



DOCTORAL DISSERTATION

# Development of lead-reduced perovskite photovoltaics

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#### Abstract

Perovskite solar cells (PSCs) are the most promising technology among third-generation solar cells and by far the most efficient solution-processable solar cells. Their greatest advantage is low-energy production and their fabrication ability on lightweight and flexible substrates. Currently, research is primarily focused on lead-based PSCs, which are the most efficient and stable of those being explored. Although they offer the potential for efficient technologies, lead toxicity is one of the factors hindering the commercialization of these solutions and poses problems related to subsequent management and disposal. Minimizing lead content in fabricated devices is the preferred approach to reducing potential lead exposure. In this dissertation, two main strategies were explored for minimizing lead content: (i) decreasing perovskite thickness and (ii) replacing lead with non-toxic tin in the perovskite composition. The next challenge in real commercialization is that most research efforts have focused on enhancing power conversion efficiency on small-area (~0.1 cm<sup>2</sup>) cells made on rigid substrates, which are far from being commercialized. Therefore, this thesis also considers advancing the development of large-area ( $\geq 1$  cm<sup>2</sup>) flexible perovskite solar cells and modules using various perovskite compositions.

The first chapter provides a brief introduction to PSC technology, outlining its theoretical aspects, working principle, and key features. The second chapter discusses concerns about lead toxicity, including environmental and health impacts associated with lead-based perovskites. It also analyses the main challenges associated with tin-based perovskites, proposed as the main alternative to lead-based ones. The third and fourth chapters provide a detailed overview of deposition and characterization techniques employed in the experimental section. The experimental section consists of a series of three publications and one patent application, all of which focus on the development and fabrication of PSCs with reduced lead content.

The first experimental chapter (Chapter 5) describes the reduction of the lead content by reducing the perovskite thickness. However, the formation of very thin, homogeneous perovskite layers becomes a challenge due to the strains present in the fabricated layers, and thus the generation of discontinuities that reduce photovoltaic performance. The study presents a working PSC with the thinnest perovskite layer reported so far, obtained using the spin-coating technique. The produced PSCs contain up to 50 times less lead than standard ones. By reducing the thickness of the remaining layers, semi-transparent PSCs have been obtained, with an application area far beyond the currently available opaque heavy silicon cells.

The second work (Chapter 6) focuses on the fundamental problem with the easy oxidation of  $Sn^{2+}$  into  $Sn^{4+}$ , resulting in poor stability of tin-based perovskites. It presents the development of a novel method for the synthesis of tin(II) iodide, a key precursor for the production of tinbased perovskites. The resulting perovskite ink and perovskite layers were characterized by significantly higher purity and stability compared to commercial precursors. This was achieved by eliminating  $Sn^{4+}$  impurities, which have an impact on material degradation and consequently reduce PSC performance. The work also demonstrates a flexible tin-based PSC with an active area of 1 cm<sup>2</sup>. The designed method has improved the performance and stability of the fabricated cells, which represents a further step towards the development of lead-free tin perovskite technology.

The third publication (Chapter 7) presents the first-ever report on a tin-based perovskite solar module fabricated by a scalable blade-coating technique. This result was achieved through a comprehensive approach that involved optimizing the perovskite composition, improving its deposition process, and enhancing crystallization by replacing the commonly used hole transport layer with its non-aqueous equivalent. An important part of the work was also optimizing the laser ablation process, which enabled an electrical connection between adjacent cells in the module. The champion device achieved 5.7% power conversion efficiency on a 25 cm<sup>2</sup> total module area.

The last part of the experimental section (Chapter 8) is about the patent application extending the method presented in Chapter 6. The described method allows to obtain a variety of metal halide salts, as well as perovskite precursor inks and powders. Perovskite layers prepared from the perovskite precursor ink, using metal halides synthesized according to the described method, are characterized by a lack or reduced amount of impurities compared to conventional synthesis or commercially available precursors.

This work aims to push further the development of sustainable photovoltaics and demonstrate that lead-reduced and lead-free PSCs can be produced on a large scale, giving them real potential for commercialization. The hypothesis that large-area perovskite solar cells and modules with a significant lead reduction can be successfully fabricated using perovskite ink engineering will be proven.

#### STRESZCZENIE

Perowskitowe ogniwa słoneczne są najbardziej obiecującą technologią spośród ogniw słonecznych trzeciej generacji i najbardziej wydajnymi ogniwami słonecznymi wytwarzanymi mokrymi technikami powlekania. Największą ich zaletą jest niskoenergetyczny koszt produkcji oraz możliwość wytwarzania na lekkich i elastycznych podłożach. Obecnie prowadzone badania są skoncentrowane na perowskitowych ogniwach słonecznych na bazie ołowiu, które są najbardziej stabilne i wydajne spośród eksplorowanych. Chociaż to one oferują duży potencjał pod kątem efektywnych technologii, to toksyczność ołowiu jest jednym z czynników utrudniających komercjalizację tych rozwiązań i stwarza realne problemy związane z ich późniejszym gospodarowaniem i utylizacją. Zminimalizowanie zawartości ołowiu w wytworzonych urządzeniach jest preferowanym podejściem w celu zmniejszenia potencjalnej ekspozycji na ołów. W niniejszej rozprawie doktorskiej zbadano dwie główne strategie minimalizacji zawartości ołowiu: (i) redukcja grubości perowskitu oraz (ii) zastąpienie ołowiu nietoksyczną cyną. Kolejnym wyzwaniem w komercjalizacji perowskitowych ogniw słonecznych jest fakt, że środowisko naukowe koncentruje się głównie na zwiększeniu wydajności konwersji energii ogniw o małej powierzchni (~0,1 cm<sup>2</sup>) wykonanych na sztywnych podłożach, które są dalekie od możliwości wprowadzenia na rynek. W niniejszej rozprawie przeprowadzono badania nad rozwojem elastycznych perowskitowych ogniw słonecznych i modułów o dużej powierzchni (≥1 cm<sup>2</sup>) dla różnych składów perowskitu.

Pierwszy rozdział stanowi krótkie wprowadzenie do technologii perowskitowych ogniw słonecznych, przedstawiając ich teoretyczny opis, zasadę działania oraz najważniejsze właściwości. W rozdziale drugim omówiona została problematyka toksyczności perowskitów na bazie ołowiu, w tym potencjalny wpływ perowskitów na środowisko oraz kwestie zdrowotne. Przeanalizowano również główne wyzwania związane z perowskitami cynowymi, które są główną alternatywą dla perowskitów ołowiowych. Rozdziały trzeci i czwarty zawierają przegląd technik osadzania i charakteryzacji stosowanych w części eksperymentalnej. Część eksperymentalna składa się z serii trzech publikacji i jednego zgłoszenia patentowego, z których wszystkie koncentrują się na rozwoju i optymalizacji wytwarzania perowskitowych ogniw słonecznych o obniżonej zawartości ołowiu.

Pierwszy rozdział eksperymentalny (rozdział 5) opisuje redukcję zawartości ołowiu poprzez zmniejszenie grubości warstwy perowskitu. Okazuje sie jednak, że wytwarzanie bardzo cienkich, jednorodnych warstw perowskitu jest dużym wyzwaniem ze względu na naprężenia obecne w wytworzonych warstwach, co może prowadzić do generowania nieciągłości

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prowadzących do zmniejszenia wydajności ogniw słonecznych. W pracy zaprezentowano działające ogniwo słoneczne z najcieńszą jak dotąd warstwą perowskitu uzyskaną za pomocą techniki powlekania obrotowego. Wyprodukowane ogniwa zawierają do 50 razy mniej ołowiu niż standardowe. Zmniejszając grubość pozostałych warstw, uzyskano półprzezroczyste perowskitowe ogniwa słoneczne, których obszar zastosowań znacznie wykracza poza obecnie dostępne nieprzezroczyste ciężkie ogniwa krzemowe.

Druga praca (rozdział 6) koncentruje się na fundamentalnym problemie szybkiego utleniania się jonów Sn<sup>2+</sup> do Sn<sup>4+</sup>, co prowadzi do niskiej stabilności perowskitów na bazie cyny. Przedstawiono w niej nową metodę syntezy jodku cyny(II), kluczowego prekursora do produkcji perowskitów cynowych. Otrzymany tusz perowskitowy i warstwy perowskitowe charakteryzowały się znacznie wyższą czystością i stabilnością w porównaniu do komercyjnych prekursorów. Osiągnięto to poprzez wyeliminowanie zanieczyszczeń jonami Sn<sup>4+</sup>, które mają wpływ na degradację materiału i w konsekwencji zmniejszają wydajność ogniwa słonecznego. W pracy zademonstrowano również elastyczne perowskitowe ogniwo słoneczne na bazie cyny o powierzchni aktywnej 1 cm<sup>2</sup>. Opracowana metoda poprawiła wydajność i stabilność wytworzonych ogniw, co stanowi kolejny krok w kierunku rozwoju technologii perowskitów bezołowiowych.

