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Chemical insights into perovskite ink stability

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Summary

Ever since the first reports on metal halide perovskite solar cells, a fundamental claim regarded a straightforward solution processability of the material, allowing for affordable and scalable processing. Therefore, understanding perovskite ink properties is a fundamental requirement toward industrialization. However, the evolution over time of these inks, which has a tremendous impact on the final performances of devices, is not yet extensively addressed. Any minute change in the ink composition can result in large variations in the photovoltaic performances, because these directly influence crystallization dynamics and final material composition. This is particularly important for the recent complex ink formulations, where the presence of numerous chemical species implies the existence of diverse interconnected equilibria. In this perspective, recent discoveries on the perovskite ink modifications over time are critically discussed, and directions for future research are proposed, including a survey of the most effective diagnostic tools used so far to investigate such inks.

Keywords: perovskite inks; stability; aging; solution chemistry; optoelectronics.

Introduction

Metal halide perovskite (MHP) semiconductors are excellent candidates for contemporary optoelectronics innovation, particularly for photovoltaics.1,2 The advantages of this class of materials derive from their hybrid nature, allowing for straightforward fabrication processes, and from their unique optoelectronic properties.3,4 A typical 3D organic-inorganic perovskite has a chemical formula of ABX3, where A is an organic cation (such as MA [methylammonium] or FA [formamidinium]), B is a metal cation (such as Pb2+), and X is a halogen anion (such as I or Br).5 However, recent advances have also explored more complex compositions embedding diverse cations/anions.6 These materials can be prepared using a plethora of methodologies spanning from thermal deposition to solution drop casting, although in the most common procedure, the material precursors dissolved in a solvent undergoes self-assembly into a perovskite structure during spin-coating onto a substrate under mild thermal annealing.5

The exceptional device performances, matching today those of crystalline silicon solar cells, call for a technological development of such devices toward industrialization.4 In this scenario, the successful scale-up of MHPs deposition methodologies requires a few key challenges to be overcome, mainly those related to a reproducible large area film manufacture and to final device stability. It is clear then how a lack of rationale upon precursors solution behavior is threatening the uptake of the technology.7, 8, 9 Particularly, the fundamental properties of the perovskite inks, along with their time-dependent evolution, are still relatively unexplored and could hinder the achievement of stable and reproducible processing protocols.10

It has been demonstrated that even for the simplest system (PbI2 + MAI —> MAPbI3), the precursor solution is a complex—and dynamic—dispersion, which contains not only solvated ions but also lead halide complexes, colloids, and aggregates of different natures and dimensions. In these complex dispersions, multiple chemical species are present and can interact—or react—between each other or with the solvent.11 The chemical reactivity of the perovskite film precursors in solution leads to ink variations over time, which, in turn, means variation in the final polycrystalline material properties. In fact, the characteristics of precursor solution eventually dictate the optoelectronic quality of resulting perovskite films.12,13 Therefore, a deep focus on the stability of these solutions is needed to understand which are the most suitable inks for in-series processing, how to store them, and for how long. Moreover, nowadays the chemical species present in the starting precursor solutions can span from simple monocation/monohalide systems, such as FAPbI3 or MAPbI3, to a far more complex solution simultaneously containing three cations (MA, FA, and Cs) and two halides (I and

Br) (in the case of the top performing multiple cation/anion perovskite nominal stoichiometry: $Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$).14,15

As an additional variable adding to the ink complexity, these solutions often contain small amounts of functional additives that can act on the processing, morphology, film stability, and crystalline phase purity.16, 17, 18, 19, 20, 21 It is commonly accepted within the scientific community that the perovskite precursor solutions need to be readily used after preparation to avoid undesirable decrease of device performances22; however, the rationale behind this empirical observation is still incomplete. To elucidate the roles of component reactivity and ink complexity on the stability of perovskite inks over time, further efforts to characterize precursor solutions and link their reactivity to film quality and device performance are needed.

In this perspective, starting from the known reactivity of the chemical species present in ink solutions, we outline the directions toward which future research efforts should be directed. We include a survey of the most effective diagnostic techniques used so far to study the species in perovskite inks and to follow their fate over time. The discussion on the chemical nature and stability of material precursors solutions is organized in two main sections, deriving from the two main components of the perovskite lattice: one is focused on the metal precursor (i.e., PbI_2), in particular on the influence of solvents, precursor nature, aging, temperature, additives, and light on the halide complexation. The second section deals with possible reactivity of organic cations, only very recently raised as one of the key points affecting the perovskite ink stability, following the discovery of reactions occurring between MA and FA.7,8 Starting from a comprehensive synopsis of the parameters and chemical species affecting the solidity of perovskite inks, we draw guidelines for the precursor solution stabilization and outline future directions for perovskite ink development.

