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REVIEW ARTICLE

Parameters that control and influence the organo-metal halide perovskite crystallization and morphology

Bat-El COHEN, Lioz ETGAR (✉)

Institute of Chemistry, The Hebrew University of Jerusalem, Casali Center for Applied Chemistry, Jerusalem 91904, Israel

Abstract This review discusses various parameters that influence and control the organo-metal halide perovskite crystallization process. The effect of the perovskite morphology on the photovoltaic performance is a critical factor. Moreover, it has a dramatic effect on the stability of the perovskite, which has significant importance for later use of the organo-metal perovskite in assorted applications. In this review, we brought together several research investigations that describe the main parameters that significantly influence perovskite crystallization, for example, the annealing process, the precursor solvent, anti-solvent treatment, and additives to the iteite solutions.

Keywords hybrid perovskite, morphology, crystallization, perovskite surface

1 Introduction

The recent entrance of organo-metal perovskite, a new, attractive material in the photovoltaic (PV) field, constitutes a breakthrough. Organo-metal perovskite has nearly all the required properties (such as simple preparation, absorbance through the entire visible range, long diffusion length) to become the next PV material. The significant organo-metal perovskite properties can be used in different solar cell architecture: planar, mesoporous, hole conductor free, and inverted configurations. However, due to the rapid development of organo-metal halide perovskite in solar cell research, there are still open issues regarding its operating mechanism, hysteresis effect, and stability. Organo-metal halide perovskite is made by a solution processed deposition technique, its crystallization process has a major influence over PV performance and stability. This review discusses several parameters influencing the perovskite morphology due to different crystallization mechanisms. Control over morphology is a key parameter to understand this attractive material; morphology control will be an additional step throughout its commercialization process. The review is divided to four parts, presenting various parameters influencing perovskite crystallization and morphology. Section 2 discusses the effect of the annealing process; Section 3 describes the precursor solvent, presenting the possible solvents being used in the deposition process; Section 4 presents the anti-solvent treatment and its effect on the cell properties; and Section 5 discusses additives that can be added to the perovskite solution before deposition.

2 Annealing

One of the main parameters controlling perovskite morphology is the annealing process of the perovskite film. The perovskite annealing is performed at various temperatures; the maximum annealing temperature for $CH_3NH_3PbI_3$ perovskite is 200°C [1]. Several reports can be found on the optimization of the perovskite annealing process on the planar [2], mesoporous [3], hole transport material (HTM) free [4] and inverted cell [5 – 7] configurations. Zhu et al. [8] investigated the effect of the ramp temperature in the annealing process on perovskite morphology in one-step deposition. Planar films of $CH_3NH_3PbI_{3-x}Cl_x$ perovskite were fabricated by spin coating and then annealed in two different ways: 1) six individual steps to 95°C or 2) direct annealing to 95°C. The six-step annealing process showed darker brown color than the direct annealing process. No structural change was observed between the samples; however, the UV-vis spectroscopy showed different absorption curves and intensity. The UV-vis intensity of the multi-step annealing was stronger than direct annealing. The scanning electron microscope (SEM) images showed that the multi-step annealing process is more uniform than the direct annealing, providing pinhole free high surface coverage. The results indicate that slow annealing encouraged slow

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E-mail: lioz.etgar@mail.huji.ac.il

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crystallization, allowing the perovskite grains to grow uniformly, while rapid crystallization led to large crystals and to pinholes in the film. PV performance of the multi-step annealed perovskite cell was remarkably improved and narrow efficiency distribution with small deviation was obtained. Better stability was observed for the films made by the slow annealing process (Fig. 1).

Another way to influence the perovskite morphology during the annealing process is by adding additives to the solvent leading to either slow crystallization or fast crystallization depending on the additive [9].

