Highly crystalline MAPbI$_3$ perovskite grain formation by irreversible poor-solvent diffusion aggregation, for efficient solar cell fabrication

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**ABSTRACT**

Energy efficient synthesis providing high quality crystalline thin films are highly desired in many applications. Here we devise a non-toxic solvent approach for production of highly crystalline MAPbI$_3$ perovskite by exploiting diffusion aggregation processes. Isopropanol solution based methylammonium lead triiodide (MAPbI$_3$) is used in this context, where the crystal growth initiation starts in an unstable suspension far from equilibrium and the subsequent crystallization is driven by the solubility parameters. The crystal formation is monitored by scanning transmission electron microscope (STEM), observing small crystallization centers growing as time evolves to large grains with high crystal purity. Energy dispersive X-ray spectroscopy (EDS) in STEM mode revealed a Pb rich core-shell structure in newly formed grains. Nano-beam Electron Diffraction (NBED) scan defined PbI$_2$ crystallites in the Pb rich shell with a single crystal MAPbI$_3$ core in newly formed grains. After a week stirring, the same aggregated suspension exhibited grains with only single crystal MAPbI$_3$ structure. The NBED analysis shows a kinetically slow transition from a core shell structure to a single crystal grain. This research presents an impactful insight on the factors that may cause sub-stoichiometric grain boundary effects which can influence the solar cell performance. In addition, the structure, morphology and optical properties of the perovskite grains have been presented. A powder of highly crystalline particles was subsequently prepared by evaporation of the solvent in a low-vacuum oven. Thin film MAPbI$_3$ solar cells were fabricated by dissolving the powder and applying it in a classical fabrication route. The MAPbI$_3$ solar cells gave a champion efficiency of 20% (19.9%) and an average efficiency at approximately 17% with low hysteresis effects. Here a strategy to manufacture the material structure without toxic solvents is highlighted. The single-crystal growth devised here opens both for shelf storage of materials as well as a more flexible manufacturing of devices. The process can likely be extended to other fields, where the intermediate porous framework and large surface area would be beneficial for battery or super capacitor materials.

1. Introduction

Finding new routes for low energy synthesis of materials promising for energy conversion and storage is a necessary and a rigorous task. Solar energy has wide availability and low environmental impact during operation, which makes it the most important renewable energy source. However, the current manufacturing routes and the recycling conflicts with many of the environmental goals. Therefore, more detailed studies to avoid negative environmental impact are of importance to find sustainable solutions for future energy conversion.

The lead halide (APbX$_3$) perovskites have reached impressively high efficiency in solar cells in the last years [1–3]. These materials are also promising candidates in light emitting diodes [4–6], lasing applications [7,8] and solar-to-fuel energy conversion devices [9,10], due to their unique optical and electronic properties. A deeper understanding of the fundamental aspects has followed with the increased research effort. Now, new types of perovskite semiconductors beyond the polycrystalline thin films are reaching the field, using nano- and
micro-crystals.

One advantage with the perovskite material is the ability to obtain high crystallinity at comparably low temperatures. With advanced techniques such as grazing-incidence small-angle scattering and wide-angle scattering the crystallization behavior, crystal orientation and structural phase transitions in new synthesis routes can be observed and tuned with additives [11]. Single crystal based perovskites are attracting interest because they possess minimal defect densities, which enables the realization of their optimal opto-physical properties [12]. The gap in performance between the single crystal properties and polycrystalline performance between the single crystal properties and polycrystalline films decrease with increasing quality of the thin film. The quality increase also encourages new routes and motivate to acquire better understanding of the crystallization of the perovskite at nano-level and grains at micro level. Solidification and crystallization of a solution determination the final properties to a large extent, and by studying the formation mechanism it can be controlled in future structure designs [13].

A challenge in perovskite technologies is the poor control of solution-mediated crystallization [14]. The formation of solution based intermediates has been shown to influence both crystallization and device performance [15–17]. It has been proven that the Lewis basicity factor of the solvent can be a predictor for the solvents ability to solvate the perovskite precursors. It is quantified by Gutmann’s donor number, DN, and describe interactions between Lewis-basic solvents and the Lewis-acidic Pb+2 center of iodoplumbate complexes in solution [18]. High DN solvents compete with I– for coordination sites around Pb+2 and prevent the formation of iodoplumbates, forming a stable precursor solution for thin-film processing. Low DN solvents coordinate less strongly with Pb+2 and thus favor iodoplumbate formation and subsequent single-crystal growth.