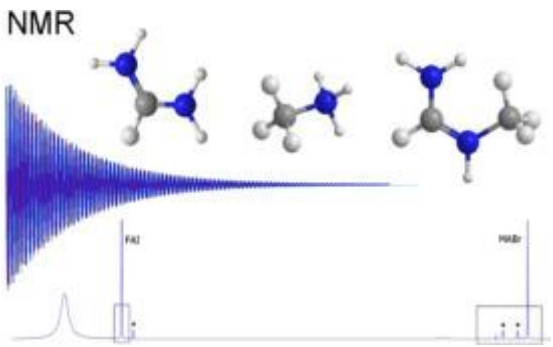
Characterizing the ink: A comprehensive picture

A deep and comprehensive characterization of the ink chemical-physical properties is a fundamental starting point for the rationalization of its evolution over time and to link this to the resulting perovskite film characteristics and device performances. Most importantly, proper ink characterization can be a predictive tool at the very first steps of the material synthesis and could help avoid wasting resources on empirical evaluation of the final devices.

Given the ink complexity, in terms of composition, chemical-physical properties, dynamic evolution, a series of complementary experimental techniques needs to be used to depict the solution characteristics. These can give different levels of information, spanning from the chemical identification to the aggregation behavior, to the dynamic evolution from solution to film of the

species constituting the solution. These approaches are summarized in Table 1 along with the details about the specific application of each technique.

Table 1. Specific techniques used to characterize perovskite inks divided by the kind of information that can be extracted, specifically on the chemical identification, on the aggregation behavior and on the transition from solution to film

<table>
<tr><td colspan="2">Chemical identification</td></tr>
<tr><td> 
</td><td>UV-vis absorption spectroscopy:
monitors diluted solutions by steady state or time resolved to follow the evolution of
inorganic-based adducts that present electronic transitions in the visible range[26]
Nuclear magnetic resonance spectroscopy (NMR):
- in solution NMR, gives information on the deprotonation of MA and the formation of a condensation product between methylamine and FA (methylformamidinium, MFA)[7,8]
- 2D NMR spectroscopy methods, such as Correlation Spectroscopy (COSY) and Nuclear Overhauser Effect Spectroscopy (NOESY), can assess the configuration of any chiral by-product formed by reactions. (i.e., the trans/cis stereoisomeric products of MFA [trans-MFA and cis-MFA])
IR spectroscopy:
- in situ attenuated total reflection infrared (ATR-IR) spectroscopy can evidence decomposition products of solvents (e.g., DMF that decomposes in formic acid)[27]
- FTIR can identify some intermediate compounds, for example, a stable MAI(Br)- PbI2 -DMSO phase[28]
X-ray spectroscopies:
identifies crystalline species isolated form solution precipitation, i.e., MAI(Br)–PbI2–DMSO adduct[28]
Predictive computational modeling:
density functional theory (DFT) can model the number of iodide ions and of solvent molecules coordinated to the Pb2+ centers and time evolution of poly-iodide species[29,30]</td></tr>
<tr><td colspan="2">Aggregation behavior</td></tr>
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<td>Dynamic light scattering (DLS):
estimates the dimensions of aggregates and their size evolution with solution aging[10]
X-ray spectroscopies:
can be performed directly on perovskite inks (i.e., in a cuvette or in a silicon microfluidic chip device with a constant flow)[9]
- small-angle X-ray scattering (SAXS) technique gives information on the mean spacing d between the centers of mass of the colloidal particles and on differences in colloidal structures with different sizes, in different solvent systems
- the extended X-ray absorption fine structure (EXAFS) measurement gives information on the local surrounding of lead complexes
Nuclear magnetic resonance spectroscopy (NMR):
diffusion-ordered spectroscopy (DOSY) separates different species according to their diffusion coefficient (D), monitors the hydrodynamic radius (rH) of MAI in solution as a function of the additive concentration,16 and probes the formation of aggregates involving MA their consumption; longitudinal and transverse relaxation times (T1,T2) are responsive to aggregation phenomena and/or to the presence of intermolecular interactions in solution[31]
Electron microscopy:
cryo-TEM (transmission electron microscopy) imaging of the frozen mother liquid can detect the presence of less soluble colloidal species present in solution (such as PbCl2)[23,32]</td>
</tr>
<tr>
<td colspan="2">Evolution from solutions to films</td>
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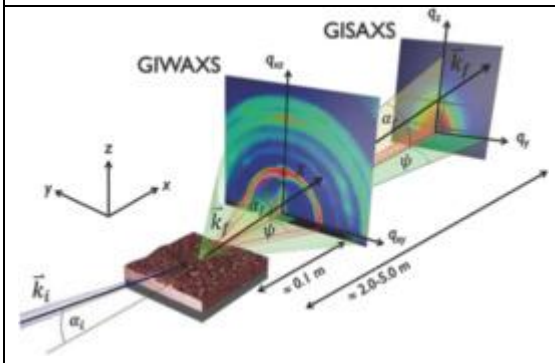
<tr>
<td> 
</td>
<td>Optical microscopy:
to monitor the crystallization of perovskite precursors from a microdroplet during solvent evaporation33 or during the annealing of films[17]
Differential scanning calorimetry (DSC):
can be used to calculate the crystallization enthalpy from the exotherms, measured by heating perovskite inks in different temperature ranges and at different scanning rate[34]
In situ electrochemical impedance spectroscopy (EIS):</td>
</tr>
</table>