In the one-step deposition process, the perovskite crystals are formed during spin coating while the solvent is evaporating. To slow down solvent evaporation, an appropriate additive could be added to the precursor solution. A possible additive might be a second solvent, which must comply with three rules: 1) the vapor pressure of the additional solvent must be lower than the vapor pressure of the main solvent; 2) the boiling point of the additional solvent must be higher than the boiling point of the main solvent; 3) the precursors should be soluble in both of the solvents. Based on these rules, three different solvents (in addition to dimethylforamide (DMF)) have been chosen: dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), and N-cyclohexyl-2-pyrrolidone (CHP). In the case of DMF, the perovskite film showed pinholes due to the fast DMF evaporation; in all cases where two solvents were used, the surface coverage improved and the occurrence of pinholes was reduced. The combination of DMF and CHP exhibits a uniform perovskite film with 100% coverage. NMP as an additive for the precursor solution was also investigated by Yang and coworkers for $CH_3NH_3PbI_3$ perovskite films [10], the NMP imply slow annealing. In addition, there are several studies discussing the contribution of low temperature annealing on the perovskite surface and morphology [11,12].

One more way to influence the perovskite morphology is through environmental conditions. Melot et al. investigated the effect of low humidity on the perovskite crystallization [13]. Yang et al. demonstrated improvement of the morphology when the annealing for $CH_3NH_3PbI_{3-x}Cl_x$ perovskite planar cells occurred in a controllable humidity environment of 35% humidity [14]. The perovskite precursors were annealed in three different environments: dry nitrogen, controllable humidity, and dry oxygen. SEM showed morphology improvement (Fig. 2) for the ambient air (controllable humidity) when pinholes and grain boundaries were reduced and the crystals size was increased. The authors reported that the grain size was increased due to moisture accumulation at the grain boundaries, which merging together adjacent grains, resulting in pinhole free morphology. The X-ray diffraction (XRD) results were correlated and supported the observation of improved crystallization. Although the specific mechanism is still unclear, it seems that while exposing perovskite to humidity during crystallization, the diffusion of the precursor ions was enhanced due to the CH_3NH_3I hydroscopic character. PV performance improved as well; a major improvement appears in open circuit voltage (V_{OC}), which increased from 0.86 to 0.99 V for cells annealed under controlled humidity. Photoluminescence (PL) measurements indicated that non-radiative decay is significantly suppressed by the perovskite annealed in a humid environment. Time-resolved PL showed triple PL lifetime for the films annealed in a humid environment, which might be due to reduced defects. Figure 2 shows top-view SEM images of the perovskite films after annealing under various environmental conditions.

3 Precursor solvent

The selection of the precursor solvent is a critical parameter affecting the perovskite morphology, in particular, in the one-step deposition technique and in the planar configuration. The main requirement is that the solvent must be polar in order to dissolve the precursors, while the physical properties, such as boiling point and vapor pressure, must to be considered regarding the

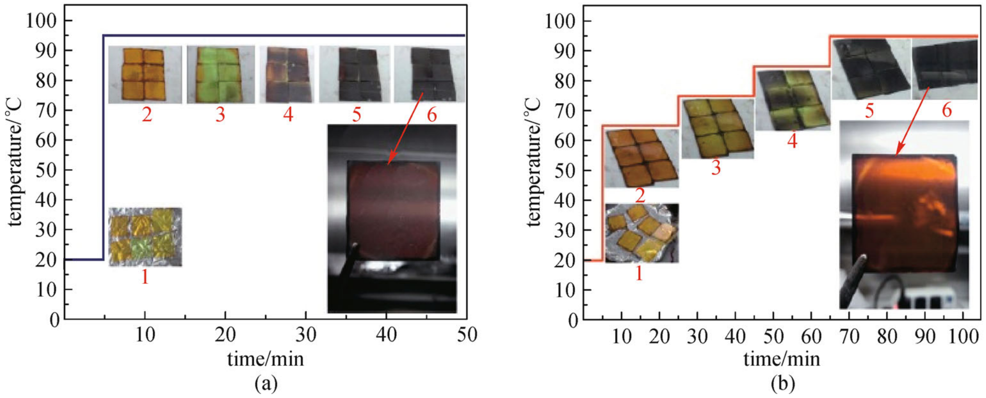

Fig. 1 (a) One-step and multi-step methods; (b) insets are photographs of perovskite films. Taken with permission from Ref. [8]