Assembly methods which also affect the crystal growth and modulate the particle interactions are evaporation-driven increase of particle concentration, destabilization by adding anti-solvents or adding an electric field during crystal growth [19–21]. Aggregation can occur when an attractive force disperse basic units which build characteristic structures called aggregates and their size increases over time as an irreversible process [22]. Thus a well ordered lattice in the aggregates depends on the initial particle concentration, different additives like surfactants and the evaporation rate [20,23].

In 2014 isopropanol was used to investigate an in-situ transformation vs dissolution-crystallization process of perovskite in an iodine rich environment [24]. First coordinated lead complexes was formed by reacting Pb(NO3)2 with KI and then recrystallized into perovskite morphology with excess CH3NH3I in isopropanol. One conclusion from this work was the determinant PbI2 morphology and CH3NH3I concentration on the final crystal geometries including rods, wires, plates and cubes. Same synthesis route was also used in a later project which confirmed perovskite structure with UV–vis NIR and FTIR spectroscopy [25]. There is one example in the literature of a direct conclusion from this work was the determinant PbI2 morphology and CH3NH3I concentration on the final crystal geometries including rods, wires, plates and cubes. Same synthesis route was also used in a later project which confirmed perovskite structure with UV–vis NIR and FTIR spectroscopy [25]. There is one example in the literature of a direct synthesis into high quality materials. To validate the optoelectronic quality gives the atomic number contrast. Together with EDS signals and nano-beam electron diffraction (NBED) techniques we could analyze the nanostructures formed in the newly mixed suspension sample and a one-week-old sample.

This enables an understanding of both the critical initial crystallization conditions as well as subsequent processes into microstructures. Thereby, increasing the possibility to control the crystal grains formation into high quality materials. To validate the optoelectronic quality and to add an applied aspect to the synthesized material, the highly crystalline grains are used in a classical solar cell manufacturing process. The results are very promising with rather high average efficiency (17%) with low hysteresis effects which opens the possibility to use premade hybrid perovskite powder into thin film processes.

2. Results and discussion

2.1. Preparation of the initial suspension

We begin our investigation where our previous project ended [27], with a component mixture of methylammonium iodide (MAI) and lead iodide (PbI2) in isopropanol, now only using a stoichiometric (1:1) molar ratio. Isopropanol is slightly more toxic than ethanol but much more benign than the typical solvents used for lead halide perovskite preparation such as DMSO and DMF. The simple formation of perovskite dispersions in isopropanol is potentially a useful and green method that can be used in perovskite solar cell manufacturing. In the first part of this work, we will focus on the formation of MAPbI3 grains in IPA. To describe the dominating kinetic interaction processes in the right order is a complicated phase space in perovskite solution chemistry including electrostatic interactions, ionic, acid-base and steric interactions. Fig. 1 shows a simple schematic of the synthesis route. In step (1) we first introduce mobile ions by dissolving methylammonium iodide in isopropanol. Isopropanol is often used as a solvent for the organic iodide in two steps processes for thin film perovskite synthesis [28]. It has a dielectric constant, εr, of 18.3 and Gutmann’s solvent donor number, DN, of 21.1 kcal mol–1. This value of DN is right in between the high donor numbers indicating a functional precursor solution and low donor numbers suitable for single crystal growth. The most utilized precursor solvents DMSO and DMF have a high DN just below 30 kcal mol–1. Acetonitrile and nitromethane have low donor numbers below 15 kcal mol–1 which indicate single crystal growth. However, for a solution, a mixture of solvent and dissolved substance down to a molecular level is required. This implies that the bonds between the dissolved MA+ and I– ions, and isopropanol has to be equally strong as the hydrogen bonds in between the isopropanol molecules. Also the entropy effects must be similar. PbI2 is a layered semiconductor with hexagonal Pb planes sandwiched between two the layers of iodine seen in Fig. 1. (2). Isopropanol as well as other alcohols are known to poorly dissolve PbI2. However, when the PbI2 is added into the solution a black suspension is immediately formed, Fig. 1. (2). This indicates a direct transition to perovskite phase which is driven by the access to iodide from the dissolved MAI in the solution. Early on in the process the aggregation starts when particles create clusters of perovskite material, Fig. 1. (3). The 0.67 M suspension is kept at room temperature throughout the process.
The reaction of PbI₂ perovskite structure starts to form. The methylammonium iodide are dissolved into IPA, (2) the lead iodide is added into the transparent solution, (3) which immediately turns to a black suspension indicating an intercalation of MA⁺ and I⁻ ions into the layered PbI₂ structure, (4) the MAPbI₃ perovskite structure starts to form.