	the real-time concentrations of the growth solution can be calculated as a function of the ohmic resistance; the slowing down of the consumption of solute can be correlated to the depletion in supersaturation, giving information on crystallization kinetics[35] **X-ray spectroscopies:** - real-time in situ GIXRD monitored the [PbI6]4- cage concentration increase upon solvent evaporation, which allow [PbI6]4- octahedra to arrange in a more stable PbI2 framework forming the MAI-PbI2 -DMF intermediate[36] - in situ grazing-incidence wide-angle X-ray scattering (GIWAX) can capture the dynamic evolution and longevity of the crystalline or disordered precursor solvates, the formation of the adduct intermediate state either with solvent or additives and eventually correlating them to the characteristics of the resulting perovskite films and to the device performance[17,37]
Representative image for the chemical identification: NMR spectrum of MFA adduct. Adapted from Valenzano et al.[8] Copyright 2021 with permission from Cell Press. Representative image for the aggregation behavior: Cryo-TEM setup. Adapted from Dutta et al.[23] Copyright 2020 with permission from American Chemical Society and from Wang et al.[24] Copyright 2018 with permission from Cell Press. Representative image for the evolution from solution to film: Time-resolved in situ GIWAX sketch. Adapted from Johannes Schlipf et al[25] Copyright 2017 with permission from WILEY-IEEE.	

“Chemical identification” methods can be used to monitor chemical species in the perovskite ink solutions, to identify their chemical structure, and to investigate their reactivity with other material precursors, solvents, and/or additives. Lead (or tin) poly-halide complexes have electronic transitions in the visible range and thus can be easily monitored in diluted solutions by UV-Vis absorption. Herein, either steady-state or time-resolved UV-Vis absorption spectroscopy is useful to follow the evolution of such species in a simple yet effective manner.26,38,39 It is very specific for determining the complexation degree of halides around the metal, as often the other species (such as solvents or additives) are very diluted or not absorbing.

On the other hand, the organic cations and their decomposition/reaction products can be effectively identified by solution nuclear magnetic resonance spectroscopy (NMR), which allows the sampling of the chemical nature and geometry of the surrounding of 1H and 13C atomic nuclei.16,31,40 This powerful tool can be used to explore different experimental conditions and directly determine how they modify the reactions kinetics, as occurs, for instance, in the perovskite ink of solutions of

different ages.7,8 It has the great advantage of monitoring the solution in the real conditions, i.e., the concentration used for the device fabrication, also taking into account effects related to viscosity of the media, diffusion of the ions, and so on.

Fourier transform infrared spectroscopy (FTIR) has been used as very direct tool to follow the evolution of decomposition products of typical solvents at different temperatures.27 It can also be used to identify some intermediate solvent/precursor compounds that form upon the dripping of a non-dissolving solvent during perovskite film formation.28 This technique applies on a formed film; therefore, the information about the solution equilibria can be extracted indirectly. Also X-ray spectroscopies can be performed both on films and on powders; intermediates solvent/precursors, for example, can conveniently be isolated in their crystalline forms by precipitation from the precursor solution and studied through X-ray diffraction (XRD), complementing the information obtained with FTIR and NMR characterization.

Finally, the results of these analyses, as well as the theoretical energetic landscape for intermediate formation, can be rationalized by using a computational approach, which represents another fundamental tool for the prediction of perovskite ink properties and time evolution of poly-iodide species, particularly as regards the future innovation of such formulations.29,30

Investigating the “aggregation behavior” of the perovskite ink solutions through monitoring the formation, evolution, and dimensions of colloidal species can give valuable information on complexation equilibria and weak short-range interactions in solution.

The colloidal nature of perovskite ink solutions has been evident from the beginning of perovskite photovoltaic era and was first identified by the typical Tyndall effects.11 That is the observation of the scattering of a laser beam passing through highly concentrated solution, usually used for solar cells, indicating that such solutions are colloidal dispersions in the mesoscale, rather than real solutions.

The dimensions of these aggregates and their size evolution with time can be monitored by dynamic light scattering (DLS) in a very first approximation,10,31 considering that DLS can only appreciate sized in the order of the scattered light wavelength. On the other hand, their crystalline structure is efficiently characterized by X-ray spectroscopies of different kinds, requiring the use of synchrotron radiation directly on the perovskite inks.9 Such high-resolution techniques give unique information on the structure of colloids with different sizes and in different solvent systems, plus mapping the local surrounding of lead complexes.

NMR spectroscopy is a powerful tool also for characterizing the aggregation phenomena and short-range intermolecular interactions. It can be used to monitor the hydrodynamic radius (rH) of organic cations (such as MA) in solution, which is directly related to their aggregation behavior, to the formation of reasonably soluble species, and to the aggregate consumption.16 The strength of intermolecular interactions existing in solution between organic cations and different additives has also been evaluated through bidimensional NMR spectroscopy.31

Physical-chemical characterization can be also refined by electron microscopy on frozen precursors solution. This approach has been used to investigate the evolution of such solution by freezing inks at different time interval after preparation, evidencing the presence of less soluble species that would act as heterogeneous nucleation sites for the formation of perovskite crystals.23,32 This is a quite complete—although not straightforward—approach that allow to acquire a "screenshot" of the solution at each aging time.24

Monitoring the nucleation and growth of perovskite polycrystals "from solution to film" with tailored operando/time-resolved measurements provides key information on how solution chemistry affects film quality. A series of complementary techniques have been specifically tailored to monitor in situ and "real-time" transition from solution to solid state, by means of operando characterizations that allowcollection of key information on the nucleation mechanism and on the labile intermediate species forming in this transition. The knowledge that comes from the analysis of the nucleation process is fundamental to follow the fate of the species in solution and to link them to the coming solid phase.

