorber coating and we believe have the greatest potential for perovskite absorber fabrication. Table 1 presents top reported PCE values (for small devices) for the four scalable

fabrication methods discussed below. The performance data are presented only for illustration and should not be interpreted to be a quantitative comparison. Device architecture, absorber composition, and even performance measurement methodology still differ greatly among groups working on perovskite solar cell fabrication, therefore exact comparison of reported performance values is not meaningful. Furthermore, for large scale fabrication champion device performance is less important than stability, reproducibility and complete fabrication cost, but these parameters will not be possible to compare until consistent testing protocols are established and used by the perovskite solar cell research community.

Table 1 Champion cell efficiencies reported for scalable fabrication methods discussed in this section. Device area in all the cases in < 1 cm².

Method	Top reported PCE	Reference
Airbrush	18.3%	[45]
Doctor blade	15.1%	[46]
Slot-die	14.7%	[22]
Ultrasonic spray	16.0%	[13]

3.1. Doctor blade

Doctor blade or "knife" coating is a simple technique for coating flat substrates. Coating is accomplished by pouring ink on the substrate and moving a blade across the surface to remove excess ink. The distance between the blade and the substrate determines the thickness of the wet film. At high coating speeds (typical of industrial processing), a good approximation for wet film thickness t is [47]:

$$t = \frac{G}{2}$$

where, G is the gap between the blade and the substrate (see Fig. 2). The relation is less accurate at slower speeds characteristic of laboratory machines, but still serves as a good guideline.

Both laboratory and industry grade blade coating machines are widely available. It is particularly appealing for laboratory testing due to the extreme simplicity of the construction. It is also important that the wet film applied by blade coating is flat almost immediately upon application. Flat wet film imposed by the shape of the blade greatly reduces the equilibration time of the wet film, but also restricts coatable substrates to flat surfaces. Other disadvantages are potentially high exposure of ink to atmosphere (while in the reservoir) and waste of excess ink in the reservoir. Several works have demonstrated perovskite absorber coating by doctor blade [25-27].
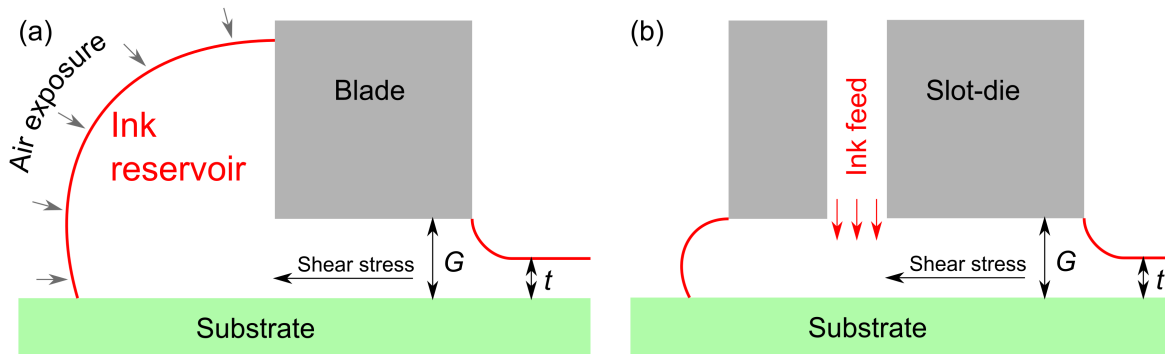
Fig. 2. Schematics of blade coating (a) and slot-die coating (b). The drawing denotes important quantities G–gap between blade/slot-die and substrate, and t–wet film thickness.

3.2. Slot-die coating

Slot-die coating is a widely used coating technology in functional film coating. It is mechanically similar to blade coating, but wet film thickness is determined directly by supplied ink quantity (see Fig. 2). The approximate relationship between blade distance and wet film thickness described for blade coating still holds, therefore blade distance needs to be adjusted accurately to achieve stable coating [47]. When operated within the stability limits, slot die coating allows adjustment of wet film thickness by changing the ink flow rate.

Slot die coating has the advantages inherent in blade coating–instantly flat wet film and relatively simple construction. It is also restricted to flat substrates. The short exposure of ink to atmosphere before being applied to the substrate is also an advantage for perovskite absorber coating. Slot die coating has been implemented for perovskite absorber coating [18-24], including pilot industrial production [48].

3.3. Airbrush spray coating

Unlike slot-die or blade coating, spray requires ink to travel a considerable distance before reaching the substrate. To accomplish delivery of ink over a distance, liquid ink is atomized into fine droplets and carried towards the substrate by gas flow. The process parameters can be customized to achieve a continuous liquid coating before the solvent evaporates, rapid drying of droplets in contact with the substrate, or even partial precipitation of solids while the droplets are in flight.

Atomization of the droplets is achieved by ejecting ink through a nozzle by a high pressure gas (see Fig. 3a). Fast motion of the gas flow causes atomization of the liquid ink into fine droplets. The same gas flow that is used to atomize the gas is also used to direct atomized droplets to the substrate. High quality films require fine atomization of ink, which necessitates high velocity of gas ejected from the nozzle. As a result, the distance between the nozzle and the substrate cannot be too small, or the carrier gas will disturb the wet film before it dries. High flow of gas can also cause considerable overspray–scattering of ink outside of coating area. Air brush spray coating has been demonstrated for perovskite absorber layer by several groups [2-7].