The reaction of PbI₂ with iodine ions has previously been explained by the formation of iodoplumbate complexes in solution [18]. The iodoplumbates can be seen in UV-vis spectrophotometry in the range of 400–600 nm, in particularly if the solution is yellow. However, the isopropanol suspension is totally black and absorbs all the light up to 800 nm, which indicate a direct transition to the perovskite phase rather than possible iodoplumbate intermediates or that the kinetics of this intermediate reaction step are below seconds. The black suspension was measured with UV–vis in our previous work [27].

As previously observed, solubility is more strongly correlated with $D_0$ than with dielectric constant which indicates that acid-base interactions between solvent and precursor, rather than electrostatics, dominate the dissolution process [29]. By evaporating a sample droplet of the suspension, seen in Fig. 1, (4), on a substrate and measure X-ray diffraction the formation of MAPbI₃ perovskite is proven by the diffracted peak pattern. The evaporation-driven increase of particle concentration in the dispersion will affect the crystal growth when adding a droplet on a substrate surface, which is seen further below.

2.2. Crystal growth observed by electron microscopy techniques

Electron microscopy techniques were used to be able to observe the crystal birth. Right after mixing the suspension a droplet was added onto the Cu grid. In Fig. 2, the crystallization is monitored by using scanning transmission electron microscopy (STEM) and transmission electron microscopy (TEM). A small and equally distant nucleation center of aggregation was observed approximately 15 min after mixing the components and evaporation on the Cu grid, Fig. 2 (a). The concentration of ions increases with the evaporation of isopropanol and the time evolution and kinetics of the aggregation must be rapid. At this point, we performed NBED on this 15 min old sample and no clear crystalline signals can be observed. Fig. 2 (b) shows a higher magnification at the background and the site of a small nucleation centrum. In a bird’s eye view, the surface of the grid have a fractal like pattern of amorphous particles/ions. In Fig. 2 (c) cubic centers are observed with high density, surrounded by particles and ions. The stringy structure is typical in aggregation mechanisms of clusters, Fig. 2 (d). Mobile iodine anions along with the respective cations has previously been reported to cluster into large isotropic fractal patterns [30]. After approximately additional 30 min and 1 h after the initial mixing, several changes have occurred and the heart of nucleation has grown clearly showing cubic grains, Fig. 2 (e). In the surrounding amorphous material, small crystals are observed, Fig. 2 (f). This has also been reported in the previous work [27]. As far as we have been able to observe, both types of crystallization, the small quantum dot crystallization from the amorphous background and the large squares of crystal grain aggregation, occur simultaneously. Fig. 2 (g) is a close up on one of the grains. Vaguely, a core shell is observed, indicated by the arrow, and also some amorphous or cluster like materials on and surrounding the grain. A high-resolution image of the surface, Fig. 2 (h), reveal a single crystalline lattices that have a 0.31 nm lattice plane spacing which is equal to MAPbI₃ (220) lattice place spacing.

2.3. Structure, morphology and optical properties of the perovskite grains

Fig. 3. (a) and (b) shows the X-ray diffraction pattern of a newly mixed solution and a one week old solution. The pattern is clearly tetragonal with space group $I4/mcm$ and lattice parameters of approximately $a=b = 8.87$ Å and $c = 12.65$ Å [31]. The most pronounced peaks for the tetragonal MAPbI₃ perovskite structure are labelled with the corresponding plane in Fig. 3. (a). The newly mixed solution also contains another pattern with peaks at 9.77°, 19.62°, 29.65° and 39.45° 20.