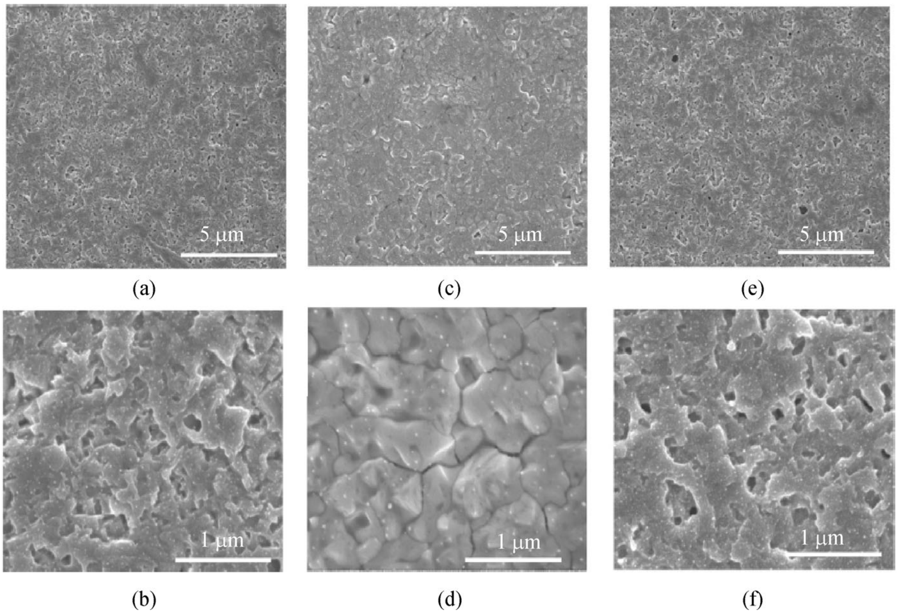

Fig. 2 SEM images of the perovskite film precursor. The films were annealed under various conditions. (a) and (b) under nitrogen; (c) and (d) in ambient air; (e) and (f) in an oxygen environment. The small white dots in the SEM images are evaporated gold particles on the perovskite film surface to reduce charge effect during SEM measurements. Taken with permission from Ref. [14]

preferred crystallization mechanism, that is, rapid or slow. γ-butyrolactone (GBL), DMSO, NMP, and DMF are the common solvents in the precursor solution, and mixing these solvents is a possibility to optimize the crystallization [15–18].

Wang et al. investigated the effect of mixing halide using DMF and DMSO as the precursor solvents in the two-step deposition sequence [19]. When considering the interactions of the solvents with PbI_2^+, DMSO coordinates better with PbI_2. Compared to DMF, DMSO has a strong interaction with PbI_2^+ that could retard the crystal growth of PbI_2 during the formation of the $PbI_2(DMSO)_x$ complex. In this study, a series of DMSO/DMF volume ratios were studied when the $PbI_2(DMSO)_x$ $(0 \leqslant x \leqslant 1.86)$ complex was formed. The size of the $PbI_2(DMSO)_x$ complex increased linearly with the addition of the DMSO, while the $PbI_2(DMSO)_x$ complex reaches its maximum size at 242 nm and then starts to decrease with additional DMSO. It was observed that adding DMSO to the DMF solution assisted in controlling the perovskite crystallization, resulting in enhanced PV performance. The morphology appears to be correlated with the results since pure DMF showed low surface coverage, whereas the coverage was improved by adding DMSO (this increased the size of the $PbI_2(DMSO)_x$ complex), until a certain point at which the surface coverage showed pinholes. At this point, the $PbI_2(DMSO)_x$ complex started to decrease in size. Figure 3 shows a schematic illustration of the crystal growth process with the addition of DMSO.