In comparison with slot-die and blade coating, the chief advantage of spray coating is the capacity to coat non-flat surfaces. A potential concern is that long distance of travel from nozzle to substrate may result in undesired exposure of ink to the atmosphere. In addition, because the wet film is formed from individual droplets, the equilibration time for the wet film can be substantial, and requirements for the substrate preparation may be more strict than for the techniques that coat flat wet films directly.

A regime of spray coating that allows ink droplets to equilibrate to a continuous wet film on the substrate is referred to as "wet" coating. A unique feature of spray coating is the capacity to coat in the "dry" regime. "Dry" coating regime is achieved when a large fraction of the solvent in atomized ink droplets evaporates in flight, and the solid is formed immediately when a droplet touches the substrate. Equilibration of the wet film does not occur in this regime. Dry coating can be advantageous because rapid formation of the dry film reduces the sensitivity to surface conditions. The texture of a dry spray coated layer is necessarily rough, however roughness can be reduced by coating many thin layers. Another major advantage of dry coating is suppressed interaction with substrate materials. This may be important if the solvent of the coated layer dissolves the substrate materials. This principle was demonstrated for dry spray coating of organic solar cell absorber [49].
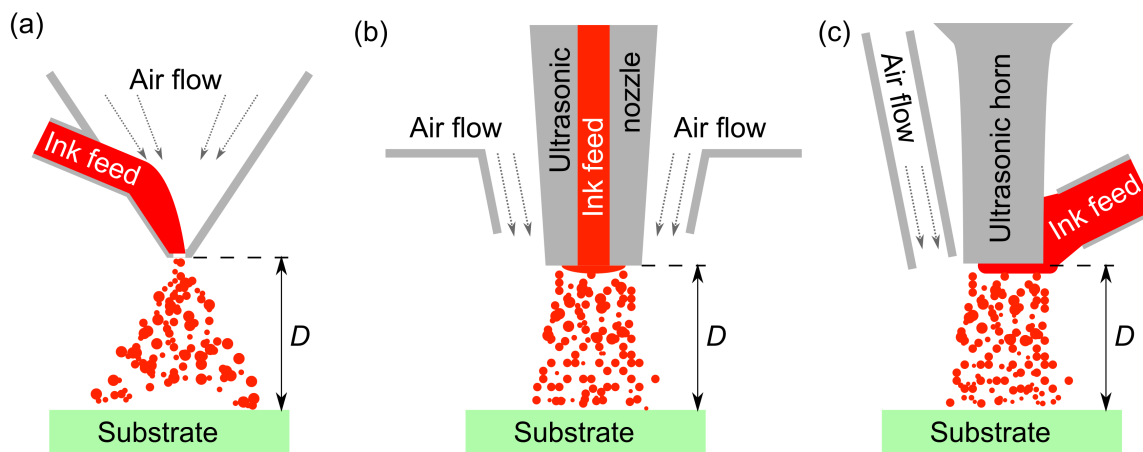
Fig. 3. Airbrush (a), ultrasonic nozzle (b), and nozzle-free ultrasonic (c) spray. *D* denotes the distance between the nozzle and substrate. For airbrush spray, *D* is around 10 cm or more, whereas for ultrasonic spray *D* can be as little as a few mm.

3.4. Ultrasonic spray coating

Ultrasonic spray coating functions on a similar principle as airbrush spray coating, but atomization and ink transport are accomplished by different processes (see Fig. 3b and c). To atomize the ink, the liquid makes contact with a surface vibrating at ultrasonic frequency. At sufficient power, ultrasonic vibration causes droplets to break off from the liquid surface, forming a mist. The size of the droplets is approximately determined by the frequency of vibration, but also strongly depends on the properties of the ink. A separate gas flow is utilized to direct the ink mist toward the substrate. In contrast with airbrush, the air flow rate can be arbitrarily low, adjusted to be sufficient to deliver droplets to the substrate at desired velocity. Gas flow may also be shaped to achieve the desired ink distribution. A low gas flow rate allows the ultrasonic spray nozzle to approach as close to the substrate as desired. This minimizes waste of ink to overspray, reduces ink exposure to atmosphere, and allows a limited degree of patterning by a narrow spray.

The concept of wet and dry coating applies to airbrush and ultrasonic spray. A greater range of coating conditions are achievable via ultrasonic spray, therefore ultrasonic spray is preferred where exact control of coating quality is required. Various regimes of roughness achievable by tuning parameters are illustrated in Ref. [33]. Ultrasonic spray has also been implemented for perovskite absorbers by several groups [8-14].

3.5. Printing

The characteristic of "printing" that distinguishes it from "coating" methods described above is the capacity of precise patterning. Printing methods that have been applied to organic or perovskite solar cell fabrication include ink jet printing, screen printing and flexographic printing. Some works have reported the applications of printing (e.g., ink-jet [15-17]) to perovskite absorber fabrication. The concerns for obtaining high quality printed layers are similar to coating technologies described above.

The chief advantage of printing versus coating is the built-in capacity for patterning, however, low cost laser-based patterning capabilities have been developed for thin film solar cells which are expected to be readily transferable to perovskite film patterning. Because integrated patterning necessitates a compromise between cost or film quality, we will not consider such patterning capabilities for perovskite films at this time.