Fig. 2. shows STEM and TEM images. Image a-d, a 15 min old suspension drop casted on a Cu grid and image, e-h, from a 1-h old solution. (a) Equidistant nucleation centers on a Cu grid, (b) closing in reveals an amorphous background, (c) a dense nucleation center (d) the amorphous dendrite like background. (e) Clearly large cubic grains begin to form, (f) as well as small nano-crystals (g) a zoom in on a perovskite grain, (h) In the STEM-HAADF image, the MAPbI₃ (220) lattice planes (marked by dashed lines) are observed when the grain is oriented to [001] zone axis. Marked areas indicate approximately the zoom ins and the arrow in (g) the core shell and (h) the lattice plane distance.
These peaks, labelled with a star in Fig. 3, (a), correspond to the methylammonium iodide salt with the planes of (001), (002), (003) and (004) for the corresponding 20 degree angle [32,33]. The crystal grains are large, approximately 1 μm, and the peaks have a full width half maxima (FWHM) similar to the instrumental broadening of 0.04° 20. There is a small contribution from PbI2 content identified as the (001) plane at 12.6° and (101) plane at 25.6° 20. This provides clear evidence that not all MAI and PbI2 have reacted after the short reaction time of 15 min. Fig. 3, (b) shows high resolution of the peaks corresponding to the diffraction planes (002) and (110) at approximately 13.9° and 14.1° 20 respectively as well as the (004) and (220) plane at 28.1° and 28.4° 20 respectively, which all indicate a pure tetragonal phase. This is different compared to our previous work where the cubic phase also influenced the diffraction pattern [27]. In Fig. 3, (c) and (d) the SEM images shows grains from a new and a one-week-old suspension with the same magnification. Both samples were prepared by adding a droplet of the suspension on a conducting substrate. When the solvent evaporates, the perovskite crystals undergo an evaporation-induced self-assembly process with the increase of concentration during evaporation. The mesoporous crystal grains (mesocrystals) have an apparent size distribution from 0.5 to 2.5 μm. One clear difference is seen at the edges of the grains, where the crystals from the old suspension have sharp and defined edges and the new solution contains grains with more soft edges. The slow crystal growth during stirring in the poor solvent, isopropanol, is essential for the assembly of single domain mesocrystals. Only cuboid grains is found in the (1:1) molar ratio, compared to our previous work with other molar ratios where rods and plates also occurs [27]. The morphology indicates a high porosity as of a powdered surface with 1 μm grains. The mesostructures are influenced by the organic-inorganic interactions and cooperative assembly.

To investigate the local variation of optical properties, steady-state photoluminescence (PL) emission mapping was performed. Two quantitative surface areas (30 × 30μm) representing newly formed and one-week-old grains respectively were measured. Fig. 4 shows the PL emission mapped over two samples with evaporated suspensions on plain glass substrates. One newly mixed (a) and (c), and one sample with an evaporated one week stored suspension (b) and (d). The PL emission spectra are seen in Fig. 4, (a) and (b). The red spectra show spectra from the spatial points exhibiting the highest and lowest PL emission intensity and the black spectra show the longest and shortest wavelength of the peak center position. The newly mixed solution has the PL emission maximum at 769 nm and a one-week-old solution at 784 nm (Fig. 4).

In addition to the 15 nm shift in peak position, the intensity from the one-week-old solution is four times higher. The increase in PL emission intensity is likely connected to higher crystal quality, which decreases trap-induced quenching of the exciton and thus increase the PL emission. Previous reports suggest that a stronger intensity from large grains are due to a reduction of surface related defects [34]. The step size in this measurement was 200 nm, while the meaningful spatial dimensions here are limited by the Abbe diffraction limit of d = λ/2NA where NA is the numerical aperture. With the super sampling, the 532 nm laser, and the objective used, this translates to a spatial resolution of 280 nm for the PL mapping, which is low enough to distinguish between the interior and the edges of the larger grains. For the fresh suspension, the blue-shift of the highest intensity PL emission peak at 769 nm indicate a general band gap broadening over the 30 × 30 μm area. In general, all the peak positions are blue-shifted in the newly mixed solution. The broader band gap occurring in the newly mixed suspension indicates either perovskite with non-stoichiometric composition or a remaining fraction of low dimensional crystals (quantum dots). The mapping of the surface seen in Fig. 4, (c) and (d) show the variation in peak position over the surface, black corresponds to shorter wavelength and red to longer wavelength. The wavelength range is different in the two images, short (black) starts at 764 nm for the new suspension and at 773 nm in the old suspension, to be compared with (a) and (b). The older solution has larger grains. The blue-shift of PL peak indicates a structural change between the newly mixed and one-week-old nanocrystals. Thus, we applied various TEM based techniques to analyze the nanocrystal grains and the grain boundaries. See also the Supplementary Information Fig. S1 for mapping of intensities.
2.4. High resolution characterization of grain structure and stoichiometry