The effect of the precursor solvent was also investigated in a one-step deposition process. Kanatzidis et al. studied lead-free perovskite $CH_3NH_3SnI_3$ crystallization using GBL, DMSO, NMP, and DMF [20] in the precursor solution. The crystallization of $CH_3NH_3SnI_3$ is faster than the crystallization of $CH_3NH_3PbI_3$ perovskite due to the greater Lewis acidity of Sn^{2+} compared to Pb^{2+}. Therefore, it is necessary to control the solvent evaporation in order to form stepwise crystallization. The difference in the crystallization process was observed when using the various solvents: (DMF > DMSO > NMP from fast to slow crystallization). SEM images show that full surface coverage and homogenous film were observed when DMSO was used as a solvent. DMSO has high coordinated affinity and a high boiling point compared with DMF. The DMSO effectively slowed the perovskite crystallization when an intermediate solvated phase formed, which can be completely removed during annealing. The intermediate phase mechanism of the DMSO is different for $CH_3NH_3PbI_3$ than for $CH_3NH_3SnI_3$. For $CH_3NH_3PbI_3$, the DMSO acts as a hydrogen bond acceptor while in the case of $CH_3NH_3SnI_3$, the DMSO directly coordinates to the Sn ion in SnI_2*3DMSO configuration, leaving the $CH_3NH_3^+$ cation to dissolve in the solvent. This mechanism implies that perovskite formation takes place on the substrate and can be controlled by the solvent evaporation rate.

Yuan and coworkers presented a new solvent for the perovskite precursor for use in the one-step deposition process leading to a smooth, dense perovskite layer [21]. The idea was to achieve rapid crystallization of the perovskite film. The solvent used for this purpose was dimethylacetamide (DMAC), forming crystallization dur-

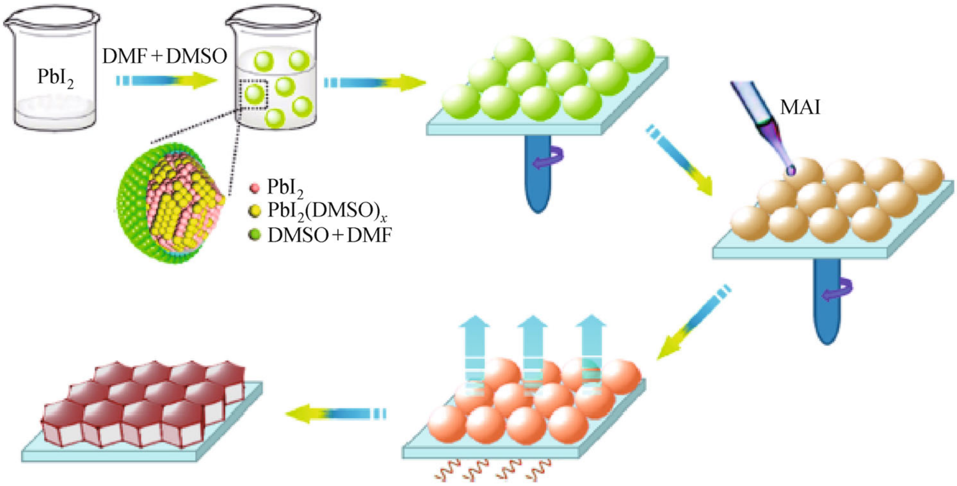

Fig. 3 Schematic view of the crystal growth process of perovskite thin film via molecular self-assembly approach in the presence of DMSO. Taken with permission from Ref. [19]

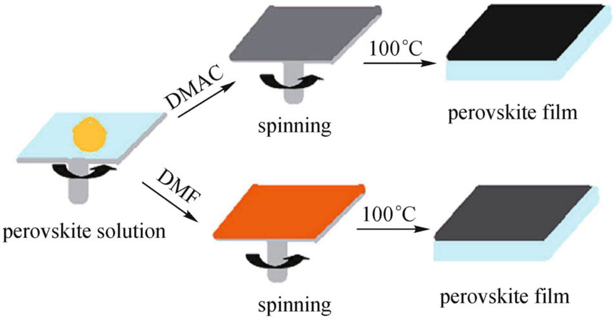

Fig. 4 Schematic illustration of spin coating process for preparing perovskite films based on a DMAC solution of $CH_3NH_3PbI_3$ (upper); based on a DMF solution of $CH_3NH_3PbI_3$ (lower). Taken with permission from Ref. [21]