4. Post-processing

Post-processing encompasses a variety of processes that are applied to a film after it is solidified. In the context of large scale manufacturing, post-processing is especially important since the conditions

for uniform deposition may not be optimal for film functionality. Post-processing provides an opportunity to fine-tune functional properties without affecting the uniformity of material distribution.

The most common post-process is heat treatment, or annealing. Heat may be applied via direct contact with a hot surface (hot plate) or a heated chamber (oven). Oven annealing is easier to implement on large scale, however due to low heat transfer rates through gas, annealing time is long and good uniformity of temperature in an oven is difficult to achieve. Hot plate application results in annealing time that is an order of magnitude shorter than oven annealing time, and uniformity of heating can be fine-tuned to a few °C. For this reason, it is preferred to develop the processes based on hot plate annealing.

Almost every published perovskite absorber coating process involves some form of heat post-processing. It would be beyond the scope of this work to review the published results under different annealing conditions, but it is important to note that environmental conditions, such as ambient gas, humidity or solvent vapor presence, ambient temperature, and illumination all affect the outcome of an annealing process. Therefore, when a process is transferred from laboratory to large scale production, it is likely to fail if these additional parameters are not properly controlled.

Mechanical compression is another type of post-process that has been reported to improve perovskite absorber performance [50, 51], including post-processing of spray coated perovskite nanoparticles [36]. Reports have indicated that mechanical compression does not affect the crystallinity of perovskite films, but is effective in reducing the number of voids and pinholes in absorber films. More compact films demonstrate more efficient collection of photogenerated charge and reduction of shunt defects. Low cost of implementation makes compression of an appealing option for large-scale post-processing.

Photo-flash annealing is a technique that is currently widely applied to sintering of solution processed metal nanoparticle inks. Intense illumination by a short pulse of light allows heating of the surface layer, without exposing the substrate to high temperatures. This technique is widely applied to the fabrication on flexible substrates with limited temperature tolerance. Photo-flash annealing was also applied to perovskite film annealing [52, 53]. It was demonstrated that with exposure duration of around a millisecond, results comparable to extended hotplate annealing could be achieved. Rapid processing and compatibility with flexible substrates make photonic annealing an attractive option for up-scaling of perovskite absorber processing.

5. Outlook for commercialization

Several methods of perovskite device fabrication have been established to consistently yield high-performance devices. In general, these methods are developed for use with spin-coating, and often rely on special characteristics of spin-coating to be effective. In this section we discuss the applicability of these methods to scalable processing technologies described above.

5.1. Antisolvent processing

Antisolvent processing is accomplished by spin coating a perovskite precursor ink containing a solvent with a low evaporation rate and rapidly removing the solvent by application of an "anti-solvent". Presence of the low evaporation rate solvent prevents the crystallization of perovskite. When the film has reached a solid state, but substantial solvent is still present, an "antisolvent", a liquid that dissolves the solvent but not the perovskite precursor is dripped on the spinning sample. Presence of the anti-solvent rapidly removes the solvent from the film, resulting in a meta-stable state that is annealed to obtain high performance perovskite films. Several anti-solvents have been employed including toluene [54], diethyl-ether [55], chlorobenzene [56], and mixed solvents [57]. As long as the anti-solvent satisfies the requirements of (a) dissolving the solvent, and (b) not dissolving perovskite, it could be implemented in this process. In practice, different anti-solvents yield dramatically different results depending on the precursor composition and environmental condition. Precise optimization of all the process parameters is crucial. In particular, the timing of anti-solvent application is important.

Solvent removal from the spin-coated ink proceeds at a rapid rate due to surrounding air movement while the sample is spinning. If spin coating is allowed to proceed until a steady state is reached (solvent

no longer evaporates from the film), anti-solvent application is no longer effective. For example, it is indicated that with a total spin coating time of 30 s, anti-solvent must be applied 25 s after starting the process [56]. Uniform application of anti-solvent is also critical. Partial application of anti-solvent creates boundary areas between treated and untreated films which cannot be repaired by further application of anti-solvent.

Application of anti-solvent processing to scalable processes presents several challenges. A key element of anti-solvent process is the rapid application of anti-solvent to the entire sample, in a transient state (partially complete spin-coating). Inevitably, different locations on a large-area film will dry at different rates. If the treatment needs to be timed with precision of seconds, it may mean that some locations on the film will not be ready while for others it is already too late. Furthermore, spin coating features a centrifugal driving force that rapidly distributes liquid across the substrate. In the absence of driving force, the only way to rapidly apply a solvent to a large area substrate would be by immersion or spray of large quantities of solvent. This would entail waste of large quantities of hazardous solvents, and risk over-exposure of the substrate to anti-solvent, since the solvent would not be removed rapidly as it is in spin coating.

These shortcomings may be addressed by advances in anti-solvent or precursor design. As demonstrated by Y. Yu et al. [57], adjusting the composition of anti-solvent mixture can be used to tune different aspects of perovskite crystal growth such as nucleation density and conversion rate. Tuning of precursor and solvent composition has also been demonstrated to increase anti-solvent processing window from seconds to minutes [58]. These results indicate that, while the commonly employed anti-solvent processing techniques are poorly compatible with scalable processing, further research may result in applications of anti-solvent process in large area fabrication.

5.2. Gas flow quench

Following the idea of controlling the solvent removal rate to control crystallization rate, an alternative to anti-solvent method is the gas quench method, as demonstrated by M. Zhang et al. [59] The gas quench method uses flow of gas over the surface of the sample to rapidly drive away the solvent vapors and accelerate drying of the film. While spin coating naturally induces air flow around the sample, engineered application of gas flow allows greater uniformity and more powerful application of gas.