To quantitatively examine chemical distributions and the structure at the surface of a grain with the grain boundary as well as the interstitial with the inner core, samples presented in Fig. 2 were further analyzed using STEM-HAADF, TEM, STEM-EDX and NBED. Fig. 5. (a) shows a newly formed grain with a clear core shell structure. Since the atomic number contrast dominates in a STEM-HAADF image, the brighter contrast generated from the shell part indicates that the shell contains heavier elements than the core of the analyzed crystal. In Fig. 5. (b) the overlapped STEM-EDS maps of Pb and I are shown. One can observe that the grain boundary contains more Pb, than the grain interiors. The iodine content, presented with green color, appears rather evenly distributed. From the intensity profiles extracted by X-ray counts, as shown in Fig. 5. (c), the peaks of Pb signal located at the shell of the analyzed grain are observed. This appearance of the two peaks at the edges of the grain indicates that the lead content is higher at the surface than in the center of the grain. There is also slightly lower signal from nitrogen and carbon at the edges of the grain, which give us a reason to conclude a bit lower content of the MA⁺ ion at the grain boundary as well. In Fig. 5. (d)–(h), an NBED scan over the grain at zone axis [201] is conducted. The indexing of diffraction spots in NBED patterns can be found in Fig. S2. The shell of the grain, seen in the NBED patterns in Fig. 5. (d) and (h) show broadened reflection rings that can be attributed

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**Fig. 4.** Photoluminescence emission spectra and PL mapping; (a) and (c) correspond to a newly mixed suspension, (b) and (d) correspond to a one-week-old suspension, (a) and (b) describe the variation in peak position (shortest and longest wavelength) and intensity (lowest and highest). In the PL maps in (c) and (d), black color represents short wavelengths (blue shifted) and red longer wavelengths.

**Fig. 5.** shows a grain from a newly mixed solution, (a) STEM-HAADF image of the grain with a core shell character (b) EDS maps using the Pb L-lines and I L-lines X-rays, (c) a EDS signal scan from the elements N, Pb, I and C, emphasized with the arrow in (b), (d)–(h) nano-beam electron diffraction over the grain, scale bar 3 nm⁻¹.
to the diffuse scattering of electrons. The intensity center of the first inner broadened ring is located at 2.534 nm$^{-1}$ ± 0.0327 nm$^{-1}$, which corresponds to the (010), (100) and (−110) reflections of PbI$_2$. These reflections cannot be overlapped with other reflection signals generated from MAPbI$_3$. Thus, the broadened reflection rings indicate that the shell has a less ordered structure (lack in long range ordering) and consist of tiny PbI$_2$ crystallites that are randomly oriented. A few steps into the grain, the NBED patterns in Fig. 5. (e) and (g) acquired at the interfacial regions, contains both broadened reflection rings and the single crystalline pattern. In the middle of the grain, the NBED pattern in Fig. 5. (f), shows only a single crystalline pattern that is generated by MAPbI$_3$ structure (see also Fig. S2) and the broadened rings have disappeared. The analysis of NBED patterns, acquired from different parts of the grain, suggests a change of nanostructure at the shell, interfacial regions and core. At the shell regions, the nanostructure is dominated by PbI$_2$ crystallites. At the interfacial regions, a mixture of both PbI$_2$ crystallites and the single crystalline MAPbI$_3$ is observed. At the core regions, only single crystal MAPbI$_3$ is detected from NBED analysis. The formation of such core-shell like structure from the newly formed sample is most likely due to a chemical gradient at the interfacial region of a metastable precipitate. The chemical inhomogeneity at the interface also provides the driven force for the grain growth unit it reaches the thermodynamic stable state. Moreover, the chemical inhomogeneity towards the grain boundaries might be responsible for the blue-shift of the PL peaks with lower emission intensities in Fig. 4. (a). There are scattered electron diffraction spots in Fig. 5. (e) and (g) that cannot be indexed by the crystalline structure of PbI$_2$ or MAPbI$_3$. This may be due to the formation of a super-lattice structure at the interfacial region, however, the suspected super-lattice structure remains unknown and will not be discussed in this article.

According to previous research in the field, grain boundaries can effectively separate charge carriers even if the grain surface have localized states [35]. The band bending at the grain boundary of a certain grain can create a built in potential and the electric field might facilitate the separation of the photogenerated charge carriers as well as ion migration over grain boundaries. In contrast to the more classical band bending, this occurs at grain boundaries in CIGS solar cells which suppress the photogenerated charge carriers [36,37]. From the NBED analysis, the results proposed an interfacial nanostructure which consists of the salt PbI$_2$ with band gap 2.3 eV and MA$^+$ and I$^-$ ions, each quantum well in the semiconducting salts set up new selection rule that affect the conditions for charges to flow through the structure.