ing spin coating (Fig. 4). In contrast to using DMF as the precursor solvent, the film color did not change during the spin coating process. Theoretical calculations showed that the interactions are different between PbI_2, CH_3NH_3I (MAI) and DMAC/DMF solvents. The bonding energy between PbI_2-DMF is larger than for PbI_2-DMAC. In the case of MAI, it seems that the interaction between MAI-DMAC is stronger than the interaction between MAI-DMF. The authors report that the DMAC based deposition allowed better control of the grain crystallization leading to better perovskite morphology. In addition, the authors find that the DMAC based films have better stability, better visible optical absorption, and improved carrier diffusion length.

4 Anti-solvent treatment

In 2014, Seok et al. were the first to report the solvent engineering process for perovskite films by using a mixture of GBL and DMSO as the precursor solvent, following by dropping toluene as an anti-solvent during the spin coating of the precursors (anti-solvent means a solvent in which the perovskite is not soluble) [16]. This report was a breakthrough for improving perovskite solar cell efficiency and for controlling the morphology. $CH_3NH_3Pb(I_{1-x}Br_x)_3$ perovskite compositions were used in this study, in which the anti-solvent treatment seems to remove the DMSO residues while forming an intermediate phase of MAI-PbI_2-DMSO resulting in smooth, uniform perovskite film with low surface roughness. Following the toluene treatment, the perovskite morphology exhibits dense grains with uniform grain size distribution and 100% surface coverage. Figure 5 describes the anti-solvent treatment.

Following work of Seok et al., there have been several publications using anti-solvent treatment on different structures, such as mesoporous TiO_2/perovskite [22], PEDOT:PSS/perovskite/PCBM [23,24] and planar perovskite cells [25], in the perovskite solar cells.

Priya et al. investigated the impact of different anti-solvents and annealing temperatures on $CH_3NH_3PbBr_3$ films [26]. Three kinds of anti-solvents were chosen according to their polarity: dichloromethane (DCM), chlorobenzene (CB) and toluene (TL). In terms of non-

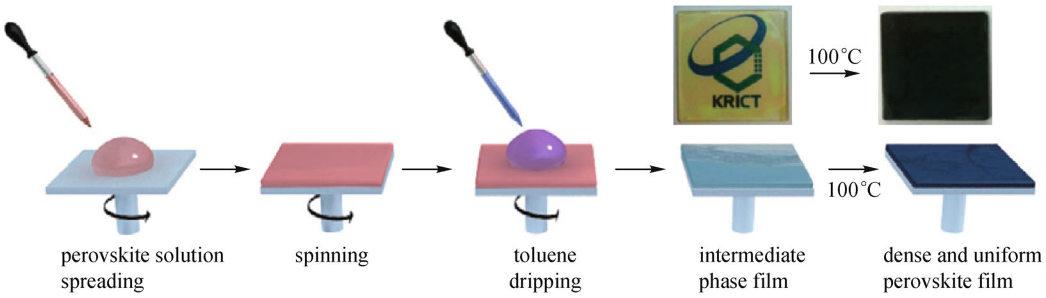

Fig. 5 Scheme of solvent engineering process. Taken with permission from Ref. [16]

polar solvents, TL is more non-polar followed by CB and DCM. The anti-solvent acts as a driving force for the crystallization as it reduces Gibbs energy. In this regard, TL has a larger driving force compared with the other anti-solvents. The toluene treated film shows a smooth, homogenous, dense perovskite layer. The CB and DCM films show less homogenous and pinhole free perovskite films, consistent with their polarity. The non-treated film shows low coverage and a non-uniform perovskite layer. The good crystallinity and the homogenous pinhole free perovskite layer had a remarkable effect on the PV performance, increasing from 3.15% efficiency for the untreated cell to 7.75% efficiency for the toluene treated cell, which showed the best results for anti-solvent treated cells.