Very simple and readily available methods can contribute to determine the kinetics of nucleation and crystallization, such as optical microscopy performed during the annealing of films prepared from perovskite solutions17 or on microdroplet of perovskite inks during solvent evaporation.33

In situ electrochemical impedance spectroscopy (EIS)35 and differential scanning calorimetry (DSC)34 methods have also been very effective in probing the kinetics of the perovskite crystallization process. Furthermore, DSC also provides the enthalpy associated to the crystallization process as estimation of the thermodynamic stability of the final perovskite material. Fundamental to the correct extraction of this value is the proper conduction of the experiment, aiming at excluding interferences from endothermic process related to the solvent evaporation that is concomitant to the exothermic perovskite crystallization.34

Among the most important contributions to monitoring the transition from solution to film was given by in situ and "time-resolved" X-ray scattering techniques, although employing very complex

experimental setups. Grazing incident X-ray diffraction (GIXRD) and custom-made time-resolved in situ grazing-incidence wide-angle X-ray scattering (GIWAX) employing synchrotron light was performed during the spin-coating.17,25,36 GIXRD has been used to reveal that perovskite crystallization occurs through the formation of intermediated [PbI6]4−-centered nanoparticles surrounded by MA+ ions and solvent. Time-resolved GIWAX allows to go through all the phases of the coating process9,17,34,37,41 and to screen in real conditions the effects of many different parameters and the influences of solvent and additives, giving much more detailed and precise information than the results of any ex situ steady-state technique.

Lead halide complexation

It is well known that metals with an s^2 electron configuration (i.e., Ti^+, Sn^{2+}, Pb^{2+}, Sb^{3+}, Bi^{3+}, and Te^{4+}) form kinetically labile complexes with halogens in a number of solvents.[42] For Pb^{2+}, these complexes are referred to as "plumbates" (e.g., PbI_3^-, PbI_4^{2-}, PbI_5^{3-}, and PbI_6^{4-}). In solution, these complexes are not stable in only one form but involved in a dynamic equilibrium that is easily influenced by the halogen concentration as by the solvent and or by other chemical species present in solution (Figures 1A and 1B).[26,39]

The formation of poly-halide complexes contributes to disaggregate the PbI_2-based colloidal aggregates (see Figure 1).[11] Such colloids are made of an intermediate soft coordination complex between inorganic and organic species dispersed in equilibrium in the mother solution, which will be easily modified by conditions, such as illumination, temperature, and time, which will inevitably affect the final perovskite material. In fact, such intermediate phases act as a framework for the perovskite polycrystal growth, and their fate governs the perovskite nucleation and growth occurring during the drying process.[11,44]

Perovskite formation process can be framed in the classical nucleation theory: formation of monomers, supersaturation along with formation of nuclei upon solvent evaporation, and diffusion-controlled growth.[12] The size and cohesion of perovskite polycrystals in the actual photoactive films is determined by the close packing and concentration gradient of the PbI_6^{4-} cages during the crystallization process (Figure 1C).[36] The formation of high-valent poly-iodide complexes leading to colloids with smaller sizes enables the deposition of a thin perovskite layer with good crystallinity and few defects.[43] Therefore, several additives have been explored to act on the PbI_2 complexation, mainly following a Lewis acid-base adduct approach.[45]