To understand the changes over time in the aggregated suspension we repeated the same measurements on the one-week-old grains. In Fig. 6. (a) a STEM-HAADF image of two grains is shown and in (b) the EDS map showing the average spread of Pb and I X-ray signals over the grain. It is impossible to see any core shell like structure from the one-week-old sample. In Fig. 6. (c), there is no peaks of Pb X-rays counts at the edge of the grain and this suggests a more uniform distribution of Pb across the analyzed grain in the one-week solution. Comparing the NBED pattern with zone axis [110] in Fig. 6. (d) and Fig. 5S with simulated data (Fig. S4) shows a good match with the perovskite MAPbI$_3$ structure [38]. When scanning over the grain, no broadened reflection rings can be detected. Instead, a single crystalline structure of MAPbI$_3$ is observed. During the week in isopropanol, the suspension has self-organized into larger stoichiometric crystals. The large stoichiometric MAPbI$_3$ structure without a shell indicates that the grain growth has reached a thermodynamically stable state after one-week. The chemical gradient at the interfacial regions disappear and the grains will less likely grow in size by time if the synthesis conditions remain the same. By combining the analysis results obtained from TEM and PL, we can further understand that the blue shift seen in the PL emission spectra for the newly mixed suspension can be attributed to the presence of tiny PbI$_2$ crystallites at the grain boundaries.

### 2.5. Solar cell manufacturing and characterization

Pure and stoichiometric MAPbI$_3$ powders are easily prepared at room temperature using the methods shown in Fig. 1. To investigate the functionality and quality of the prepared MAPbI$_3$ powders, solar cells were fabricated with standardized methods. The synthesized MAPbI$_3$ suspension is made into a powder by drying in a low-vacuum oven at low temperature (65 ◦C). Then the powder is subsequently dissolved using the classical DMF and DMSO solvents for spin-coating onto the substrates for thin film layer formation, see the experimental part. The main question here is if it is possible to use the powder in a manufacturing process. This can then facilitate and shortening the time for synthesizing the material used in solar cell production. The thin film perovskite solar cell architecture is seen in Fig. 7. (b). The device structure is glass/FTO/SnO$_2$/perovskite/spiroMeOTAD/Au. In Fig. 7. (a) a SEM image of the cross section of the solar cell is shown. No significant differences are observed compared to a perovskite thin film layer prepared from a standard precursor solution, see SI Fig. S6. To the right in Fig. 7. (a) colors enhance and help to understand the layers from the SEM image and in (c) the schematics of the solar cell design in the lab is drawn with the evaporated gold on top.

To investigate the optoelectronic quality of the material the photovoltaic performance were measured. The reproducibility of the solar cell devices based on the powder method were rather promising, using only MAPbI$_3$ without any additional mixture of ions. Two batches of totally...
28 MAPbI₃ solar cell samples were manufactured and gave a champion efficiency of 20% (19.89%) and an average efficiency close to 17% with low hysteresis effects, Fig. 7. (e). The hysteresis index (H-index) gave a value of 0.033, SI Fig. S7 shows an even lower H-indexed solar cell. The hysteresis index (H-index) is calculated from the photocurrent efficiency (PCE) and hysteresis (H) index, (e) shows statistics of PCE from 28 solar cell samples out of two experimental batches.

Elemental analysis and NBED on newly formed larger grains displayed a core-shell structure with enriched content of Pb at the surface that leads to the formation of PbI₂ crystallites at the shell and interfacial regions. The NBED pattern reveals a single crystal core that is made of MAPbI₃. After storage, the same aggregated suspension showed grains with only single crystal structure of MAPbI₃. The approach provide an energy efficient irreversible process for aggregation of crystalline grains of tetragonal crystalline phase and cuboid grain shape. Thin films MAPbI₃ solar cells were fabricated by dissolving the powder and reuse it in a classical fabrication route. The MAPbI₃ solar cells gave a champion efficiency of 20% (19.9%), see SI Fig. S10, and an average efficiency of approximately 17% with low hysteresis effects. The single-crystal growth devised here, under low energy crystallization by using the poor-solvation effect, can likely be extended to mixed halides and multiple A-site cations in perovskite synthesis but also have an impact on other fields, where the intermediate porous framework and large surface area would be beneficial for battery or super capacitor materials. The approach opens both for shelf storage of materials as well as a more flexible manufacturing of devices by separating the initial crystallization process from the deposition process. The approach can also be seen as pre-crystallization step as the powder is re-crystallized in the secondary pre-crystallization step as the powder is re-crystallized in the secondary creation of thin films. Low energy crystallization by using the poor-solvation evaporation, effectively separates the processes of high crystalline material formation and subsequent thin film production. As the perovskites represent a rich material class relevant for a plethora of applications, we envision that this approach can also be of use for application areas not specifically addressed in this contribution with the hope of extending the use for this class of materials.