Trzecia publikacja (rozdział 7) przedstawia pierwsze w historii doniesienie na temat perowskitowego modułu słonecznego na bazie cyny wykonanego za pomocą skalowalnej techniki powlekania raklowego. Wynik ten został osiągnięty dzięki kompleksowemu podejściu, które obejmowało optymalizację składu perowskitu, udoskonalenie procesu jego osadzania oraz poprawę krystalizacji poprzez zastąpienie powszechnie stosowanej warstwy transportującej dziury na jej bezwodny odpowiednik. Ważną częścią pracy była również optymalizacja procesu ablacji laserowej, która umożliwiła połączenie elektryczne między sąsiednimi ogniwami w module. Najlepszy moduł osiągnął sprawność konwersji energii na poziomie 5,7% na powierzchni całkowitej modułu wynoszącej 25 cm<sup>2</sup>.

Ostatni rozdział części eksperymentalnej (rozdział 8) dotyczy zgłoszenia patentowego rozszerzającego metodę przedstawioną w rozdziale 6. Opisana metoda pozwala na otrzymywanie różnych soli halogenków metali, a także perowskitowych tuszy oraz proszków. Warstwy perowskitu przygotowane z roztworu prekursorów, wytworzonego przy użyciu halogenków metali zsyntezowanych zgodnie z przedstawioną metodą, charakteryzują się brakiem lub zmniejszoną ilością zanieczyszczeń w porównaniu do konwencjonalnej syntezy lub komercyjnie dostępnych prekursorów.

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Niniejsza praca ma na celu dalszy rozwój zrównoważonej fotowoltaiki, pokazując, że perowskitowe ogniwa i moduły słoneczne o obniżonej zawartości ołowiu mogą być produkowane na dużą skalę, co daje im realny potencjał komercjalizacji. Udowodniona zostanie hipoteza, że perowskitowe ogniwa słoneczne i moduły o dużej powierzchni o znacznie zredukowanej zawartości ołowiu mogą być z powodzeniem wytwarzane dzięki odpowiedniej inżynierii tuszu perowskitowego.

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# Motivation and hypothesis

The widespread adoption of perovskite solar cells (PSCs) is currently limited by the use of toxic lead, raising critical environmental and regulatory concerns. As a promising lead-free alternative, tin-based perovskites offer comparable optoelectronic properties while potentially mitigating toxicity issues. However, their commercialization remains challenging due to their inherent instability, particularly the rapid oxidation of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  under ambient conditions. Although various material engineering strategies have been explored, reliable and scalable synthetic methods for producing high-purity, oxidation-resistant tin(II) iodide are still lacking. Overcoming this bottleneck is essential for enabling the development of efficient, stable, and environmentally friendly PSCs.

This dissertation aims to improve methods for the fabrication of lead-reduced perovskite solar cells. The motivation for the research was outlined in Chapter 1.1 and is further expanded in Chapter 2, where both the toxicity of lead-based perovskites and the potential alternative of tinbased perovskites are discussed. Two deposition techniques were used to fabricate the perovskite layers: spin-coating and blade-coating. In addition, a wide range of structural, optical, and electrical characterization methods were used to assess material quality and device performance, which are described in Chapter 4 and the Supporting Information section of the related publications.

The structure of this dissertation is organized to reflect a logical progression from motivation and hypothesis through experimental methods and results, concluding with innovation and future perspectives. The hypothesis presented in the dissertation is that large-area perovskite solar cells and modules with a significant lead reduction can be successfully fabricated using perovskite ink engineering. To verify the hypothesis, detailed studies were carried out as outlined in Chapters 5, 6, and 7. These chapters are complemented by the patent application described in Chapter 8, which is an extension of the method reported in Chapter 6. The dissertation presents three different experimental approaches to verify the hypothesis:

1. **Fabrication of uniform ultra-thin perovskite layers** using a tailored perovskite ink composition based on highly pure precursors. The developed methodology enabled the production of lightweight semi-transparent perovskite solar cells with significantly reduced lead content.

- 2. **Development of a method allowing the** *in-situ* **synthesis** of tin-based perovskite ink with minimal impurities affecting the quality and stability of the produced films and devices. The new approach enabled the fabrication of completely lead-free perovskite solar cells with remarkable performance and long-term stability.
- 3. **Demonstration of the first-ever tin-based perovskite solar modules** achieved through optimization of the perovskite ink composition and additive engineering.

# 1 Introduction

## 1.1 Global warming and renewable energy sources

Global warming is one of humanity's biggest problems in the 21<sup>st</sup> century. It is the result of an increase in greenhouse gases concentration (mainly carbon dioxide, methane, and nitrous oxide) in the atmosphere, which then traps heat energy from the Earth's surface [1]. Radiative imbalance leads to an increase in the average temperature of the planet, triggering a range of adverse environmental changes. Some of these changes amplify the warming, causing an avalanche effect. For instance, an increase in the average temperature of the planet causes glaciers to melt, reducing Earth's albedo and thus absorbing more heat.

The main idea to tackle global warming is to minimize the production of greenhouse gases. The strategy now needs to change to keep warming below 1.5°C, as set out in the Paris Agreement and reinforced in the Glasgow Pact. Many countries have committed to net-zero emission targets by 2050 (including the European Union, United Kingdom, Japan, South Korea), 2060 (China), or 2070 (India) [2]. Quite a large amount of greenhouse gases is produced by burning fossil fuels, which still contribute about 80% of the world's energy production [3]. One possible solution is replacing fossil fuels with zero-carbon energy technologies, which include solar, geothermal, and wind power.

Photovoltaic technology, which directly converts solar energy into electricity, offers a practical and sustainable solution to meet the growing global demand for energy. Since the introduction of the first generation of crystalline silicon solar cells in 1954, photovoltaics has undergone significant evolution. Today, high-purity crystalline silicon remains the dominant photovoltaic product for commercialization, achieving power conversion efficiencies (PCEs) exceeding 27.6% and demonstrating long-term operational stability [4]. In principle, a solar cell absorbs a specific spectrum of sunlight, and by the photoelectric effect, pairs of charge carriers are generated. By separating and transporting electrons and holes to the corresponding electrodes, a potential difference is created, and the generation of an electric current flow is possible. Currently, the most popular material for absorbing solar radiation is crystalline silicon, providing about 97% of total production [5]. The main disadvantages of such cells are the low chances of further improvements in efficiency due to fundamental physical limitations, the weight due to thick substrates, and the need to use high temperatures during the manufacturing process, which has a direct effect on production costs. Although the price of silicon cells is

constantly decreasing, other solutions are being explored, which would be cheaper, more efficient, and allow for expanding the area of potential applications.

The next generations of solar cells relate to thin-film cells, which require much less absorbing material and can be deposited on flexible, lightweight substrates. The best-known types of second-generation cells are those based on amorphous silicon, cadmium telluride (CdTe), copper indium selenide (CIS), and copper indium gallium selenide (CIGS) [6]. The third generation of cells includes dye-sensitized solar cells (DSSCs), organic solar cells (OSCs), quantum dot solar cells (QDSCs), or perovskite solar cells (PSCs) [7]. Currently, the majority of third-generation solar cells have certain drawbacks and limitations - in the case of DSSCs, it is the liquid electrolyte, while in QDSCs the limitation is the high binding energy of the exciton [8–9]. These concepts have both advantages and disadvantages. However, it is not necessary to see them as a strict black and white contrast. There remains an area of the market where silicon cells cannot be used. The fact that the new generation of solar cells can be manufactured on flexible substrates allows them to be easily installed in many places inaccessible to heavy and rigid silicon cells [10–11].

This thesis relates to the most promising technology from third-generation photovoltaics – flexible perovskite solar cells.

#### 1.2 Metal halide perovskites

Metal halide perovskites are a great candidate for absorber material for solar cells due to their high absorption coefficient, tunable bandgap, and good charge transport properties [12]. The term perovskite refers to materials with a general chemical formula  $ABX_3$  and crystal structure adopted by the mineral called perovskite, which consists of calcium titanium oxide (CaTiO<sub>3</sub>) [13]. The crystal structure of perovskite is shown in Figure 1.



Figure 1. Cubic perovskite crystal structure. Reproduced with permission from Springer Nature [14].

Perovskite can be composed of many different elements. In the case of photovoltaic applications, the A-site cation is usually methylammonium (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, MA<sup>+</sup>), formamidinium (CH(NH<sub>2</sub>)<sub>2</sub><sup>+</sup>, FA<sup>+</sup>) or cesium cation (Cs<sup>+</sup>), the B-site cation is lead (Pb<sup>2+</sup>) or tin (Sn<sup>2+</sup>) cation, and the X-site anion is iodide ( $\Gamma$ ) or bromide (Br<sup>-</sup>) anion. To form a photoactive perovskite structure ABX<sub>3</sub>, the Goldschmidt tolerance factor *t* needs to be in the range 0.8 < *t* < 1, where

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)},\tag{1}$$

and  $r_A$ ,  $r_B$ , and  $r_X$  is the ionic radius of the corresponding atom [15]. If t is greater than 1, it is possible to form a two-dimensional layered structure. Usually, it is done by increasing the size of the A-site cation [16]. Calculated tolerance factors for a few different A-site cations are shown in Figure 2a.