Similar to anti-solvent coating, gas quench is applied in the last stages of spin coating when the film is already solid, but before solvent evaporation from the sample reaches a steady state. When implemented with spin coating, the gas quench method requires the application of treatment to a transient state of the film. However, it is important to note that unlike anti-solvent processing, gas quench can be applied to a fully wet film, before solid state is achieved. Because the effect of the gas flow is limited to the surface of the film, it may be applied as soon as a flat wet film is formed. In contrast, the application of liquid anti-solvent to a wet film would result in an uneven mixing of two liquids and uncontrollable morphology. Consequently, the timing constraints for application of gas quench are potentially more relaxed than for anti-solvent. Gas quench has been successfully applied to improve the morphology of a slot-die coated PbI_2 film by Hwang et al. [19]. When gas quench was applied to a fully wet film immediately after coating, improvement of dry film morphology was observed.

From the environmental perspective, gas application is more desirable than liquid application, as no liquid waste is produced. Direct ink application coating processes like slot-die or blade coating can be combined with gas quench to improve the coating morphology. Spray based processes (ultrasonic spray coating, airbrush) cannot be easily combined with gas quench, as close proximity between ink spray and gas quench would cause interference with ink application. A barrier could be designed to block the interference from quench nozzle to tspray nozzle, but such a design would have little advantage over direct application via slot-die coating.

In summary, gas flow quench has a slight advantage over anti-solvent processing for large area fabrication due to the reduced waste and relaxed timing constraints. It may be applicable to large area coating of perovskite films, for direct-application methods such as slot-die and doctor blade.

5.3. Sequential conversion

5.3.1. Liquid phase conversion

Sequential conversion was introduced soon after the significance of perovskite absorber was recognized [60]. The basic idea is, instead of mixing all the precursors in a single ink and allowing the functional film to form when the solvent evaporates, one of the precursors is coated on the substrate and then allowed to react with the other precursor to form the functional film. To implement this process, it is necessary that one of the precursors is soluble in a solvent that does not dissolve the final functional film. For the case of $MAPbI_3$ that is accomplished by coating PbI_2 and exposing it to MAI dissolved in isopropyl alcohol.

A key feature of this process is that large scale uniformity of the perovskite film is driven by the uniformity of the first precursor layer. The final thickness of perovskite is also determined by the first precursor thickness, as the reaction with the second precursor is allowed to run to saturation. A notable drawback of this process is that penetration of the second precursor can be limited, which limits the maximum achievable perovskite thickness [61].

From the standpoint of large area coating, sequential conversion has a clear advantage over one-step deposition. Separation of functional film formation from film coating allows separate optimization of the two processes. Fast processing is desired, however optimizing process condition for two unrelated processes (perovskite crystal growth and uniform coating) inevitably introduces additional costs that will outweigh the advantages of faster processing.

A possible problem of sequential conversion is achieving uniform exposure to the second precursor over a large area. Reaction with the second precursor commences immediately on contact with the liquid solution, and any partial coverage results in boundary areas that are not "healed" by additional exposure. In practice, it means that the substrate has to be immersed in the second precursor very rapidly, avoiding any partial coverage. It may be challenging and wasteful to rapidly immerse a large substrate into liquid precursor.

Sequential conversion has been implemented for doctor blade [26], slot-die [19, 22, 24] and ultrasonic spray [13, 14] coated PbI_2 films. Several groups have also demonstrated spray application of the second precursor [4-6], but it remains unclear if the problem with non-uniform application of second precursor is avoided by the spray process. Slot-die coating has also been demonstrated as means to apply MAI precursor to PbI_2-coated substrates [19, 20, 22, 24]. In this case, it is also not clear if the short exposure to MAI is sufficient to form optimized perovskite films.

5.3.2. Gas-phase / CVD conversion

An alternative method to process a sequential conversion is to apply the second precursor in gas phase. This process has been implemented in several variations, including exposure to MAI vapor [62, 63], MA gas [64], MA and HI gases [65], FA gas [66] etc.

In addition to the improved morphology and functionality of the perovskite film, the gas-phase conversion process holds several advantages for large scale production. First of all, the application of gaseous precursor avoids the problem of defects due to the partial or slow immersion into a liquid precursor (described above) because a gas cannot sustain sharp boundaries of concentration. Absence of liquid solvents eliminates the concern of solvent disposal.

Gas process also introduces an important simplification by eliminating the interaction between solvent of the second precursor (because there is no solvent in a gas process) and perovskite film. The process described in Section 5.3.1 is built on the assumption that the solvent of the second precursor does not interact with the perovskite film. This assumption seems to be good in cases of short exposure, but at longer exposures many groups reported peeling of perovskite $MAPbI_3$ films due to the over-exposure to IPA. Similar slow interactions can be expected to occur for other types of perovskite films, and it is advantageous to completely eliminate the solvent from the process.

5.3.3. Intramolecular exchange

Intramolecular exchange, another variant of the sequential conversion, aims to overcome one of the limits of sequential deposition–limited penetration of the second precursor into the solid film. The basic principle is to form a two-component precursor film, with one component being a perovskite precursor and the other, a weakly-bound inert molecule that is easily replaced by the second perovskite precursor. One implementation [67] employs PbI_2 as the perovskite precursor, and DMSO as the inactive component. This particular work employed anti-solvent processing to obtain high quality PbI_2-DMSO films, however it is conceivable that such films could also be fabricated using other methods.