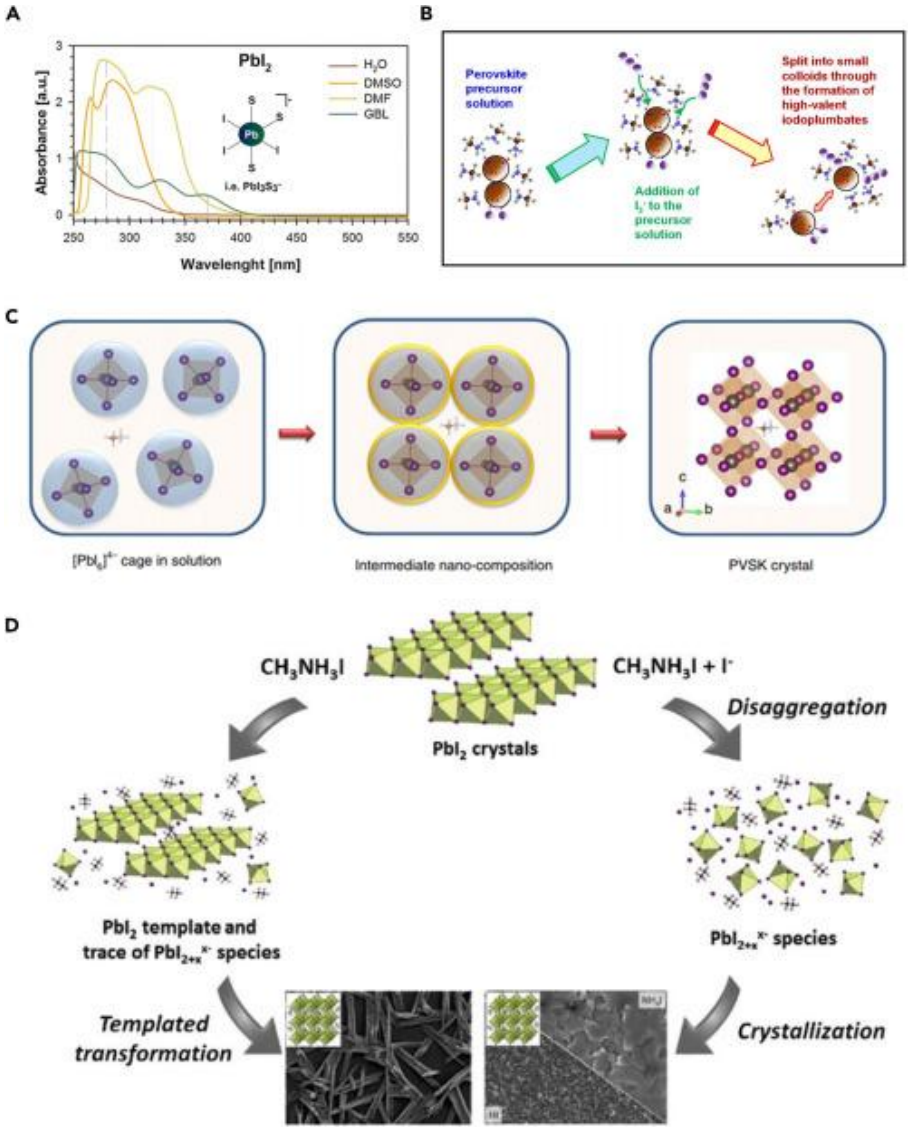


Figure 1. The role of poly-halide species in solution in the perovskite formation

(A) Absorption spectra of solutions containing PbI_2, showing the different coordination capability of a range of different solvents. Reproduced from Rahimnejad et al.[39] Copyright 2016 with permission from Wiley-IEEE.
(B) A scheme of the formation of high-valent iodoplumbates with the inclusion of iodide additive into perovskite precursor solution. Adapted from Kim et al.[43] Copyright 2020 with permission from American Chemical Society.
(C) A sketch of the perovskite polycrystal growth from the PbI_4^- cage to the intermediate state and finally to the perovskite structure. Adapted from Hu et al.[36] Copyright 2017 under a Creative Commons license CC BY 4.0 Springer Nature Ltd.
(D) A representation of the two perovskite formation mechanisms: the templated transformation that occurs without the use of additives and the disaggregation-crystallization that occurs by including iodide additives. Reproduced from Mastria et al.[44] with permission from the Royal Society of Chemistry Copyright 2017.

The inclusion of halogenated additives (I_3^-, HI, and NH_4I),[43,44,46, 47, 48, 49] allows an increase in the complexation capability of PbI_2, leading to the disaggregation of PbI_2 seeds[11,44] (see Figures 1B and 1D). In the case of iodide additives, the perovskite growth occurs through a disaggregation/crystallization mechanism leading to smaller grains evenly distributed in a fully covered morphology (Figure 1D).[44] These enable more uniform nucleation and modulate crystallization kinetics, ultimately improving the film quality in the perovskite active layer.[38,50]

The coordination ability of the different solvents employed (for example, dimethylsulfoxide DMSO, dimethylformanide DMF, γ-Butyrolactone GBL, etc.) also influences the formation of poly-iodide species. High-coordinating solvents compete with halogen ions to fill the metal coordination sphere; therefore, solvent changes modify the proportions of differently coordinated iodoplumbate species.[29,39] (Figures 1A and 2A) Conversely, weak coordinating solvents generate iodoplumbate species richer in iodide.[51] The DMSO solvent, which forms a stable intermediate phase (PbI_2-MAI-DMSO), is often used to retard the perovskite crystallization in combination with the solvent engineering method to obtain smooth and homogeneous film morphology.[28,52] Modulating the solvent coordination, i.e., addition of highly volatile solvents in combination with strong coordination Lewis base additive, has been demonstrated as an alternative strategy to achieve densely packed perovskite films on a large area.[53]

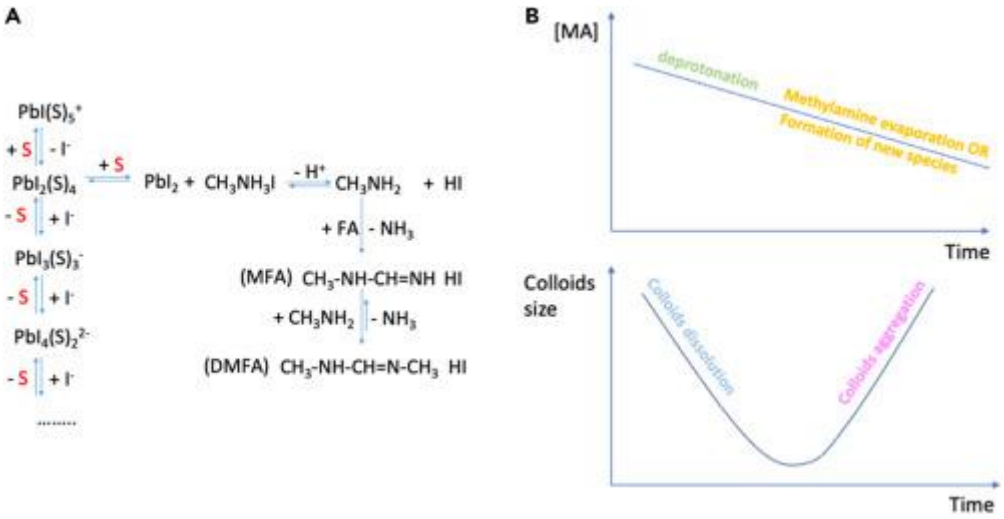


Figure 2. Summary of the most relevant reactions in solution and their effect on the MA concentration and colloids size in solution