Figure 2. (a) Goldschmidt tolerance factor of APbI<sub>3</sub> perovskite with different A-site cations: Cs – cesium, MA – methylammonium, FA – formamidinium, DMA – dimethylammonium, EA – ethylammonium, GA – guanidinium, AA – acetamidinium. Reprinted with permission from [16]. (b) Absorption coefficient spectra of MAPb(Br<sub>x</sub>I<sub>1-x</sub>)<sub>3</sub>. Reproduced from [17] with permission from the Royal Society of Chemistry.

The X-site anion and B-site cation have the main influence on the bandgap. An exchange of the X-site anion modifies the dimensions of the perovskite unit cell and thus the bandgap. A lower bandgap is obtained for a bigger anion. In the case of MAPbX<sub>3</sub>, the bandgap can be tuned from about 1.6 eV for MAPbI<sub>3</sub> to 2.3 eV for MAPbBr<sub>3</sub> [17]. Absorption coefficient spectra for different MAPbI<sub>3</sub> to MAPbBr<sub>3</sub> ratios are shown in Figure 2b.

#### 1.3 Perovskite solar cells

#### 1.3.1 Architectures and materials

The first perovskite solar cells originated from dye-sensitized solar cells, where the photoactive material was incorporated into a mesoporous structure responsible for collecting and transporting the generated charge carriers [18]. However, with the discovery of ambipolar transport in perovskite and their large diffusion lengths of carriers, the mesoporous structure was no longer required [19]. This advancement led to a much thinner planar architecture, where all layers are separated. Typically, the perovskite layer is sandwiched between layers responsible for selective carrier transport. The side through which light enters the solar cell determines its architecture. In the n-i-p architecture, the light first passes through the electron transport layer (ETL) and then the perovskite. Conversely, in the p-i-n architecture, light first passes through the hole transport layer (HTL). Depending on the chosen architecture, different materials are used for ETL and HTL to optimize performance. For ETL in n-i-p architecture, the most common are TiO<sub>2</sub> and SnO<sub>2</sub>, and for HTL 2,2',7,7'-tetrakis[N,N-di(4methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) [20]. Unfortunately, Spiro-OMeTAD requires some highly hygroscopic additives to improve conductivity, which can further affect the stability of PSC [21]. It can be overcome by the implementation of the p-i-n architecture, where for HTL many more materials can be used. From inorganic materials, the most promising are NiO<sub>x</sub>, CuSCN, and CuI, and from organic - poly[bis(4-phenyl)(2,4,6trimethylphenyl)amine] (PTAA), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and poly(3-hexylthiophene-2,5-diyl) (P3HT) [20]. The typical materials for ETLs are fullerene C60 and its derivatives [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) or 1',1'',4',4''-tetrahydro-di[1,4]methanonaphthaleno[5,6]fullerene-C60 (ICBA) [22]. The reason for different transport materials for n-i-p and p-i-n architecture is mainly the requirement of high transparency of the first layer and solvent compatibility for material deposited on top of the perovskite layer. For example, PEDOT:PSS aqueous dispersion is suitable as HTL in pi-n architecture but cannot be used directly as HTL in n-i-p architecture, as the water content would dissolve the perovskite layer.

#### 1.3.2 Working principle

In PSCs, the material responsible for absorbing light is perovskite. Photons of high enough energy reaching the perovskite layer excite electrons in the valence band, leading to the formation of an electron-hole pair. To generate current flow, these carrier pairs must be separated and transported to the appropriate electrodes. Figure 3 illustrates this mechanism.

Due to the low binding energy of the exciton and high mobility of charge carriers, they can easily reach the transport layers and then the electrodes. Charge carrier transport is enabled by an electric field and diffusion driven by the concentration gradient [23]. However, the charge carriers can recombine, which reduces the solar cell efficiency. In an ideal solar cell where only radiative recombination occurs, it is possible to achieve the theoretical efficiency limit proposed by Shockley and Queisser [24]. However, any non-radiative recombination results in efficiency loss, varying from the Shockley-Queisser limit. Non-radiative recombination typically arises from the presence of trap states, which form at grain boundaries in the perovskite or the interface between different materials [25].

The predicted maximum efficiency for a single junction solar cell with an optimal absorber bandgap close to 1.1 eV and a standard solar spectrum (AM1.5G, 1000 W/m<sup>2</sup>) is set at 33%. That value can be increased if calculations are done for different light sources (white fluorescent lamp, phosphor light-emitting diode). Maximum efficiency of about 57% is calculated for a bandgap of 1.82 - 1.96 eV and an artificial light source [26]. That bandgap can be obtained for perovskites, which opens a new area of application for them – indoor photovoltaics [11]. Shockley-Queisser limit can also be overcome by tandem solar cells, where two or more absorber layers are connected in one device [27].



Figure 3. Band diagram and main processes in PSC: 1) absorption of photon and free carrier generation; 2) charge carrier transport; 3) charge extraction to electrodes. Reprinted from [28] with permission from Elsevier.

# 2 Choice of perovskite absorber layer

## 2.1 Toxicity aspects of lead-based perovskites

The optical and electrical properties of perovskites based on lead are nearly ideal for solar cell applications. However, lead is a highly toxic element, raising significant concerns about potential leaching from PSCs and resulting environmental contamination. Nevertheless, the standard perovskite absorber is very thin (hundreds of nanometers). For example, in the case of the MAPbI<sub>3</sub> layer, approximately 33% of its mass is attributed to Pb. As a result, the total Pb content in PSC is less than one gram per square meter. Despite this, small amounts of lead contamination from PSCs pose a potential risk to soil and groundwater, where it could further transfer to plants, wildlife, or humans, depending on the environmental context. The proper management and disposal of PSCs at the end of their life cycle are essential to mitigate the risk. However, minimizing lead content in perovskite composition or replacing it entirely with nontoxic alternatives remains a critical goal. This is particularly important from the application point of this technology, such as wearable electronics, where devices are in close contact with humans.

Lead contamination can pose a significant risk at various stages of PSCs production and use. The first stage, cell fabrication, involves two main processes: perovskite ink preparation and ink deposition. During ink preparation, workers handle lead-based compounds, such as lead(II) iodide, often in powder form. This introduces potential exposure through dermal contact, ingestion, or inhalation if proper precautions are not taken. Similarly, during the ink deposition process, organic lead compounds, which are more bioavailable than inorganic forms, are used, further increasing the risk of contamination [29–30]. However, these risks can be significantly mitigated by adhering to proper work safety regulations.

The situation becomes more complicated when switching to the use and utilization of the cells at the end of their life cycle. At this stage, the cells may be deployed in poorly controlled environments such as on building rooftops. This raises concerns about potential sudden damage and lead leakage into the environment. Regarding the utilization of cells, an important issue here will be appropriate regulations for the collection and storage of used cells. However, it will also be impossible to fully control where the used perovskite cell will go, especially when it comes to smaller devices such as wearable electronics. To address these concerns, reducing the amount of toxic lead or eliminating it entirely is a critical step in developing and commercializing perovskite solar cells. In Chapter 5, the protocol for depositing ultrathin perovskite layers was presented with the demonstration of the thinnest spin-coated perovskite layer reported to date. The prepared PSCs contain up to 50 times less Pb than standard high-performing analogs. By reducing the perovskite layer and silver electrode thickness, semi-transparent PSCs were developed, enabling their use in many different applications such as building-integrated photovoltaics.

#### 2.2 Tin-based perovskites

To overcome the toxicity of lead-based perovskite solar cells, alternative perovskite formulations were investigated. Apart from low toxicity, ideal Pb-free candidates for solar cell absorbers should have narrow direct bandgaps, high optical absorption coefficients, high charge-carrier mobilities, low exciton-binding energies, long charge-carrier lifetimes, and excellent stability. Among all candidates, tin-based perovskites have gained the most attention due to their very similar properties compared to lead-based perovskite, while offering significantly reduced toxicity [30]. Tin has a comparable atomic radius and belongs to the same Group IVA of the periodic table. Furthermore, tin-based perovskites feature a narrower bandgap (1.2 -1.4 eV), which results in a higher theoretical limit of power conversion efficiency [31]. Unfortunately, tin-based perovskites have a few different features that negatively impact their efficiency and stability. One key issue is their higher conduction band minimum and valence band maximum level, which results in an energy mismatch with the charge transport layers commonly optimized for lead-based perovskites. This mismatch leads to losses in both opencircuit voltage and fill factor. However, the design of new transporting materials can prevent these deficits. This is a dynamic and growing area of research within the PSCs.