4. Material and methods

4.1. Sample preparation

A 0.67 M perovskite suspension was prepared by dissolving 1 mmol (159 mg) methyl ammonium iodide (MAI) in 1.5 mL isopropanol and then adding 1 mmol (462 mg) lead iodide (PbI₂) powder under stirring (all chemicals were of pro-analysis (PA) and purchased from Sigma-Aldrich except the PbI₂ which is from TCI). The solution immediately...

Fig. 7. (a) shows a SEM cross section of the MAPbI₃ solar cell produced from the perovskite powder, with a scale bar of 1 μm with schematics of the layers colored to the right. (b) The lab solar cell layout. (c) J-V measurement of a perovskite solar cell with forward and reverse scan, (d) data of Jsc, Voc, FF, PCE and hysteresis (H) index, (e) shows statistics of PCE from 28 solar cell samples out of two experimental batches.

3. Conclusions

We have explored an approach for production of high quality MAPbI₃ perovskite powder using only non-toxic solvent, isopropanol. The crystallization is an irreversible process of aggregation ending up in a porous framework of cuboid crystalline grains far from the polycrystalline thin film used is solar cells. Analysis of the initial crystal formation revealed high purity crystal grains as observed by STEM. The approach opens both for shelf storage of materials as well as a more flexible manufacturing of devices by separating the initial crystallization process from the deposition process. The approach can also be seen as pre-crystallization step as the powder is re-crystallized in the secondary creation of thin films. Low energy crystallization by using the poor-solvation evaporation, effectively separates the processes of high crystalline material formation and subsequent thin film production. As the perovskites represent a rich material class relevant for a plethora of applications, we envision that this approach can also be of use for application areas not specifically addressed in this contribution with the hope of extending the use for this class of materials.
turned from transparent to black while pouring PbI₂ into the MAI iso-
propanol solution. All reactions were carried out at room temperature. 
The solution was drop casted at different time interval onto a Cu-grid for 
the TEM measurements and on a carbon tape for the SEM analysis.

4.2. Material characterisation

To analyze the structural and chemical properties of nanocrystals, we 
employed STEM-HAADF imaging technique and STEM-EDS analysis on 
an aberration-corrected TEM, TitanThemis. The microscope equipped with 
ultra-bright XFEG electron gun, coupled with Super-X quad EDS 
detectors for elemental analysis. The acceleration voltage is at 200 kV. 
The STEM-HAADF images were acquired by scanning a focused electron 
probe (1 Å) across the sample and recording the high angle scattered 
electrons on an annular detector. To a good approximation, the brighter 
contrasts in a STEM-HAADF image indicate the existence of heavier 
atoms. For the chemical analysis, firstly, the selected crystal grain was 
tilted off from a low-index zone axis in order to minimize the electron 
channeling effect. In the FEI Titan Themis 200 features, a three 
condenser system, the C₂–C₃ zoom can be employed to ensure beam 
parallelity over a range of illuminated area sizes. In this work, we set a 
parallel beam with an illumination area of 5 nm for NBED technique. 
Before doing the NBED, the selected crystal grain was tilted into [201] 
zone axis. For the NBED pattern acquisition, FEI Ceta 16 M camera at a 
resolution of 1024 × 1024 pixels was used and dwell time at 1s for 
acquisition. The calibration of pixel size was accomplished using a 
standard gold nanoparticle sample at the same camera length before the 
NBED patterns were recorded. The calibrated pixel size for NBED pat-
terns is 0.0327 nm⁻¹. A line scan of NBED was made across the crystal 
grains.

The surface morphology and grain sizes of the formed nanostructures were 
characterized with scanning electron microscopy (SEM), using a 
LEO 1550 FEG instrument (LEO Electron Microscopy Ltd., Cambridge, 
UK) with in-lens detector operating at 3 kV. X-ray diffraction (XRD) 
patterns were recorded from the crystalline perovskite grains of the 
 evaporated isopropanol solution (powder) using a Bruker D8 TwinTwin 
instrument with Bragg Brentano set-up and resolution of 0.05° (2θ). The 
CuKα influence was corrected for using the program software Eva.

The photoluminescent mapping was carried out using a Renishaw 
InVia Reflex micro Raman spectrometer using a frequency-doubled YAG 
laser (532 nm) and a 1200 lines/mm grating yielding a spectral reso-
nance of 0.1 nm. A 150x objective (N.A 0.95) was used and gave a laser 
spot with 0.75 µm diameter with 0.2 mW intensity on the sample. An edge 
filter was used to remove the Rayleigh line of the 532 nm laser, cutting 
85 cm⁻¹ into the Stokes part of the spectra and neutral 
density filters reduced the laser power to prevent that the PL intensity 
exceeded the detector saturation threshold, so that a full relative in-
tensity count could be achieved. The area mapped was 30 × 30μm and the step size was 200 nm with an intentional oversampling.