(A) Summary of the most relevant equilibria established in solution around PbI_2 and MAI species: left, dissolution of PbI_2 in a generic solvent (S) and competitive reaction between iodide ions and solvent molecules leading to different plumbates ions; right, deprotonation of MA to give methylamine that can either evaporate or react with a FA ion to give the mono- or double-addition

products MFA and DMFA; the alternative pathway represented is the addition of a generic additive A that inhibits MA^+ deprotonation.

(B) Schematic representation of the effect of aging time on the MA concentration and colloids size in the perovskite inks.

When the ink composition changes, as in the case of the recently introduced complex perovskite stoichiometries, the solvent effect should be specifically evaluated. For example, PbI_2·N-methylpyrrolidone (NMP)[54,55] allowed the realization of FA-based perovskite films without the use of antisolvent dripping and in ambient air. The stable PbI_2·NMP can react *in situ* with FAI/CsI cations favoring a lead halide-templated crystallization and lower the formation energy of the conductive α-phase FA perovskite.

To stabilize the PbI_2-solvent-MAI complex, different additives have been included,[56] starting from Lewis bases, such as urea thiourea, methylamine, pyridine, aniline, thioacetamide, etc., which can function as O-donors, S-donor, or N-donors in forming coordination complexes with Pb(II) halides.[45,]57, 58, 59

Bromide, chloride, thiocyanates, and other pseudo halide anions have been proven to outcompete solvent or iodide for PbI_2 ion coordination already in solution.[1,]60, 61, 62, 63, 64, 65, 66, 67

Besides solvent choice and additives, illumination and temperature can also interfere with the complex equilibrium of ionic species in solution and with the complexation and size of poly-iodide colloids. Recently, it has been proven that less than 1 h of illumination (1 sun) can modify the iodoplumbate equilibrium state toward high-valent iodoplumbate either for $MAPbI_3$ than $FAMAPbI_3$.[68] This is caused by light-induced DMF expulsion from the lead coordinative sphere. This perturbation promotes the formation of perovskite materials with larger and more homogeneous grains and solar cell devices with higher performance and reproducibility. A similar effect was obtained in $MAPbI_3$ perovskites by exploiting a time-dependent mild annealing of the precursor solution (65°C).[69] Nonetheless, prolonged annealing under UV radiation induces the oxidation of I^- to I_2 leading to the formation of metallic lead (Pb^0) and iodide interstitial that, being deep trap states for charge carriers, are detrimental to solar cell performance.[70,71]

Clearly, all the mentioned complexation equilibria occur with specific kinetics that will determine the properties of the perovskite ink with time. Very recent works have focused on this time evolution, in particular for the dimension of aggregates. Tsai et al. demonstrated that the optoelectronic properties, crystalline size, and device performance of $MAPb(I_{1-x}Cl_x)_3$ were affected by the perovskite precursor solution aging.[10] They correlated the aging time to the in solution formation of progressively larger

seeds, finding that influencing the nucleation process induces the growth of a more crystalline perovskite thin film with better coverage and fewer traps. Their optimized aging duration was 48 h. Boonmongkolras et al. also revealed that precursor solution aging has a great influence on the colloidal size distribution of the solution.[72] They revealed that the formation of micron-sized colloidal intermediates in the triple-cation precursor solution when aged longer than the optimum hours (6 h) led to a degradation of the phase purity of the resulting films and, consequently, to poorer device performance.

The addition of hydrohalic acids (HI, HBr) was found to induce a dynamic dissolution of lead poly-halide colloids, which occurs over a period of tens to hundreds of hours for triple-cation (MA, FA, and Cs) perovskite inks.[73] Therefore, aging is a rather crucial parameter affecting the size and concentration of colloidal species.

Reactivity of organic cations

Chemical reactions involving organic cations can occur even when the only organic players involved are MA and the solvent. MAI is a weakly acidic salt that in the solid state can easily experience a proton transfer to I^- with a minimum activation energy. This deprotonation is mostly responsible for the thermal decomposition of $MAPbI_3$ with the production of gaseous methylamine (CH_3NH_2) and HI:

$$CH_3NH_3^+ + I^- \rightarrow CH_3NH_2\ (g) + HI\ (g)$$

This process, although endothermal, has a positive entropy variation and therefore is favored by a temperature increase.[74]

In solution (MAX + PbX_2+ solvent) an increase in proton activity has been observed before any heating,[27] as a result of the deprotonation of MA to CH_3NH_2 and H^+. Clearly, any external stimulus, such as temperature or illumination, may affect this equilibrium. Focusing on the simplest ink formulation, one must consider that the most common solvents (DMF or GBL) also have acid-base activity. In fact, DMF can decompose into formic acid and dimethylamine and GBL can decompose to g-hydroxybutyric acid.[75,76] In contrast, DMSO produces no acidic component upon decomposition.