The main challenge for tin-based perovskites stems from their chemical nature, particularly the easy oxidation of  $Sn^{2+}$  into  $Sn^{4+}$ , which results in p-type doping and deterioration of optoelectronic properties. In lead-based perovskites, electrons in the 6s orbital of Pb<sup>2+</sup> are electromagnetically screened by electrons on 4f and 5d orbitals, and they remain unshared, which is called an inert-pair effect (lanthanide contraction) [32]. Electrons in the 5s orbital of  $Sn^{2+}$  are screened only by electrons on the 4d orbital, making oxidation into  $Sn^{4+}$  much easier (Figure 4a). The redox potential of the  $Sn^{2+}/Sn^{4+}$  couple is only 0.15 V, compared to 1.60 V for the Pb<sup>2+</sup>/Pb<sup>4+</sup> relative to the standard hydrogen electrode (SHE). This oxidation can occur *via* external oxidizing agents or intrinsic instability. Within the perovskite lattice,  $Sn^{4+}$  defects are metastable, allowing for the reverse reaction to occur:

$$Sn^{4+} \rightarrow Sn^{2+} + 2h^+,$$
 (2)

which will result in p-type doping of the perovskite [33]. Thus, it is crucial to ensure that a tinbased perovskite precursor solution contains as few  $\text{Sn}^{4+}$  ions as possible. Unfortunately, even highly pure commercial  $\text{SnI}_2$  (declared as 99.999% purity) can contain up to 10%  $\text{SnI}_4$ impurities due to its inherent instability, which significantly impacts the optoelectronic properties and stability of the resulting perovskite layers [34–35]. On the perovskite surface, a disproportionation reaction may also occur, leading to the formation of  $\text{Sn}^{4+}$  and metallic tin:

$$2 \operatorname{Sn}^{2+} \to \operatorname{Sn}^{4+} + \operatorname{Sn} + \operatorname{V}_{\operatorname{Sn}}^{2-}.$$
 (3)

The formed tin vacancy defects  $V_{Sn}^{2-}$  can act as electron traps, promoting lattice degradation into  $A_2SnI_6$  and  $SnI_4$ . Combined with p-type doping, this leads to a shift of the absorption onset to higher energies due to the Burstein-Moss effect. Consequently, increased non-radiative recombination and reduced charge-carrier mobility significantly deteriorate the final performance of PSCs [36].



Figure 4. Difference between Pb<sup>2+</sup> and Sn<sup>2+</sup>: (a) electron screening, (b) Lewis acidity. Reprinted with permission from [37]. Copyright 2021 American Chemical Society.

One additional challenge with tin-based perovskites arises from the high Lewis acidity of  $\text{Sn}^{2+}$ , which influences the crystallization rate of the perovskite (Figure 4b). Rapid crystallization results in smaller crystal grains and higher defect density. Combined with the inherent oxidation, these effects induce several unfavorable structural changes in the perovskite. Furthermore, exposure to oxygen and moisture can lead to decomposition of tin-based perovskites, as described by the following equations [34]:

$$2 \operatorname{ASnI}_3 + \operatorname{O}_2 \to \operatorname{SnI}_4 + \operatorname{SnO}_2 + 2 \operatorname{AI}, \tag{4}$$

$$\mathrm{SnI}_4 + 2\,\mathrm{AI} \to \mathrm{A}_2\mathrm{SnI}_6,\tag{5}$$

$$\operatorname{SnI}_4 + 2\operatorname{H}_2\operatorname{O} \to 4\operatorname{HI} + \operatorname{SnO}_2, \tag{6}$$

$$4 \text{ HI} + 0_2 \rightarrow 2 \text{ I}_2 + 2 \text{ H}_2 0, \tag{7}$$

$$ASnI_3 + I_2 \rightarrow SnI_4 + AI. \tag{8}$$

To suppress the decomposition of tin-based perovskite, minimizing the presence of  $Sn^{4+}$  species in the precursor ink or perovskite layer is crucial. Various strategies have been employed to reduce/eliminate  $Sn^{4+}$  content, with most reports highlighting the use of  $SnF_2$  additive (optionally  $SnCl_2$ ). This approach was first demonstrated in 2014 for the CsSnI<sub>3</sub> perovskite [38].  $SnF_2$  not only helps reduce  $Sn^{4+}$  content in the perovskite structure but also influences the film crystallization, leading to an improved perovskite film morphology. Interestingly,  $SnF_2$ does not act as a direct reducing agent for  $Sn^{4+}$ . Instead, it coordinates with  $Sn^{4+}$  through a ligand exchange reaction between fluorides from  $SnF_2$  and iodides from  $SnI_4$ , resulting in the formation of  $SnF_4$ , which remains mostly at the grain boundaries and is unlikely to be incorporated into the perovskite lattice [39].

Another option for minimizing  $\text{Sn}^{4+}$  content is the use of reducing additives such as Sn powder, hypophosphorous acid, or hydrazine derivatives [40–42]. The addition of bulky organic cations was also investigated [43–44]. In general, additives can function in three different ways: as reducing agents that directly convert  $\text{Sn}^{4+}$  to  $\text{Sn}^{2+}$ ; as antioxidants that prevent  $\text{Sn}^{2+}$  oxidation by reacting with O<sub>2</sub>, or by coordinating with  $\text{Sn}^{2+}$ , thereby providing protection against O<sub>2</sub>; similar to the ligand exchange mechanisms observed for  $\text{SnF}_2$  [45]. A schematic of these mechanisms is shown in Figure 5.



Figure 5. A schematic of three different general working mechanisms of additives used in tin-based perovskites. Reproduced from [45] with permission from the Royal Society of Chemistry.

Most strategies for improving tin-based perovskite quality involve the use of additives in the precursor solution, typically prepared from commercial SnI<sub>2</sub>. Alternatively, the quality of SnI<sub>2</sub> can be improved through synthesis and purification methods. However, processes are often complex and time-consuming, highlighting the continued need for innovative strategies. Chapter 6 discusses a novel approach to the *in situ* preparation of tin-based perovskite ink, offering a simple and rapid method that effectively eliminates p-type doping by preventing the formation of Sn<sup>4+</sup> impurities in perovskite ink and deposited layers. Chapter 7 expands on this by presenting a combination of different strategies, including the use of a quasi-2D perovskite structure, a reducing agent, and an additive to control crystallization dynamics.

# 3 Deposition techniques

#### 3.1 Perovskite ink preparation

A thin perovskite layer can be deposited by thermal evaporation of solid-state precursors or by wet methods in which the perovskite crystallizes from the precursor solution. Thermal evaporation is a well-known method for obtaining highly uniform layers, but it is more challenging to optimize for new perovskite compositions. In the research presented in this thesis, thermal evaporation was used only for deposition of ETL and the top electrode, while perovskite layers were fabricated using wet processes - spin-coating or blade-coating techniques. Both methods require the prior preparation of the perovskite precursor solution. In general, this involves dissolving perovskite precursors in an appropriate solvent mixture. However, numerous factors influence the quality of the perovskite layer and final device performance, starting with precursors purity, stochiometry, additives, preparation conditions, and the time between solution preparation and deposition. The purity of materials is important both for tin-based perovskites as well as lead-based as discussed in this thesis. The colloidal precursor ink depends on the particle-solvent interactions, and the used precursors significantly affect colloid formation, which influences the final morphology of perovskite layers. Impurities can also act as non-radiative recombination centers or trap states, which deteriorate the optoelectronic properties [46-47]. A more detailed description of ink chemistry was provided in Chapter 5.

Stochiometry also plays a critical role in both lead-based and tin-based perovskites. Many reports detailed that an excess of PbI<sub>2</sub> is beneficial for the final PSC efficiency [48–50]. In quasi-2D perovskites, stochiometry has a strong impact on the crystallization and orientation of perovskite grains [51–52]. Considering these relationships, detailed optimization of the perovskite ink is essential for obtaining high-quality layers and efficient PSCs. The optimal time for deposition can also vary among different compositions and used precursors. Achieving a balance between precursor dissolution, intermediate species formation, and the aggregation of complexes due to aging varies for each system and depends on its specific composition and precursors.

## 3.2 Perovskite crystal growth

Perovskite crystal growth can be effectively described in the framework of the classical nucleation theory, which involves the formation of monomers, supersaturation achieved

through solvent evaporation, and diffusion-controlled crystal growth. The free energy of a nucleus in this process is defined as [53]:

$$\Delta G(r) = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_V, \tag{9}$$

where *r* is the radius of the nucleus,  $\gamma$  is the surface free energy per unit area, and  $\Delta G_V$  is the free energy per unit volume of a crystal expressed as the difference between the free energy of the monomer in the crystal and solution.  $\Delta G(r)$  plot and critical radius  $r_c$  are shown in Figure 6a. To minimize free energy, nuclei smaller than  $r_c$  cannot grow further and will re-dissolve into smaller monomers. Only nuclei with a radius larger than  $r_c$  can exist and grow further.



Figure 6. (a) Free energy versus particle radius (solid line). Contributions from the surface and volume terms are plotted as dashed lines. Reprinted with permission from [54]. Copyright 2009 John Wiley & Sons, Inc. (b) LaMer diagram illustrating the nucleation and growth dynamics. Reproduced from [55] with permission from the Royal Society of Chemistry.

Crystal growth of perovskites is induced by solvent evaporation and can be described using the LaMer model. The process involves three stages, illustrated in the LaMer diagram shown in Figure 6b. In the first stage, monomer concentration increases as the solvent volume decreases over time. In the second stage, the concentration reaches a critical threshold known as the supersaturation stage. Nucleation starts, and it leads to a reduction in monomer concentration. Once the concentration falls below the critical supersaturation level  $[M]_{min}^*$ , no further nucleation occurs (starting of stage 3). Crystal growth continues and is completed when the monomer concentration drops below the solubility limit  $[M]_{sol}$  [55].