Upon exposure to the second precursor solution, DMSO molecules are replaced by FAI molecules that have a greater affinity for PbI_2. The advantage of this method over simple sequential conversion, is deeper penetration of FAI into PbI_2 films and absence of volume change (and associated stress) during the conversion. Volume change is avoided because volume occupied by FAI is similar to DMSO and molecules are replaced 1 for 1.

As with basic sequential conversion, intramolecular exchange has the advantage of separation of precursor coating and perovskite crystal formation. Once the PbI_2 film is formed, the uniformity of the perovskite film is driven by the uniformity of PbI_2.

5.3.4. Textured precursor

An alternative method to address limited penetration of the second precursor during sequential conversion, is to substitute the compact film of the first precursor with a textured or porous film. Fabrication of such films has been demonstrated by incorporating additives into PbI_2 ink, that are later removed by annealing, leaving a porous precursor film [68, 69]. A high density of pores smaller than the perovskite grains in the final product allows rapid penetration of second precursor and does not introduce non-uniformity into the converted film. While the texturization of the films appears to introduce an additional annealing step into the process, the added reproducibility and improved speed of subsequent conversion are likely to be favorable for large scale fabrication.

In summary, sequential conversion is fundamentally advantageous for large scale production, due to the separation of film coating and functional crystal growth. Gas-phase or CVD conversion further enhances the scalability and reduces waste from the sequential conversion process. The shortcomings of sequential conversion, such as a limited second precursor penetration and slow conversion rate, may be addressed by the techniques such as intramolecular exchange of texturized first precursor films.

5.4. Additive assisted coating

The concept of additives can imply a very broad range of changes to precursor composition. When considering coating process design, the important additives are those that affect wet film surface tension, evaporation rate, viscosity, and/or precipitation rate. These additives generally have little effect on the active properties of the film, but strongly affect the uniformity of coating. A separate class of additives is used to tune the functional properties of the film, with little effect on coating uniformity, but it will not be discussed in this work.

Polymer additives are frequently used to adjust the viscosity of the film. Large polymer molecules allow continuous tuning of liquid viscosity by changing polymer concentration. Increased viscosity may be desirable when sharp edges to a coated film are desired. For example, a film with low viscosity, applied by slot die coating will rapidly spread beyond the width of slot-die head, but a high viscosity liquid will maintain a sharp edge. Increasing viscosity will necessarily increase the equilibration time of the wet film, so this application is most suitable for the coating technologies that inherently produce flat wet films (e.g., slot-die, blade coating).

Surfactant additives are added to reduce the surface tension of the ink, improving the wetting quality of the substrate. While many organic solvents have relatively low surface tension (30–40 dyn/cm), water has notably high surface tension (74 dyn/cm) and generally requires surfactant additives to obtain a flat wet film.

A common feature of polymer and surfactant additives is that they remain incorporated into the film after solvent evaporation is complete. For this reason, the quantity of additive must be minimized to avoid affecting the functionality.

Solvent additives are a particularly important class of additives to perovskite film coating. Solvent additives are distinct from polymer or surfactant additives in that they are eventually removed from the film by annealing. This greatly relaxes the constraints on the amount of additive that can be used, because it is not incorporated into the film.

A typical function of solvent additive is to prevent the crystallization of perovskite, or to increase the solubility of precursors. Preventing crystallization of perovskite in liquid films, allows the crystallization to be triggered at a later stage, when conditions are optimal. The general principle of operation is as follows: the additive is chosen to be soluble in perovskite precursor ink, and has a much lower vapor pressure than the main solvent. Presence of the additive should also impede the formation of perovskite crystals. When the main solvent evaporates from the wet film, a solid film is formed with the additive present (and no perovskite crystallization). Subsequently, additive evaporation is triggered by annealing and perovskite film is formed. This principle has been demonstrated for different additives in a number of works [70, 71]. The key advantage of this technique is that functional crystal formation does not take place in the wet film, and it can be triggered when conditions are optimal. Separation of coating and functional film formation is key to the development of a well-controlled process.

Increasing solubility of precursors in the ink is advantageous, because it allows to achieve higher concentrations of precursors before nucleation occurs. Higher precursor concentrations, result in higher nucleation densities and consequently smoother films. A common additive to DMF based PbI_2 precursor inks is DMSO, because it dramatically increases the solubility of PbI_2 in DMF at fractions that do not dramatically affect the evaporation rate of the mixture. For example, DMSO was used to formulate spray coating inks [14] that allow coating of thin wet films and uniform PbI_2 dry films.

Additives that increase precursor solubility and retard crystallization are equally applicable to coating of precursor films for sequential conversion. Precursors, such as PbI_2 suffer from problems similar to perovskite films. Rapid crystallization leads to dendritic crystal growth and highly non-uniform coating. Suppressing crystallization and increasing nucleation density result in smooth amorphous films that can be converted to smooth perovskite films.

The types of additives listed above illustrate only some of the aspects that need to be considered. From the stand point of large area coating, additives are applicable (and necessary) to all the coating technologies. Systematic research on additives that enhance the coating properties without damaging functional properties will be key to the eventual commercialization of perovskite-based solar cells.