In addition to the effect of the anti-solvent on the morphology, a recent report revealed that the anti-solvent treatment also affected the electronic properties of the perovskite [27]. In this work, a HTM free perovskite based solar cell was fabricated using toluene anti-solvent treatment. As reported previously, the toluene treatment improved the perovskite film coverage and roughness, achieving 11.2% efficiency. In addition to the morphology improvement, conductive atomic force microscopy (cAFM) demonstrated the increase in the conductivity of the perovskite film following the toluene treatment, while *I-V* measurement on a single perovskite grain shows negligible hysteresis after the toluene treatment. It was suggested that the anti-solvent treatment removes residues of halides and methylammonium ions from the surface, creating a net positive charge on the Pb atoms, resulting in an enhanced conductive perovskite surface.

5 Additives

Additives are one more factor influencing the perovskite morphology. They can be added to the precursor solution. There are various additives mentioned in the literature for different perovskites. As reported by Han et al., one

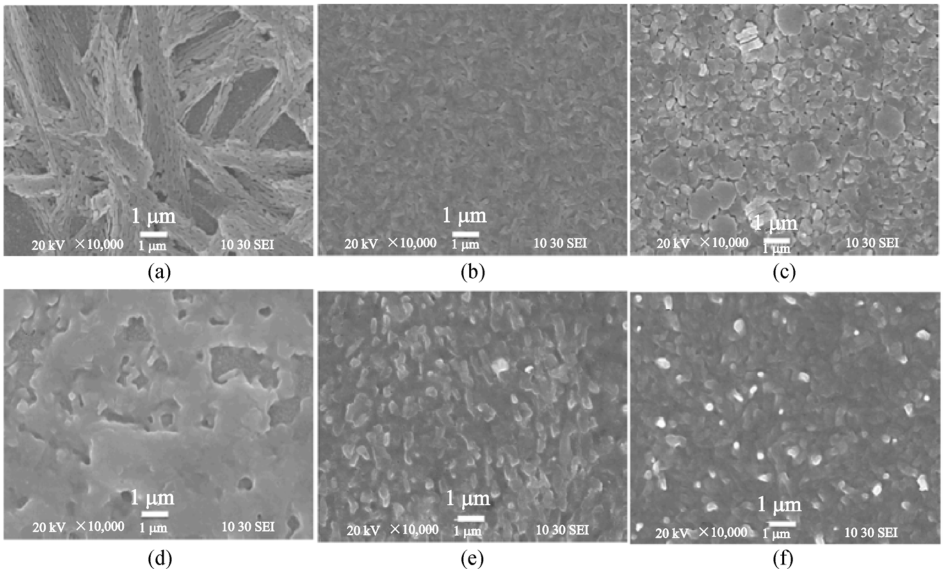

Fig. 6 Topographical SEM images (a–c) pristine PbI_2 with HI and PbI_2 with HCl on the TiO_2 dense layer coated FTO, respectively. (d–f) $CH_3NH_3PbI_3$, $CH_3NH_3PbI_3$ + HI, and $CH_3NH_3PbI_3$ + HCl, respectively, after sequentially reacting with CH_3NH_3I. Taken with permission from Ref. [30]

additive is the use of acids in the one-step solution for 5-ammoniumvaleric acid (5-AVA) iodide and for $CH_3NH_3PbI_3$ perovskite [28]. Snaith et al. have also reported using hydroiodic acid (HI) as an additive for the formamidinium lead trihalide perovskite [29]. Leung et al. used the two-step deposition sequence for perovskite deposition, when halogen acids were added for the PbI_2 precursor solution [30]. The effect of HI and hydrochloric acid (HCl) on PbI_2 crystallization, perovskite morphology, device performance, and stabilization was studied. The addition of the halogen acids into the PbI_2 precursor solution promotes homogeneous nucleation and crystal growth due to the change in the crystalline PbI_2 morphology. When adding HI or HCl, the morphology of PbI_2 transforms from rod-shaped crystals into hexagonal-plate crystals. The plates morphology of PbI_2 creates full coverage of the TiO_2 dense layer in the planar structure, which is followed by full coverage of the perovskite. The use of additives, in particular, the addition of HCl, improved the solar cell performance and stability. Figure 6 shows the film morphology after adding the acids.