Another model that can be applied to perovskite growth description is Ostwald ripening [56]. This model suggests that smaller particles dissolve, which causes the growth of large ones. According to the Gibbs-Thomson theory, smaller particles dissolve more easily due to their higher chemical potential [57]. This creates a concentration gradient between particles of

different sizes. The concentration of dissolved components is higher around smaller perovskite grains than larger ones. As described by Fick's first law, this gradient drives mass transport from smaller to larger grains [58]. Consequently, large grains with lower chemical potential continue to grow, while smaller grains gradually disappear.

#### 3.3 Spin-coating

Spin-coating is a simple thin-film deposition technique that is widely used. Generally, in this method, the material is applied to a substrate that is rotated at high speed. The centrifugal force acting on the solution causes it to spread on the substrate. The final thickness of the film depends most on the solution concentration and viscosity, as well as the spin-coater rotational speed. However, conventional spin-coating can result in a low density of nuclei due to slow evaporation of the perovskite host solvent. To produce uniform and dense layers, a high density of nucleation centers is required at the same time. This is typically achieved by using antisolvent treatment. The antisolvent is a solvent that is miscible with the perovskite host solvent is applied by dripping it onto the spinning substrate. It induces instant supersaturation in the precursor solution by reducing the solubility of perovskite monomers, thereby promoting nucleation. A schema of the fabrication of perovskite films with antisolvent treatment is presented in Figure 7.



Figure 7. A schema of the perovskite layer fabrication process made with the spin-coating technique. Reprinted from [59] under CC-BY 4.0 license.

In addition to standard parameters like spin-coating speed and perovskite solution concentration, the quality of the resulting layer is strongly affected by the choice of antisolvent and timing of its application. The timing can be considered in two aspects: the moment of application of the antisolvent during the spin-coating process and the duration of its application. In the first case, the optimal application time depends on spin-coating parameters, and it needs to be optimized for every process. In the second aspect, controlling the application duration is

more challenging, as it mainly depends on the operator's technique. Therefore, the quality of the produced layers and the performance of solar cells may vary depending on the pipetting method used. With a fixed volume of antisolvent and a specific type of pipette, this application duration depends only on the speed at which the pipette trigger is pressed.



Figure 8. Different types of antisolvents and mechanisms involved in perovskite film formation. Reprinted from [59] under CC-BY 4.0 license.

In general, the addition of the antisolvent on top of the perovskite precursor layer during spincoating involves two key processes. The first one is the diffusion of perovskite host solvents into the antisolvent, which initiates nucleation and further growth of the perovskite layer. The second process is the diffusion of precursor molecules, which is undesirable. The efficiency of host solvent extraction while preserving the precursor composition is determined by the relative differences in solvent-precursor interactions in the chosen antisolvent. Based on these interactions, antisolvents can be classified into three categories [59]. The first category includes solvents such as ethanol or isopropanol, which have high solubility of organic precursors and high miscibility with host solvents. When such antisolvents are used, a significant portion of the organic precursor is removed, leaving an excess of inorganic compounds (PbI<sub>2</sub>, SnI<sub>2</sub>) in the fabricated layer. Antisolvents of this type require a short contact time to effectively remove the host solvents without significantly extracting organic halides. The second group consists of antisolvents that exhibit low solubility for organic compounds while being well miscible with the host solvents. Due to large differences in diffusion rates, good morphology layers can be achieved by fast as well as slow antisolvent dripping rates. These solvents are, for example, chlorobenzene, anisole, or ethyl acetate. The last type includes antisolvents that are relatively poor miscible with the perovskite precursor host solvents and require longer contact time to provide efficient diffusion of host solvents into the antisolvent. Examples of such solvents include toluene. A summary of the described processes for different types of antisolvents is shown in Figure 8.

#### 3.4 Blade-coating

Blade-coating is a technique commonly used to coat large-area substrates. In this method, the ink is deposited by the movement of the blade along the substrate. A schematic illustration of the blade-coating technique is shown in Figure 9. One key advantage of blade-coating over spin-coating is cost-effectiveness, as it requires significantly less ink to coat the same area. On the other hand, optimizing the blade-coating process is more complex because it involves numerous factors that influence film thickness and morphology. The most important factors are the speed of the blade and the gap between the blade and the substrate, although ink viscosity and surface energy of the substrate must also be considered [60]. Apart from those facts, the key difference between the blade-coating and the spin-coating is the inability to use the antisolvent in the blade-coating process. To achieve the supersaturation in this method, a different approach must be used. In this technique, supersaturation is achieved through strong gas flow (gas quenching method). Typically, an air knife is placed just behind the blade, where the ink is distributed. The gas flow enhances the solvent evaporation, leading to rapid supersaturation of the perovskite ink. Another method of increasing the solvent evaporation rate during blade-coating is heating the substrate. For optimal morphology and a uniform layer, the applied temperature should be close to the boiling point of the perovskite host solvents [61]. Unfortunately, typical perovskite host solvents like N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) have a boiling point above 150 °C, making it impractical to apply such high temperatures to flexible poly(ethylene terephthalate) (PET) substrates. Thus, other solvents with a lower boiling point and high vapor pressures are being explored for use in perovskite solar cells fabrication with the blade-coating technique [62].



Figure 9. A schematic illustration for gas-assisted blade-coating of perovskite thin films. Reprinted from [62] under CC-BY-NC 4.0 license.

## 4 Characterization techniques

### 4.1 Current-voltage measurements

The most common types of measurement techniques for every solar cell are current-voltage characteristics. Perovskite solar cells are typically characterized under the standard AM1.5G radiation spectrum (1000 W/m<sup>2</sup>) or low-light illumination conditions (typically 200 - 1000 lx). The AM1.5G spectrum represents the yearly average irradiance in the temperate latitudes on the Earth (for AM1.5, the solar zenith angle is equal to 48.2°). The performance of the solar cell can be described by three parameters derived from the measurement: the short-circuit current ( $I_{sc}$ ), the open-circuit voltage ( $V_{oc}$ ), and the fill factor (FF). The  $I_{sc}$  is the current generated under illumination when the voltage across the solar cell is zero. The  $V_{oc}$  is the maximum voltage that a solar cell can generate when no current flows through the circuit. The FF is defined as the ratio of the maximum power  $P_{max}$  generated by the solar cell to the product of the  $V_{oc}$  and  $I_{sc}$ :

$$FF = \frac{P_{max}}{V_{oc}I_{sc}}.$$
 (10)

Graphically, it is the ratio of the area of the largest rectangle that fits under the current-voltage (I-V) curve to the area of the rectangle determined by the values of  $V_{oc}$  and  $I_{sc}$ . The higher values of these parameters lead to increased power conversion efficiency (*PCE*). The *PCE* is defined as the ratio of the maximum power to the input power  $P_{in}$  of the radiation:

$$PCE = \frac{P_{max}}{P_{in}} = \frac{V_{oc}I_{sc}FF}{P_{in}}.$$
(11)

The short-circuit current is generally determined by the energy gap of the perovskite and the thickness of its layer. However, if the charge collection is not sufficient, it can be significantly reduced. The plot of theoretical values of short-circuit current density ( $J_{sc}$ ,  $I_{sc}$  divided by the active area of the solar cell) as a function of the absorber layer energy gap is shown in Figure 10a. Those calculations assume an optimal thickness of the absorber layer. However, if the carrier diffusion lengths are insufficient relative to the layer thickness, significant current losses can occur. Improving perovskite layer quality by reducing defect density can enhance diffusion lengths, enabling better charge extraction and overall performance [63].

In the case of  $V_{oc}$ , the maximum theoretical value is also determined by the energy gap. A larger bandgap generally leads to a higher theoretical  $V_{oc}$ , but on the other hand, it leads to lower  $J_{sc}$ .

The relationship between  $V_{oc}$  and the energy gap is shown in Figure 10b. In an ideal case, the  $V_{oc}$  can be expressed as:

$$V_{oc} = \frac{E_{Fn} - E_{Fp}}{q},\tag{12}$$

where *q* is the elementary charge,  $E_{Fn}$  and  $E_{Fp}$  are the quasi-Fermi energy levels of electrons and holes, respectively [64–65]. Fermi energy level splitting results from the excitation of electrons into the conduction band under external illumination. However, direct calculation of  $V_{oc}$  from the difference between  $E_{Fn}$  and  $E_{Fp}$  is not possible for PSCs due to energy gap tail states – the density of states distribution in perovskites extends far into the energy gap [63–66].



Figure 10. (a) The short-circuit current density  $J_{sc}$  and (b) the open-circuit voltage  $V_{oc}$  calculated for the AM1.5G irradiance as a function of the energy gap of the absorber. Reprinted from [67] with permission from Elsevier.

Considering the solar cell as an equivalent circuit comprising a constant-current source, a diode, and an external load, the  $V_{oc}$  can be expressed as:

$$qV_{oc} = nk_BT \cdot \ln\left(\frac{J_{sc}}{J_0} + 1\right),\tag{13}$$

where *n* is the ideal coefficient of the diode,  $k_B$  is the Boltzmann constant, *T* is the cell temperature, and  $J_0$  is the reverse saturation current density. The  $J_0$  is the sum of currents generated by radiative and non-radiative recombination [63]. The radiative recombination and associated voltage losses are inevitable [68]. Therefore, the non-radiative recombination is the critical factor influencing  $V_{oc}$ , and it can lead to significant variations in  $J_0$ . In the tin-based PSCs, one of the main causes of  $V_{oc}$  loss is the oxidation of Sn<sup>2+</sup> to Sn<sup>4+</sup> [69–70]. Strategies to mitigate this voltage loss by eliminating Sn<sup>2+</sup> oxidation in PSCs are presented in Chapter 6.