6. Conclusions

In this review we have considered scalable technologies that are leading candidates for large area manufacturing of perovskite films, and their compatibility with methods that have been developed to obtain high-performing perovskite films in the laboratories. Slot-die coating is the most explored of all the technologies and has even been applied to pilot production outside of academia. Ultrasonic spray coating offers the capability to coat non-flat substrates and is also being explored by several laboratories. Airbrush or blade coating is appealing due to their simplicity, but will likely be superseded in industry by slot-die and ultrasonic spray coating due to greater capacity for process control.

Considering the pathways that have led to top performing cells via spin-coating, we find that anti-solvent processing is poorly compatible with industrial scaling up. Gas flow quench is a more scalable method for rapid solvent removal, but it may still be very challenging to achieve uniform application of gas flow over a large surface. Sequential conversion holds a distinct advantage of separating film coating and perovskite growth into two steps. Rapid single-step processing is appealing in laboratory research, but in industrial manufacturing, the far greater demands on yield and optimization favor the capability to optimize process steps individually. Gas-phase sequential conversion also holds promise for a high-yield process with minimized solvent waste. Any of the processes above will require

extensive research to reach commercial viability, and further advances may yet make processes like anti-solvent processing practical for industrial applications.

Almost inevitably, an industrial perovskite absorber fabrication process will involve additive incorporation. Adjustment of ink properties by additives is the standard pathway of all the solution coating technologies to achieving high-uniformity coatings. In many cases additives act negatively on functional properties of the film, but the advantages of greater uniformity and reproducibility outweigh the performance loss. In this review we discuss additives that affect the coating properties of ink, including surface tension, viscosity, evaporation rate, and solubility. These are an important set of the properties that need to be considered, but further research will reveal which properties are most crucial to perovskite film formation and may yet indicate that other ink properties need to be tuned as well.

Acknowledgements

References

[1] NREL Efficiency Chart, https://www.nrel.gov/pv/assets/images/efficiency-chart.png (accessed: 2017/08/01).

[2] Z. Liang, S. Zhang, X. Xu, N. Wang, J. Wang, X. Wang, Z. Bi, G. Xu, N. Yuan, J. Ding, RSC Adv., 5 (2015) 60562-60569.

[3] S. Gamliel, A. Dymshits, S. Aharon, E. Terkieltaub, L. Etgar, J. Phys. Chem. C, 119 (2015) 19722-19728.

[4] K.M. Boopathi, M. Ramesh, P. Perumal, Y.-C. Huang, C.-S. Tsao, Y.-F. Chen, C.-H. Lee, C.-W. Chu, J. Mater. Chem. A, 3 (2015) 9257-9263.

[5] Y.-S. Jung, K. Hwang, F.H. Scholes, S.E. Watkins, D.-Y. Kim, D. Vak, Sci. Rep., 6 (2016) 20357.

[6] F. Shao, L. Xu, Z. Tian, Y. Xie, Y. Wang, P. Sheng, D. Wang, F. Huang, RSC Adv., 6 (2016) 42377-42381.

[7] Z. Bi, Z. Liang, X. Xu, Z. Chai, H. Jin, D. Xu, J. Li, M. Li, G. Xu, Sol. Energy Mat. Sol. Cells, 162 (2017) 13-20.

[8] W.-C. Chang, D.-H. Lan, K.-M. Lee, X.-F. Wang, C.-L. Liu, ChemSusChem, 10 (2017) 1405-1412.

[9] A.T. Barrows, A.J. Pearson, C.K. Kwak, A.D.F. Dunbar, A.R. Buckley, D.G. Lidzey, Energy Environ. Sci., 7 (2014) 2944.

[10] S. Das, B. Yang, G. Gu, P.C. Joshi, I.N. Ivanov, C.M. Rouleau, T. Aytug, D.B. Geohegan, K. Xiao, ACS Photon., 2 (2015) 680-686.

[11] J.G. Tait, S. Manghooli, W. Qiu, L. Rakocevic, L. Kootstra, M. Jaysankar, C.A. Masse de la Huerta, U.W. Paetzold, R. Gehlhaar, D. Cheyns, P. Heremans, J. Poortmans, J. Mater. Chem. A, 4 (2016) 3792-3797.

[12] D.K. Mohamad, J. Griffin, C. Bracher, A.T. Barrows, D.G. Lidzey, Adv. Energy Mater., 6 (2016) 1600994.

[13] H. Huang, J. Shi, L. Zhu, D. Li, Y. Luo, Q. Meng, Nano Energy, 27 (2016) 352-358.

[14] M. Remeika, S.R. Raga, S. Zhang, Y.B. Qi, J. Mater. Chem. A, 5 (2017) 5709-5718.

[15] S.-G. Li, K.-J. Jiang, M.-J. Su, X.-P. Cui, J.-H. Huang, Q.-Q. Zhang, X.-Q. Zhou, L.-M. Yang, Y.-L. Song, J. Mater. Chem. A, 3 (2015) 9092-9097.

[16] Z. Wei, H. Chen, K. Yan, S. Yang, Angewandte Chemie, 126 (2014) 13455-13459.

[17] M. Bag, Z. Jiang, L.A. Renna, S.P. Jeong, V.M. Rotello, D. Venkataraman, Mater. Lett., 164 (2016) 472-475.