Importantly, all those equilibria can be perturbed in one direction or in one other (protonation or deprotonation of the acid), in order to restore or create an ideal situation for material deposition. When the transformation is irreversible, i.e., with the evaporation of a product, the solution composition permanently changes, with a potential impact on the formation of perovskite, as well as its properties. Very recently it has been determined how fractional changes in the stoichiometry of the precursor

solution have an enormous effect on the properties (surface composition and energetics, photoluminescence, crystallinity, energetic disorder etc.) of perovskite films, which can impact the final device performance and stability, even as the films show apparently identical microstructures.[13]

Another example of a largely used monocation perovskite is $FAPbI_3$, which is a very good candidate for optoelectronic applications because of its ideal band gap (1.48 eV)[77] and the superior thermal stability of the film. The latter shows the appearance of the decomposition product 1,3,5-triazine only if treated above 95°C,[78] and in solution it is revealed in traces only for inks aged at 65°C.[7] Deprotonation of FA ion is much less favorable with respect to MA, both in film and in solution. However, in solution, other processes can decrease the stability of FA-based inks. It has been demonstrated[68] that under illumination, FA^+ participates in the reduction in solution of Pb^{2+} to produce Pb metal.[70] In contrast to MA, FA ions have −CH=NH double bonds, which are chemically more reactive than $-CH_2-NH_2$ single bonds. The light-induced FA ion degradation process is thought to occur through the redox reaction between the organic CH=NH bonds and inorganic $PbBr_2$ where −CH=NH double bonds of FA ions gradually oxidize into −CH=O, although this reaction is not obvious in the solid state.

The situation becomes more complicated when more than one cation is simultaneously present in solution. This is the case of double- or triple-cation perovskites, widely exploited materials to stabilize the conductive perovskite phase (α) of $FAPbI_3$.[79] One of the methods to enhance the phase stability of α -$FAPbI_3$ is to introduce in the lattice small size cations, such as MA of Cs.[77] Unfortunately, a non-perovskite phase always appears in the mixed perovskite films and has been attributed to δ- $FAPbI_3$ according to the diffraction peak that appears at 11.5°.[63,80, 81, 82, 83] It has also been observed that the amount of this impure phase changes over aging.[81, 82, 83] Wang et al.[7] hypothesized that the diffraction peak observed at 11.5° belongs to a mixed perovskite containing a MA-FA condensation product, N-methylformamidinium (MFA), rather than δ-$FAPbI_3$. In fact, they isolated the perovskite phase containing DMA (i.e., $MA_xFA_xMFA_x(NH_4)_xCs_xPbI_3$), which shows a diffraction peak at 11.47°. Very interestingly, a peculiar reactivity between MA and FA has been proved in mixed cation precursor inks through in-depth solution NMR analysis[7,8]: in the concomitant presence of MA and FA, a small amount of MA, formed from deprotonation of MA^+, volatilizes away from the solution, whereas the residual MA condensates in presence of FA iodide (FAI) to form N-methyl FAI (MFAI) and N, N-dimethyl FAI (DMFAI). The smaller MFA can be included in the perovskite structure to form the impure phase with diffraction peak at 11.5°.

$$CH_3NH_3I \xrightarrow{-H^+} CH_3NH_2 + HI \xrightarrow{+H_2N-CH=NH\cdot HI(FA)} \underset{(MFA)}{CH_3NH-CH=NH\cdot HI}$$

$$\xrightarrow{+CH_3NH_2} \underset{(DMFA)}{CH_3-NH-CH=N-CH_3\cdot HI}$$

Such side reactions irreversibly consume the precursor materials, producing a secondary phase in the perovskite films, which is detrimental to their performance and causes obvious changes in the perovskite solution stoichiometry. Because of such reactions, solutions aged longer than 1 day led to reduced device performances. Liu et al. have also unveiled that this side reaction occurs more quickly during the evaporation of residual solvent when the films are annealed at elevated temperatures. They found that a combination of room temperature aging and vacuum treatment of the spin-coated wet film is beneficial to reduce the side reactions and improve the perovskite phase purity.[84] We have found[8] that the presence in trace of water or small amounts of basic impurities (such as PbO), which could typically be contained in the less-pure PbI_2 reactant, significantly catalyzes the degradation reaction. Instead, cesium ions appear to slow down FA–MA reactivity.[8] This species can indeed behave as a Lewis acid, coordinating part of the formed methylamine via a soft acid—soft base interaction, subtracting it from the formation equilibrium of the new species *N*-methylformamidinium (MFA) and *N*,*N*′-dimethylformamidinium (DMFA).