The final parameter affecting PCE is the fill factor, which represents resistive losses in the circuit. Both series resistance and shunt resistance influence the fill factor. Low FF is often caused by high series resistance, which includes resistances of all layers and contacts, or low

shunt resistance. The shunt resistance is often connected with the leakage current through pinholes in the perovskite layer, where HTL and ETL may come into direct contact. Additionally, non-radiative recombination can also affect this parameter [71]. Values of shunt and series resistances can be extracted from the current-voltage curve (Figure 11).



Figure 11. Series ( $R_s$ ) and shunt resistance ( $R_{sh}$ ) extraction from a single I-V curve under illumination. Reprinted from [72] under CC-BY 4.0 license.

#### 4.2 External quantum efficiency

The external quantum efficiency (EQE) is the standard measurement method for solar cells, complementary to the current-voltage measurements. This method can validate  $J_{sc}$  value obtained from the current-voltage scan. Discrepancies between these values may arise from an incorrectly calibrated solar simulator, inaccuracies due to a small device area, or differences in measurement conditions (such as light intensity, measuring time) [73]. The EQE represents the ratio of charge carriers generated and collected by the solar cell to incident photons at each wavelength. The carrier flow at each wavelength can be calculated by multiplying the EQE spectrum by the AM1.5G spectrum. Integrating the results over the entire wavelength range gives  $J_{sc}$  of the solar cell:

$$J_{sc} = q \int_0^\infty \varphi(\lambda) EQE(\lambda) d\lambda , \qquad (14)$$

where  $\varphi(\lambda)$  is the AM1.5G photon flux. The EQE spectrum also provides information about wavelength ranges where the solar cell generates current inefficiently. Ideally, the EQE should be equal to 100% for photon energies above the absorber bandgap and 0% below it. In practical solar cells, the EQE is below 100% due to optical losses, such as absorption of the light by inactive layers, and non-radiative recombination or insufficient charge carrier collection by transport layers and electrodes. Due to the different penetration depths of the light, EQE reduction in the high-energy region is associated with recombination at the front surface, while for longer wavelengths it is associated with recombination at the rear surface. The EQE spectrum and current density-voltage curve of a typical perovskite solar cell are shown in Figure 12.



Figure 12. Current density-voltage curve and the EQE spectrum of a typical perovskite solar cell. Reprinted from [74] under CC-BY 4.0 license.

Because of its direct relationship with the light absorption, the EQE measurement can provide an estimated bandgap value of the absorber layer. Various methods are used to extract bandgap value from EQE measurements, but for perovskite solar cells, the most accurate method showing minimal deviation compared to absorption measurements is determining the inflection point of the EQE curve derivative [75].

The standard EQE setup consists of the light source, monochromator, and current meter. Usually, the light beam is modulated using an optical chopper, enabling measurement with a lock-in amplifier. This allows the application of white light bias to simulate conditions similar to current-voltage measurement. The lock-in amplifier isolates and measures only the current generated by monochromatic probe light. The output current is then normalized to the number of incident photons by reference to a solar cell with a known spectral response. Some of the EQE setups allow simultaneous measurement of the test cell and reference cell for better accuracy.

In the case of PSCs, slight discrepancies can often be observed between  $J_{sc}$  obtained from the EQE and  $J_{sc}$  from current-voltage measurements. This difference arises from a few possible mechanisms. During measurements, ion migration within the perovskite layer can alter the local crystal structure and cause defect migration [76]. The EQE measurement requires a much longer time and thus may amplify these effects. On the other hand, ion movement can also be triggered by external bias during current-voltage measurement. Additionally, due to the long response time of PSCs, a high modulation frequency of the light beam can distort the measured current [74–77]. Considering these factors, it is crucial to evaluate various conditions and preconditioning protocols for PSCs to ensure accurate and reliable EQE measurement.

## 4.3 UV-Vis absorbance spectroscopy

Absorbance spectroscopy is a simple and quick method for optical characterization of thin layers. It measures how much light the sample absorbs at each wavelength. The basic absorbance setup includes a broadband light source, a monochromator, and a detector. Absorbance (A) is closely related to the transmittance spectrum through the following equation:

$$A = \log_{10} \left( \frac{I_0}{I} \right), \tag{15}$$

where  $I_0$  is the transmittance of the reference sample (e.g., glass or flexible foil), and I is the transmittance of the measured sample. If the sample thickness is known and the reflectance is negligible, the absorption coefficient ( $\alpha$ ) can be calculated using the Bouguer-Beer-Lambert law [78]:

$$\alpha = \frac{1}{d} \ln\left(\frac{I_0}{I}\right) = \frac{A}{d} \ln(10) \approx 2.303 \frac{A}{d},\tag{16}$$

where d is the thickness. Knowing the spectrum of the absorption coefficient, the bandgap value can be easily extracted. The most suitable method is using Tauc's relation [79]:

$$(\alpha h v)^{\frac{1}{n}} = B(h v - E_g), \tag{17}$$

where *B* is a proportional constant, *h* is the Planck constant, *v* is the frequency of light,  $E_g$  is the bandgap energy, and *n* depends on the electronic transition type. For a direct bandgap with an allowed transition, *n* is equal to 0.5; for an indirect bandgap, *n* is equal to 2. By plotting the

left side of the above equation against the photon energy hv and extrapolating the linear region to 0, the bandgap of the material can be determined (Figure 13).



Figure 13. (a) Tauc plot for semiconductors with a direct bandgap and (b) with an indirect bandgap. Reprinted from [80] under CC-BY-NC-ND 4.0 license.

#### 4.4 X-ray diffraction

X-ray diffraction (XRD) is a useful technique for determining a material's crystallographic structure. Additionally, XRD can be used to evaluate perovskite grain size and intrinsic strains. The working principle of XRD is based on Bragg's law. When the X-ray beam is directed at the sample, the material diffracts it. At specific angles ( $\theta$ ), the path difference between rays diffracted from adjacent atomic planes ( $2d \sin\theta$ ) is equal to a multiple of the wavelength ( $n\lambda$ ), resulting in constructive interference (Figure 14):

$$2d\sin\theta = n\lambda\,,\tag{18}$$

where *d* is the distance between atomic planes,  $\theta$  is the angle between the X-ray beam and the atomic plane (Bragg angle), and  $\lambda$  is the X-ray wavelength [81]. By scanning across a range of angles, the diffraction pattern is generated, providing insight into the material's structural properties.



Figure 14. A schematic diagram showing Bragg's law. Reprinted from [82] with the permission of AIP Publishing.

The main element in the laboratory-scale XRD setup is the X-ray source, where X-rays are generated by high-energy electron collisions with a target metal. Electrons emitted from a tungsten cathode are accelerated by an electric field to the anode. The characteristic radiation is metal-specific, consisting of discrete emission signals with energy corresponding to the difference between specific energy levels of the metal atom. The anode material must also possess a high melting point to withstand the heat generated by incident electrons. The most common are copper anodes, producing X-rays with a wavelength of 1.54 Å [83]. Heavier elements than copper, such as molybdenum or silver, generate shorter wavelengths, leading to contracted XRD patterns and reduced resolution. On the other hand, shorter wavelengths increase penetration depth and can be used for specific samples with high X-ray absorption. Synchrotron sources can also generate X-rays by bending high-energy relativistic electrons from their path. That radiation is used for more advanced experiments such as grazing-incidence wide-angle x-ray scattering (GIWAXS).

The most suitable for measuring flat samples is the Bragg-Brentano geometry, where X-rays are diffracted from the sample, and the detector is placed at the same angle as the source [84]. It is also called reflection-based diffraction geometry. In the Debye-Scherrer geometry, a transmission-based method, the X-rays pass through the sample [85]. The measurement can be performed in two scanning modes: by moving the source and the detector simultaneously  $(\theta - \theta \text{ scan})$  or by rotating the sample and the detector  $(\theta - 2\theta \text{ scan})$ .

The XRD measurement produces a plot of diffraction intensity versus  $2\theta$  angle. Beyond identification of the crystallographic structure of the material, XRD provides insights into the microstructure, including crystallite sizes and microstrains. The crystallite size *D* can be calculated using the Scherrer equation:

$$D = \frac{K\lambda}{FWHM\,\cos\theta},\tag{19}$$

where *K* is the Scherrer constant,  $\lambda$  is the X-ray wavelength, *FWHM* is the full-width at halfmaximum of the diffraction peak, and  $\theta$  is the Bragg angle [86]. Scherrer constant depends on the shape of the crystallite. In the case of a sphere, the Scherrer constant is equal to 0.89, and often that value is used for calculation, where the shape of crystallites is not known [87]. However, the obtained result may contain significant errors, due to the assumption that the peak broadening is solely caused by crystallite size, which often is not true for samples with numerous structural defects. The presence of those defects causes strains in the crystal lattice, and that phenomenon can also cause the broadening of diffraction peaks [88]. Additional broadening  $\beta_{strain}$  is expressed as:

$$\beta_{strain} = 4\varepsilon \tan\theta, \tag{20}$$

where  $\varepsilon$  is a parameter related to microstrain [89]. The total broadening (proposed by Williamson and Hall) is therefore given as [90–91]:

$$FWHM = \frac{K\lambda}{D\cos\theta} + 4\varepsilon\,\tan\theta.$$
(21)

In other form, it can be expressed as:

$$FWHM \cos\theta = \frac{K\lambda}{D} + 4\varepsilon \sin\theta.$$
 (22)

Plotting the *FWHM cos* $\theta$  as a function of  $4 \sin\theta$  for each Bragg peak should result in a linear function with the intercept equal to  $\frac{\kappa\lambda}{D}$ , and the slope equal to the microstrain parameter  $\varepsilon$ .