[18] Z. Gu, L. Zuo, T.T. Larsen-Olsen, T. Ye, G. Wu, F.C. Krebs, H. Chen, J. Mater. Chem. A, 3 (2015) 24254-24260.

[19] K. Hwang, Y.-S. Jung, Y.-J. Heo, F.H. Scholes, S.E. Watkins, J. Subbiah, D.J. Jones, D.-Y. Kim, D. Vak, Adv. Mater., 27 (2015) 1241-1247.

[20] T.M. Schmidt, T.T. Larsen-Olsen, J.E. Carlé, D. Angmo, F.C. Krebs, Adv. Energy Mater., 5 (2015) 1500569.

[21] G. Cotella, J. Baker, D. Worsley, F. De Rossi, C. Pleydell-Pearce, M. Carnie, T. Watson, Sol. Energy Mater. Sol. Cells, 159 (2017) 362-369.

[22] T. Qin, W. Huang, J.-E. Kim, D. Vak, C. Forsyth, C.R. McNeill, Y.-B. Cheng, Nano Energy, 31 (2017) 210-217.

[23] J. Ciro, M.A. Mejía-Escobar, F. Jaramillo, Sol. Energy, 150 (2017) 570-576.

[24] D. Vak, K. Hwang, A. Faulks, Y.-S. Jung, N. Clark, D.-Y. Kim, G.J. Wilson, S.E. Watkins, Adv. Energy Mater., 5 (2015) 1401539.

[25] A.T. Mallajosyula, K. Fernando, S. Bhatt, A. Singh, B.W. Alphenaar, J.-C. Blancon, W. Nie, G. Gupta, A.D. Mohite, Appl. Mater. Today, 3 (2016) 96-102.

[26] S. Razza, F. Di Giacomo, F. Matteocci, L. Cinà, A.L. Palma, S. Casaluci, P. Cameron, A. D'Epifanio, S. Licoccia, A. Reale, T.M. Brown, A. Di Carlo, J. Power Sources, 277 (2015) 286-291.

[27] X. Xu, Z. Liu, Z. Zuo, M. Zhang, Z. Zhao, Y. Shen, H. Zhou, Q. Chen, Y. Yang, M. Wang, Nano Lett., 15 (2015) 2402-2408.

[28] A. Mei, X. Li, L. Liu, Z. Ku, T. Liu, Y. Rong, M. Xu, M. Hu, J. Chen, Y. Yang, M. Gratzel, H. Han, Science, 345 (2014) 295-298.

[29] K. Cao, Z. Zuo, J. Cui, Y. Shen, T. Moehl, S.M. Zakeeruddin, M. Grätzel, M. Wang, Nano Energy, 17 (2015) 171-179.

[30] S.C. Hong, G. Lee, K. Ha, J. Yoon, N. Ahn, W. Cho, M. Park, M. Choi, ACS Appl. Mater. Interfaces, 9 (2017) 7879-7884.

[31] R.D. Deegan, O. Bakajin, T.F. Dupont, G. Huber, S.R. Nagel, T.A. Witten, Nature, 389 (1997) 827-829.

[32] H. Hu, R.G. Larson, J. Phys. Chem B, 110 (2006) 7090-7094.

[33] S. Bose, S.S. Keller, T.S. Alstrøm, A. Boisen, K. Almdal, Langmuir, 29 (2013) 6911-6919.

[34] C. Li, Q. Guo, W. Qiao, Q. Chen, S. Ma, X. Pan, F. Wang, J. Yao, C. Zhang, M. Xiao, S. Dai, Z.a. Tan, Org. Electron., 33 (2016) 194-200.

[35] L. Zhao, D. Luo, J. Wu, Q. Hu, W. Zhang, K. Chen, T. Liu, Y. Liu, Y. Zhang, F. Liu, T.P. Russell, H.J. Snaith, R. Zhu, Q. Gong, Adv. Funct. Mater., 26 (2016) 3508-3514.

[36] B.A. Nejand, S. Gharibzadeh, V. Ahmadi, H.R. Shahverdi, Sci Rep., 6 (2016).

[37] H. Chen, F. Ye, W. Tang, J. He, M. Yin, Y. Wang, F. Xie, E. Bi, X. Yang, M. Grätzel, L. Han, Nature, (2017) DOI: 10.1038/nature23877.

[38] J. Ciro, R. Betancur, S. Mesa, F. Jaramillo, Sol. Energy Mater. Sol. Cells, 163 (2017) 38-42.

[39] H.-S. Ko, J.-W. Lee, N.-G. Park, J. Mater. Chem. A, 3 (2015) 8808-8815.

[40] C.K. Miskin, W.-C. Yang, C.J. Hages, N.J. Carter, C.S. Joglekar, E.A. Stach, R. Agrawal, Prog. Photovoltaics Res. Appl., 23 (2015) 654-659.

[41] W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, D.B. Mitzi, Adv. Energy Mater., 4 (2014) 1301465.

[42] R. Søndergaard, M. Hösel, D. Angmo, T.T. Larsen-Olsen, F.C. Krebs, Mater. Today, 15 (2012) 36-49.

[43] Contact cleaning for defect reduction in 21st century PCB manufacture, Contact cleaning for defect reduction in 21st century PCB manufacture.pdf (accessed: 2017/09/01).

[44] J. Vig, J. LeBus, IEEE Trans. Parts Hybrids Packag., 12 (1976) 365-370.