At the origin of many problems with ink variability lies the deprotonation of methylammonium, which generates free methylamine that can either evaporate, causing an unbalanced stoichiometry in solution, or can react with other species, i.e., FA (see Figure 2A). Different additives have been tested to inhibit the MA deprotonation. One is the previously mentioned Cs^+, which is an unintentional, but still effective, method to stabilize MA in its acidic form,[8] thereby slowing down the reaction between MA and FA. Thiethylborate (TEB) has been shown to fulfill the same function[7] and sulfur seems to be effective in the inhibition of the MA deprotonation thanks to amine-sulfur coordination.[82]

Toward ink stability

The primary paths for the solution components interaction, summarized in Figure 2A, translate into two main problems. One is the change in the composition of the solution, with obvious implications on the properties of perovskite thin films; the second is the change in the complexation equilibrium of the inorganic colloidal framework and thus of the colloidal aggregates, with direct implications for the nucleation process and growth of perovskite crystals (Figure 2B). It appears clear today that gaining control over the chemical-physical processes of the solution is a key step toward effective industrialization of PSCs, where “gaining control” means rationalizing the proper timing of ink

utilization withstanding its unavoidable evolution. This condition is composition dependent, as we highlighted within the perspective, since the behavior with time, illumination, and temperature (the environmental conditions that should be applied for hypothetical ink storage) strongly depend on solvent, the nature and number of cations, solution concentration, and the inclusion of additives—all parameters that would trigger a different kind of chemical reactivity/equilibrium.

Although we can assume that all inks should be stored in dark and at room temperature, the parameter "optimal aging time" will need to be defined for each system and it is not easy to be standardized. Indeed, the aging time reported by the prior studies differs significantly, ranging from hours to hundreds of hours. Trying to rationalize the reasons behind these differences, one needs again to consider the two main phenomena analyzed within the perspective: colloidal dispersion and organic cations reactivity. Considering the colloidal dispersion, the optimal time is likely a balance between the dissolution of colloids due to halide complexation or the formation of intermediate species due to interactions with the solvent, organic cations, and/or with additives, as well as the re-aggregation of these species as a consequence of aging, as sketched in Figure 2B. Organic cations show a reactivity characterized by a different kinetics, usually triggered by a deprotonation of methylammonium, followed by the transformation/evaporation of the resulting methylamine, with a consequent reduction of MA concentration. In a first approximation the optimal aging time would be given by the combination of both these kinetics (Figure 2B). The strategies devised to improve ink stability are conceived to enlarge the time window in which these two species remain available. One approach would rely on the use of additives, with the function of forming more stable colloids on one hand, and on the other hand, to inhibit—or slow down—the deprotonation of methylammonium, or more generally the reactivity between the organic cations (Figure 2A).[82] Another potentially complementary strategy could employ the use of less reactive solvents, which would not be involved in acid-base equilibrium but could efficiently coordinate the Pb-complexes to give stable intermediates.[30]

However, we need to highlight the intrinsic instability of perovskite inks, whose reactivity, due to the high complexity of the system and the tight interconnection between the described processes, is difficult to avoid, as well as to predict precisely. Therefore, in order not to make these stabilization strategies rather a palliative than a radical solution, we could consider the option of simplifying the system as much as possible. In this scenario, it is interesting to observe how going back toward a monocation perovskite is indeed, the current scope of many researchers, and the reasons behind these choices find their bases, not only in the superior properties of the final film, but also on the higher stability of the precursor ink. The stabilization of pure $FAPbI_3$ conductive phase, not including additional cations, such as MA, is surely a winning direction to avoid unwanted reactions; however,

the development of additives for the α-phase stabilization must consider the possible reactivity of FA with them.[85] Nowadays a well-established approach to stabilize the α -$FAPbI_3$ is the inclusion of MACl salt in the precursor solution. However, the reactivity between MA-FA by using the MACl additive is not assessed and should be considered. For this reason, the search for other agents that might stabilize the α-phase without interfering to the stability of the precursor solution is of paramount importance. Recently, the use of formamidine disulfide dihydrochloride (FASCl) have been proposed. FAS^{2+} ion form an intermediate phase with lead halide species $x[FAS^{2+}]_2[PbI_2Cl_x]^{x-}$, which might intervene in the perovskite crystallization, eventually stabilizing the α -$FAPbI_3$ black phase.[86]

The complex nature of poly-halide colloids has been one of the main reasons for the perovskite deposition irreproducibility. The nucleation seeds are, in fact, difficult to control and to reproduce in number, dimension, and crystallinity. Herein, another strategy toward material deposition control could foresee the use of crystalline nucleation seeds, as probably occurred for chloride-containing inks ($PbCl_2$ is less soluble than PbI_2).[87,88] In the future it could be possible to introduce crystallites having a structure in line with the material target and being in the proper concentration for the specific deposition processing envisioned.

Another interesting development front would be the use of pre-synthesized perovskite powder through (solvent-free) mechanosynthesis[89] (obtained either by ball milling or manually grinding) that would be solubilized when needed. These materials demonstrate an exceptional intrinsic stability;[90] therefore, they can in principle be stored for a longer time, and perovskite powder would be more easily produced in large quantities, which is important for scaling up the production of perovskite devices. Additionally, mechanosynthesis can guarantee improved reproducibility and accessibility to disparate perovskite compositions with a precise stoichiometry control and phase pure materials,[91] not only for ternary halide perovskites but also mixed perovskites.

All these directions should contribute to a path toward large-scale manufacturing of perovskite-based solar cells, as this industrialization requires a superior knowledge of solution properties, which will allow economical, sustainable, and reproducible production of these devices.

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