### 4.5 Scanning electron microscopy

Scanning electron microscopy (SEM) was employed to investigate the topography of the fabricated perovskites in this thesis. The main components of an SEM setup include an electron source, an accelerating column, detectors, a vacuum pump, and a sample chamber (Figure 15). Electrons are generated at the top of the column, accelerated, and passed through a series of magnetic lenses to produce a finely focused beam. The beam position is controlled by electromagnetic coils placed above the lenses. This allows point-by-point scanning of the sample surface to generate a complete image. Additionally, to minimize electron scattering caused by air molecules, measurements are conducted in a high-vacuum environment.


Figure 15. A schema of the SEM setup. Reprinted from [92] under CC-BY-NC-ND 4.0 license.

The SEM measurement employs a focused beam of high-energy electrons to generate signals from the investigated sample. The energy of the incident electrons is dissipated in the form of signals that include secondary electrons (SE), backscattered electrons (BSE), and X-rays. Secondary and backscattered electrons provide information about the surface of materials. Secondary electrons originate from atoms near the surface region, offering detailed information about the topography of the sample. Backscattered electrons are reflected from deeper regions of the sample and are sensitive to the size of atoms; a higher atomic number results in more electrons being reflected to the detector. X-rays are produced by inelastic collisions between the electron beam and electrons in the atomic shells of the sample. As the excited electrons return to lower energy states, they emit X-rays with wavelengths specific to the type of transition and the atom involved. This principle underlies the operation of the X-ray source in XRD measurements. Consequently, scanning electron microscopy can also be used to analyze the elemental composition of the sample through energy-dispersive X-ray spectroscopy (EDX) [93]. A schematic diagram showing the various signals is presented in Figure 16.

The electron beam penetrates the sample to a depth determined by the electron accelerating voltage and the size of the atoms in the material. Greater penetration depth increases the volume of the sample contributing to the signal, reducing spatial resolution. Therefore, the acceleration voltage must be carefully selected based on the sample type and the desired information. Another requirement is the good conductivity of the investigated material. For non-conductive samples, a conductive coating is required to ensure high-quality imaging and accurate analysis.

Otherwise, the charge accumulation can occur, distorting the electron beam and resulting in a deformed image [94–95].



Figure 16. A schematic diagram showing different types of signals generated during SEM measurement. Reprinted from [96] with permission from Elsevier.

# 4.6 Other methods

This chapter provides a detailed description of the main characterization techniques in which the author was directly involved. An understanding of the physical principles underlying these methods has served as a fundamental tool for analyzing and interpreting the results, as well as for formulating scientific conclusions. Several other measurement techniques, such as photoluminescence (PL), dynamic light scattering (DLS), Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and nuclear magnetic resonance (NMR), were also utilized in the presented publications. The author has participated in some of these measurements, although to a lesser extent. Detailed measurement parameters are provided in the supplementary material (Supporting Information) attached to the respective publications.

# 5 Facile Preparation of Large-Area, Ultrathin, Flexible Semi-Transparent Perovskite Solar Cells via Spin-Coating

# 5.1 Overview

The publication presents an innovative approach to addressing environmental concerns in PSCs by significantly reducing lead content through minimizing the thickness of the perovskite layer. A groundbreaking achievement was realized with the fabrication of semi-transparent PSC, utilizing the thinnest perovskite layer ever produced by the spin-coating technique. This marks a significant advancement, as previous attempts to produce thinner layers by spin-coating (<50 nm) often resulted in non-uniform films with island-like structures. In the broader context, the state-of-the-art for obtaining ultrathin perovskite layers mainly relies on vacuum deposition techniques, which offer precise control over film thickness and uniformity. However, these methods are often costly and less scalable compared to solution-based approaches. This study bridges this gap by demonstrating that spin-coating can achieve comparable results in terms of ultrathin layer fabrication. It shows both the technical feasibility and scalability of producing efficient semi-transparent PSCs, which are excellent candidates for building-integrated photovoltaics. This work not only sets a new benchmark for spin-coated PSCs but also paves the way for future advancements in thin-film photovoltaics. By addressing challenges related to uniformity, lead content, and scalability, it represents a critical step forward in the quest for sustainable PSC technologies that are in line with modern energy and architectural demands.

# 5.2 Author's contribution

Wiktor Żuraw performed and optimized the fabrication process of semi-transparent perovskite solar cells presented in the article, carried out their current-voltage characteristics, and participated in the preparation of the original manuscript text. The author also performed transmittance, external quantum efficiency, and scanning electron microscopy measurements, with the analysis and interpretation of the obtained results. Wiktor Żuraw and Łukasz Przypis (co-supervisor) contributed equally to this work.

# 5.3 Publication

# Facile Preparation of Large-Area, Ultrathin, Flexible Semi-Transparent Perovskite Solar Cells via Spin-Coating

Łukasz Przypis,<sup>\*, $\nabla$ </sup> Wiktor Żuraw,<sup> $\nabla$ </sup> Miłosz Grodzicki, Mateusz Ścigaj, Robert Kudrawiec, and Artur P. Herman



nm thick silver electrode. We present a simple yet elegant fabrication procedure for semitransparent perovskite solar cells without any additional antireflective layers. Furthermore, we fabricated working perovskite solar cells with the thinnest active layer of spin-coated MAPbI<sub>3</sub> reported so far (10 nm) exhibiting 1.9% PCE and 41.1% AVT (62.9% AVT without electrode). These results hold great promise for the integration of perovskite-based semitransparent solar cells into real-world applications, advancing the landscape of renewable energy.

KEYWORDS: semitransparent solar cells, flexible solar cells, metal halide perovskites, spin-coating, methylammonium lead iodide

#### INTRODUCTION

Metal halide perovskites (MHPs) and in particular hybrid organic inorganic perovskites (HOIPs) appear as a truly gamechanging family of materials for energy conversion due to the unique combination of optoelectronic properties and relatively facile fabrication processes, which have contributed to their widespread exploration as a potential alternative to conven-tional solar cell technologies.<sup>1–5</sup> Perovskite solar cells (PSCs) are by far the most efficient solution-processable solar cells, with a record power conversion efficiency (PCE) of 26.1% for single-junction opaque solar cells.<sup>6</sup> Despite impressive efficiencies and acceptable stability levels, there are still current limitations that impede their widespread commercialization. One area of particular interest within the field of MHP-based optoelectronic devices is the development of semitransparent ultrathin solar cells. The semitransparent perovskite solar cell (ST PSC) design represents an innovative approach, offering alternative and potentially faster pathways toward commercialization, even without achieving a PCE comparable to the dominating silicon (Si) modules. The integration of semitransparent perovskite layers in solar cells offers exciting opportunities for applications such as building-integrated photovoltaics (BIPV).<sup>7</sup> Semitransparent photovoltaic technol-

Visible Transmittance (AVT) of 21.5% for full device architecture with a 10

ogy not only generates power but also contributes to creating a comfortable natural living environment. Allowing natural light to enter the building, it simultaneously reduces the energy consumption. Additionally, it can control the spread of heat, providing both temperature and visual comfort.<sup>8–10</sup> In addition to the high PCE, the PSCs have a good application prospect in the field of semitransparent photovoltaic devices owing to the high absorption coefficient and the low-temperature preparation processes.<sup>11</sup>

The quest for semitransparent perovskite layers involves overcoming several technical challenges. One of the primary concerns is maintaining uniform ultrathin film coverage while minimizing the occurrence of pinholes and voids, which is critical for attaining high-quality perovskite layers. Insufficient reproducibility and homogeneity result in a spread of performance in the resulting photovoltaic devices. Semi-