[45] J.H. Heo, M.H. Lee, M.H. Jang, S.H. Im, J. Mater. Chem. A, 4 (2016) 17636-17642.

[46] Y. Deng, E. Peng, Y. Shao, Z. Xiao, Q. Dong, J. Huang, Energy Environ. Sci., 8 (2015) 1544-1550.

[47] L. Wengeler, M. Schmitt, K. Peters, P. Scharfer, W. Schabel, Chem. Eng. Process.Process Intensif., 68 (2013) 38-44.

[48] M. Osborne, Solliance partners create perovskite mini-module with 10% conversion efficiency, https://www.pv-tech.org/news/solliance-partners-create-perovskite-mini-module-with-10-conversion-efficie (accessed: 2017/08/01).

[49] S. Colella, M. Mazzeo, G. Melcarne, S. Carallo, G. Ciccarella, G. Gigli, Appl. Phys. Lett., 102 (2013) 203307.

[50] B. Abdollahi Nejand, S. Gharibzadeh, V. Ahmadi, H.R. Shahverdi, J. Phys. Chem. C, 120 (2016) 2520-2528.

[51] J. Xiao, Y. Yang, X. Xu, J. Shi, L. Zhu, S. Lv, H. Wu, Y. Luo, D. Li, Q. Meng, J. Mater. Chem. A, 3 (2015) 5289-5293.

[52] J. Troughton, M.J. Carnie, M.L. Davies, C. Charbonneau, E.H. Jewell, D.A. Worsley, T.M. Watson, J. Mater. Chem. A, 4 (2016) 3471-3476.

[53] J. Troughton, C. Charbonneau, M.J. Carnie, M.L. Davies, D.A. Worsley, T.M. Watson, J. Mater. Chem. A, 3 (2015) 9123-9127.

[54] N.J. Jeon, J.H. Noh, Y.C. Kim, W.S. Yang, S. Ryu, S.I. Seok, Nat. Mater., 13 (2014) 897-903.

[55] D.-Y. Son, J.-W. Lee, Y.J. Choi, I.-H. Jang, S. Lee, P.J. Yoo, H. Shin, N. Ahn, M. Choi, D. Kim, N.-G. Park, Nat. Energy, 1 (2016) 16081.

[56] M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M.K. Nazeeruddin, S.M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, M. Grätzel, Energy Environ. Sci., 9 (2016) 1989-1997.

[57] Y. Yu, S. Yang, L. Lei, Q. Cao, J. Shao, S. Zhang, Y. Liu, ACS Appl. Mater. Interfaces, 9 (2017) 3667-3676.

[58] M. Yang, Z. Li, M.O. Reese, O.G. Reid, D.H. Kim, S. Siol, T.R. Klein, Y. Yan, J.J. Berry, M.F.A.M. van Hest, K. Zhu, Nat. Energy, 2 (2017) 17038.

[59] M. Zhang, J.S. Yun, Q. Ma, J. Zheng, C.F.J. Lau, X. Deng, J. Kim, D. Kim, J. Seidel, M.A. Green, S. Huang, A.W.Y. Ho-Baillie, ACS Energy Lett., 2 (2017) 438-444.

[60] J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M.K. Nazeeruddin, M. Grätzel, Nature, 499 (2013) 316-319.

[61] S.-Y. Kim, H.J. Jo, S.-J. Sung, D.-H. Kim, APL Mater., 4 (2016) 100901.

[62] Q. Chen, H. Zhou, Z. Hong, S. Luo, H.-S. Duan, H.-H. Wang, Y. Liu, G. Li, Y. Yang, JACS, 136 (2014) 622-625.

[63] M.R. Leyden, L.K. Ono, S.R. Raga, Y. Kato, S. Wang, Y.B. Qi, J. Mater. Chem. A, 2 (2014) 18742-18745.

[64] S. Pang, Y. Zhou, Z. Wang, M. Yang, A.R. Krause, Z. Zhou, K. Zhu, N.P. Padture, G. Cui, JACS, 138 (2016) 750-753.

[65] S.R. Raga, L.K. Ono, Y.B. Qi, J. Mater. Chem. A, 4 (2016) 2494-2500.

[66] Y. Zhou, M. Yang, S. Pang, K. Zhu, N.P. Padture, JACS, 138 (2016) 5535-5538.

[67] W.S. Yang, J.H. Noh, N.J. Jeon, Y.C. Kim, S. Ryu, J. Seo, S.I. Seok, Science, 348 (2015) 1234-1237.

[68] H. Zhang, J. Mao, H. He, D. Zhang, H.L. Zhu, F. Xie, K.S. Wong, M. Grätzel, W.C.H. Choy, Adv. Energy Mater., 5 (2015) 1501354.

[69] Y. Zhao, K. Zhu, J. Mater. Chem. A, 3 (2015) 9086-9091.

[70] P.-W. Liang, C.-Y. Liao, C.-C. Chueh, F. Zuo, S.T. Williams, X.-K. Xin, J. Lin, A.K.Y. Jen, Adv. Mater., 26 (2014) 3748-3754.

[71] Y.-J. Jeon, S. Lee, R. Kang, J.-E. Kim, J.-S. Yeo, S.-H. Lee, S.-S. Kim, J.-M. Yun, D.-Y. Kim, Sci. Rep., 4 (2014).

TOC

Issues specific to large area coating need to be considered when transiting from laboratory fabrication to low-cost, high-throughput production of perovskite solar cells.

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