One more possibility is the use of HI as a new precursor compound of $HPbI_x$. [31] $HPbI_x$ precursor is formed through the reaction of PbI_2 and HI in DMF. This precursor was used together with formamidine iodide (FAI) in DMF for a one-step perovskite solution. The perovskite formed from this precursor showed a pure crystalline phase with orientation preference in the (110) direction. The perovskite was formed by a slow crystallization process which involved the exchange of H^+ and FA^+ ions in the PbI_6 octahedral framework, as well as elimination of water in the precursor solution state. The $HPbI_x$ precursor yields highly uniform perovskite film with full coverage of the TiO_2, leading to top efficiency of 17.5% for planar $FAPbI_3$ perovskite solar cells. Figure 7 shows the configurations of PbI_2, $HPbI_3$ and $FAPbI_3$ and the solubility of PbI_2 and $HPbI_3$ in DMF.

Grätzel and Han et al. reported on the use of phosphonic acid ammonium as an additive to the one-step solution to create cross linking between neighbor perovskite grains [32]. In this work, alkylphosphonic acid ω-ammonium was added to the precursor solution. The alkylphosphonic acid ω-ammonium has biofunctional groups, which form a hydrogen bond between the perovskite halide anions and the phosphonic acid groups. In addition, biofunctional group form the ammonium species to fit the periphery of the octahedral structure. The unique chemical mechanism results in a smooth perovskite layer and increased loading of perovskite into the mesoporous TiO_2, improving and increasing light harvesting and charge carrier percolation. The outcome of this cross-linked morphology is improved cell stability. Long-term stability under a series of factors such as humidity, light soaking, and heat treatment was studied, revealing high stability for the alkylphosphonic acid ω-ammonium based cell. Additional additives were investigated [33–36], with the chloride additive being widely reported [37–39]. An interesting and unique additive is 4-*tert*–butylpyridine (TBP) which was added to the PbI_2 precursor solution in the two-step deposition sequence [40]. TBP is a nitrogen donor ligand. When it is mixed with the PbI_2 precursor solution, it forms $PbI_2 \cdot x$ TBP complex after volatilization of the DMF. At an annealing temperature of 70°C, the PbI_2 complex is formed with small pores, which can be controlled using different concentrations of TBP. This crystalline PbI_2 affects the penetration of the MAI molecules and could decrease the reaction time with the MAI. A high concentration of MAI results in a smooth, continuous perovskite thin film without PbI_2 residues.

The film with the TBP-PbI_2 solution showed a dramatic

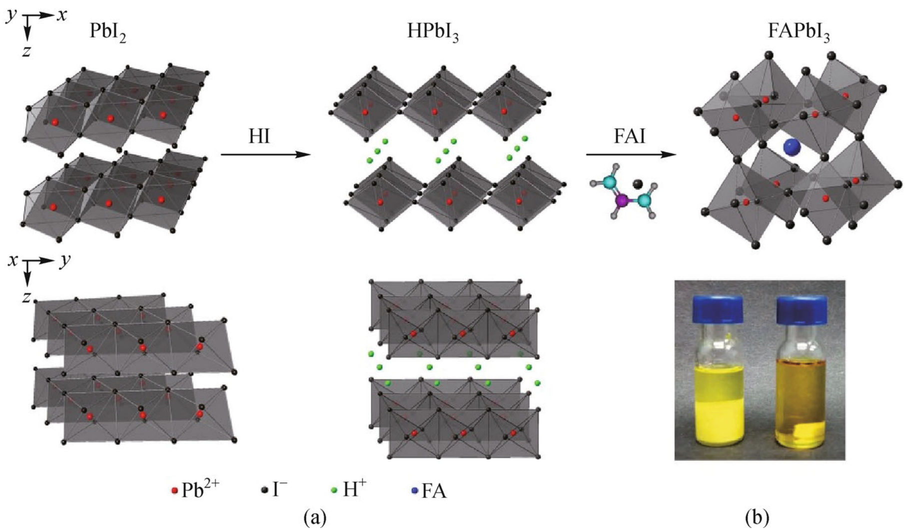

Fig. 7 (a) Schematic illustration of the configurations of PbI_2, $HPbI_3$ and $FAPbI_3$; (b) solubility comparisons of PbI_2 (left) and $HPbI_3$ (right) in DMF. Both solutions have a concentration of 2 mol/L and have been stirred for 24 h. Taken with permission from Ref. [31]