4.3. Solar cell device fabrication

Etched FTO-coated glass substrates (TEC 15) were cleaned with 
detergent, acetone, and ethanol in an ultrasonic bath for 30 min, 
respectively. The cleaned substrates were UV-ozone treated for 20 min 
before use. The SnO₂ colloidal nanoparticles were diluted in DI water as 
volume ratio of 1:4. The SnO₂ solution was spin-coated on the UV-ozone 
treated substrate at 3000 rpm for 30 s and the film was dried at 150 °C for 
30 min. The SnO₂ coated substrates were cooled down to room-
temperature and treated with UV-ozone for 15 min prior to perovskite 
coating. The perovskite precursor solution was prepared by dissolving 
930 mg of black MAPbI₃ perovskite powder, 117 mg of DMSO in 1 mL of 
DMF at room temperature. The dissolved solution was filtered with 0.45 
µm PTFE filter. The perovskite solution was coated on the substrate at 
4000 rpm for 20 s and 0.5 mL of diethyl ether was dripped on the rotating 
substrate at 12 s after the spin coating starting. The transparent film was 
heated at 100 °C for 10 min in order to obtain a dense perovskite film. 
After cooling to room temperature, 40 µl hole transport layer was coated 
by spin coating at 4000 rpm for 20 s. The hole transport layer solution 
consisted of 100 mg of spiro-MeOTAD, 39 µl of 4-tert-butyl pyridine, 23 
µl of lithium bis(trifluoromethanesulfonyl)imide (Li- TfS) solution (540 
mg Li-TFSI in 1 mL acetonitrile), 10 µl of tris [2-(1H-pyrazol-1-yl)-4-tert-
butylpyridine]cobalt (III)tris [bis(trifluoromethylsulfonyl)imide 
(FK209) solution (375 mg FK209 in 1 mL acetonitrile) in 1.1 mL of 
chlorobenzene. Finally, 80 nm of gold metal was thermally evaporated on 
top of the device to form the back contact.

4.3.1. Solar cell characterization

The photovoltaic performances of the cells were recorded by using a 
Keithley 2400 source meter with a scan rate of 50 mV s⁻¹ under air mass 
(AM) 1.5 G (1000 W m⁻²) illumination with a solar simulator (Newport 
model 91,160), which was calibrated with a standard Si solar cell 
(Fraunhofer ISE), and the power supplier was a Newport Oriel (model 
69,911). The solar cells were masked during the measurement, and the 
active area was defined as 0.125 cm².

Author contributions

The manuscript was written through contributions of all authors. All 
authors have given approval to the final version of the manuscript. M. B. 
J. planned and designed the experiments, developed the material syn-
thesis and characterized the material with SEM, XRD and TEM and 
and wrote the original draft. L.X. characterized the material with HAADF-
STEM, NBED, EDS and contributed with editing the manuscript. B.J.K. 
fabricated the solar cells and characterized them and edited the manu-
script. J.T. measured the PL emission mapping and edited the manu-
script. T.K. draw the describing images and edited the manuscript. E.M. 
J.J., M.G., and T.E. contributed with discussion and edited the manu-
script. G.B. contributed with financial support and edited the manu-
script.

Declaration of competing interest

The authors declare that they have no known competing financial 
interests or personal relationships that could have appeared to influence 
the work reported in this paper.

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Appendix A. Supplementary data

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References

[1] J.P. Correa Barra, et al., Highly efficient planar perovskite solar cells through band 
alignment engineering, Energy Environ. Sci. 8 (2015) 2928–2934.
[2] M. Saliba, et al., Incorporation of rubidium cations into perovskite solar cells 
 improves photovoltaic performance, Science 354 (2016) 206–209.
[3] K. Aitoa, et al., Carbon nanotube-based hybrid hole-transporting material and 
selective contact for high efficiency perovskite solar cells, Energy Environ. Sci. 9 
(2016) 461–466.
[4] Z.-K. Tan, et al., Bright light-emitting diodes based on organometal halide 
perovskite, Nat. Nanotechnol. 9 (2014) 687–692.
[5] H. Cho, et al., Overcoming the electroluminescence efficiency limitations of 
perovskite light-emitting diodes, Science 350 (2015) 1222–1225.
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