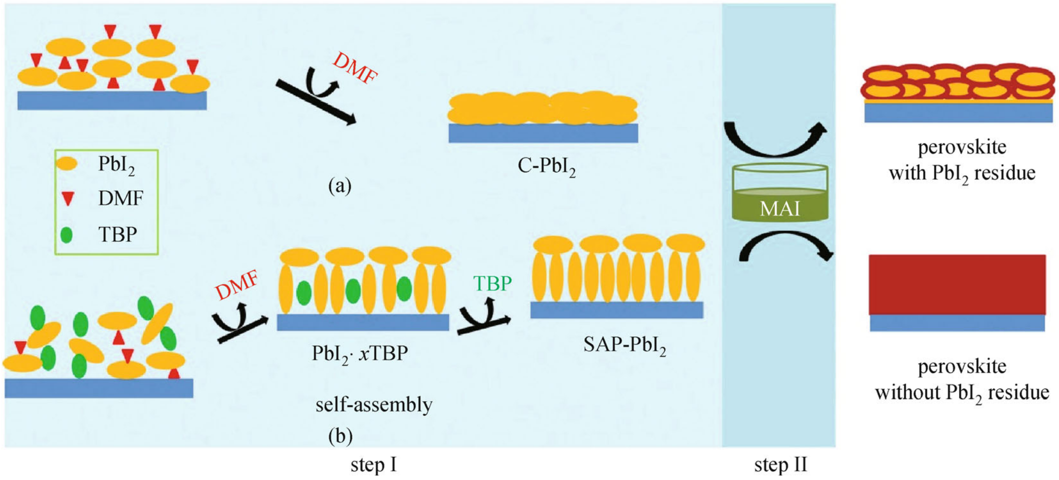

Fig. 8 Schematic of the processes of fabricating PbI$_2$ and perovskite films: (a) C-PbI$_2$ and (b) SAP-PbI$_2$. Taken with permission from Ref. [40]

improvement in the PV performance and in the long-term stability. An impressive performance of 16% efficiency was achieved for this planar solar cell structure. Figure 8 is a schematic showing the processes of the fabrication for two different PbI$_2$ precursors.

6 Summary and outlook

This review presented parameters that control and influence perovskite morphology. The effect of the annealing process was discussed in terms of the influence of multi-step annealing and of direct annealing on the observed results. It was explained that the precursor solvent affects the crystallization process, and an anti-solvent treatment after the perovskite deposition has also a major effect on PV performance. Finally, a discussion of several additives that could be added to the precursor solution, resulting in different crystallization rates and different morphologies, was presented. In summary, perovskite crystallization and morphology have a major effect on the PV performance and stability, underlining the importance of understanding the parameters discussed in this review.

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Bat-El Cohen is an M.Sc. student at Dr. Lioz Etgar's laboratory from the Institute of Chemistry at the Hebrew University of Jerusalem, Israel. Bat-El's research focuses on the investigation of hole conductor free perovskite based solar cells. Bat-El received her B.Sc. degree in chemistry from the Hebrew University of Jerusalem.

Lioz Etgar obtained his Ph.D. degree (2009) at the Technion-Israel Institute of Technology and was post-doc with Prof. Michael Grätzel (2009 – 2012) at EPFL, Switzerland. During his post-doc, he received a Marie Curie Fellowship, and won the Wolf Prize for young scientists. Since 2012, he is a senior lecturer in the Institute of Chemistry at the Hebrew University. Etgar's research group is focusing on the development of innovative solar cells. He is seeking for new excitonic solar cells structures/architectures while design and control the inorganic sensitizer structure and properties in order to improve the PV parameters. Dr. Etgar was awarded the Krill Prize of the Wolf Foundation for excellent young researchers.