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#### Table 1. Characteristics of Semi-Transparent PSCs with Active Layer Thickness below 100 nm

active area	device architecture	thickness	PCE	AVT (%), spectral range	ref
glass 0.06 cm <sup>2</sup>	FTO/c-TiO <sub>2</sub> /AAO(honeycomb shaped scaffold) + MAPbI <sub>3-x</sub> Cl <sub>x</sub> /Spiro-OMeTAD/ MoO <sub>x</sub> /ITO	90 nm <sup>a</sup>	8.50%	43, 400-800	21
glass, 0.16 cm <sup>2</sup>	FTO/c-TiO <sub>2</sub> /MAPbI <sub>3</sub> /Spiro-OMeTAD/MoO <sub>x</sub> /Au/MoO <sub>x</sub>	54 nm <sup>a</sup>	5.30%	31, 370-740	22
glass 0.06 cm <sup>2</sup>	ITO/PTAA/Cs <sub>0.1</sub> FA <sub>0.9</sub> PbI <sub>2.9</sub> Br <sub>0.1</sub> /PCBM/BCP/Al/Ag	50 nm <sup>b</sup>	6.93%	31, —	20
flex 0.08 cm <sup>2</sup>	ITO/MoO <sub>x</sub> /TaTm/MAPbI <sub>3</sub> /C <sub>60</sub> /BCP/Cu/Ag	50 nm <sup>b</sup>	4.03%	19, —	23
glass 0.12 cm <sup>2</sup>	ITO/PEDOT:PSS/MAPbI <sub>3</sub> /PCBM/Au/LiF	40 nm <sup>b</sup>	3.40%	35, 400-800	24
glass 0.05 cm <sup>2</sup>	ITO/PTAA/PEA-CsPbI <sub>3</sub> /PCBM/BCP/Al/Ag	10 nm <sup>b</sup>	3.60%	54, —	20
This work:					
flex 1.00 cm <sup>2</sup>	IZO/PEDOT:PSS/MAPbI <sub>3</sub> /C <sub>60</sub> /BCP/Ag	30 nm <sup>a</sup>	5.70%	21.5, 300-900	
flex 1.00 cm <sup>2</sup>	IZO/PEDOT:PSS/MAPbI <sub>3</sub> /C <sub>60</sub> /BCP/Ag	10 nm <sup>a</sup>	1.90%	41.1, 300-900	
<sup><i>a</i></sup> Spin-coated. <sup><i>b</i></sup>	Vacuum deposited perovskite layer.				

transparent perovskite films can be obtained using diverse wellestablished deposition techniques such as spin-coating,<sup>12</sup> blade-coating,<sup>13</sup> and dip-coating.<sup>14</sup> These methods are very convenient considering further scaling-up, however, thickness control within the crucial for transparency sub-100 nm range is significantly limited.<sup>15</sup> Therefore, new approaches to overcoming these obstacles have been developed.

First, the so-called spontaneous dewetting, which employs the treatment of as-prepared perovskite thin film with low-vapor-pressure solvent.<sup>16</sup> This method results in an archipelago-like microstructure (randomly grown perovskite islands) of an active layer providing the neutral color of full devices. Another alternative is mesh-assisted deposition which leads to a similar microstructure with partial coverage of the perovskite film on the substrate which is achieved by controlled growth in a grid structure.<sup>16-19</sup> The major disadvantage of these two methods, putting aside the additional processing step, is that electron- and hole-transporting materials (ETM and HTM respectively) are in direct contact. Quite recently preparation of conformal perovskite 10 nm layer using vacuum evaporation has been reported.<sup>20</sup> Despite promising results, the entire fabrication process is much more complex, though, and therefore more challenging for scaling up. Hence, the preparation of sub-100 nm perovskite films with a conformal profile in the wet process is still a challenge. In Table 1, we provide a summary that compares our results to previously reported solution-processed and thermally evaporated semitransparent perovskite devices.<sup>21-24</sup> Here it is worth noting that taking into account active area and flexible substrate our results are unprecedented in terms of PCE and AVT. Furthermore, one should note that considering real-world applications and technological significance our process is the only one which does not require vacuum evaporation or specially prepared substrates.

Understanding the formation mechanism of solid perovskite film from precursor solution is one of the fundamental rules for the preparation of high-quality perovskite films. However, few studies have focused on the effect of colloidal characteristics on the formation of perovskite films. In our work, we deem that high-quality spin-coated ultrathin perovskite films can be obtained by designing and controlling the colloidal characteristics of the perovskite precursor. A comprehensive understanding of precursor solution impurities and their effect on the material properties is essential for the improvement of photovoltaic performance. It directly impacts the thin film quality and device performance. Precursor purity in solution is also considered to affect the characteristics of the perovskite films such as crystal growth, charge carrier recombination dynamics, and electron/hole diffusion length.<sup>25</sup> Even common methods, such as raw material mixing, can yield lead polyhalide coordination complexes. Solvent molecules may compete as ligands for  $Pb^{2+}$ . The presence of these complexes, intermediate phases, or impurities hampers nucleation and crystal growth, affecting the physiochemical properties and reproducibility. Precursor ink, typically colloidal, depends on particle—solvent interactions. The size and concentration of colloids affect the film quality and morphology. Lead polyhalide networks in the solution impact the crystallization rate and final properties. Colloid formation and stabilization are influenced by precursor purity. Defects and grain boundaries cause performance losses.

Importantly, our objective was not to optimize the device structure for the best performance or PL emission. Instead, our aim was to demonstrate that using simple processing, i.e., spincoating of an ultrathin perovskite layer by one-step methodology, we are still able to obtain good performance with high transparency of PSCs on large-area flexible substrates. We are convinced that our methodology is not limited solely to spincoating, but it holds great promise for other wet fabrication methods of PSCs such as blade-coating or slot-die-coating as they also rely on ink chemistry.

#### RESULTS AND DISCUSSION

Keeping in mind all the complexities related to the precursor ink composition, we decided to follow the quote 'simplicity is the keynote of all true elegance' by Coco Channel, i.e., we used highly pure raw materials without additives. To avoid the use of hydroiodic acid and accompanying hypophosphorous acid (HPA) stabilizer, we synthesized MAI using molecular iodine as a halide source, which was subsequently reduced in situ by formic acid, resulting in the production of highly pure methylammonium iodide.<sup>26</sup> Furthermore, this method enables effective purification of MAI, particularly from residual iodine, which contributes to its exceptional stability without the requirement for external stabilizers, as evidenced in Figures S3 and S4. Additional discussion on the precursor ink chemistry is detailed in the Supporting Information. Although in this work we used freshly synthesized MAI, in Figure S1 two year old MAI without any evidence of aging is presented (i.e., no yellowing which originates from the presence of free-iodine can be observed). As a lead source, we used commercial PbI<sub>2</sub> of high purity (see Figure S2). The inks were prepared by dissolving precursors in DMF:DMSO mixture (9.0:1.1, v/v).





Figure 1. (a) Colloidal properties of perovskite precursors at room temperature-size distribution by dynamic light scattering for fresh inks: black -0.085 M, pink -0.050 M, red -0.037 M; (b) aged ink 0.050 M: pink-fresh, magenta -48 h, ruby -7 days; (c) FTIR spectra of perovskite precursors with different concentrations: blue -1.00 M, green -0.050 M, re -0.037 M.

The resulting dispersion was stirred for 2 h at room temperature to get the transparent inks.

First, we started the characterization of the prepared perovskite precursor solution by the rheological properties of the perovskite precursor solution. We measured dynamic light scattering (DLS). The perovskite precursor inks prepared by our strategy demonstrated a narrow size distribution of colloidal particles with a distribution around 100 nm (Figure 1a). The presence of a small and narrowly distributed particle size is beneficial for the creation of dense and compact packed grain structures in the resulting films.<sup>27,28</sup> Additionally, it is noteworthy that the elimination of larger micrometer-sized particle distribution is accomplished through the use of ultrapure precursors.

Plausible, in our philosophy, using ultrapure methylammonium iodide and lead iodide, the solvation of perovskite precursors in the DMF/DMSO solvent system was systematic. Colloidal nuclei were well-formed, and the dissolution of the precursor occurred at a similar rate. Finally, a narrow size distribution of the particles in the solution was obtained. These nanosized particles are not likely iodoplumbate complexes but are probably perovskite-solvent complexes like the intermediate phase. In contrast, in the typical MAPbI<sub>3</sub> precursor ink, the formation of the colloid may be affected by insoluble impurities, which introduce the seeds leading to the growth of bigger particles. Furthermore, we conducted an investigation into the stability of our inks over time, performing DLS measurements after 48 h and 7 days. Impressively, our inks exhibited remarkable stability over time, showing no signs of particle aggregation (Figure 1b). For the investigation of the chemistry of precursor solutions, MAPbI3 inks with various concentrations at RT were studied by using FTIR spectroscopy. It can be clearly seen in. Figure 1c that the position of bands is independent of the concentration of perovskite.

The following spectral features for each ink can be distinguished; S-O and C-S stretching vibrations related to interactions of DMSO with Pb2+ at ~1000 cm-1; N-H stretching in the range between 3200 and 3450 cm<sup>-1</sup>; and C-H stretching in the range of  $2800-3000 \text{ cm}^{-1}$ . Moreover, there is a sharp feature at 1650 cm<sup>-1</sup> which most likely can be ascribed to the C=O bond of pure DMF. Therefore, one can conclude that the affinity of MAI toward PbI2 is higher than that of DMF toward PbI2, so the colloidal clusters of perovskite-solvent complexes are formed by the substitution of MAI for DMF. Similar observations and effects were reported in the literature. $^{29,30}$  It is worth mentioning that a small shoulder observed for the band at 1650 cm<sup>-1</sup> may be ascribed to MAI well-solvated by the DMF molecules. This interaction may play an important role in the formation of small colloidal clusters in precursor ink. We further used the as-prepared inks to fabricate perovskite layers on glass substrates using an antisolvent quenching approach. The spin-coating of the perovskite precursor solution involves an antisolvent treatment to facilitate the removal of the host solvent(s) molecules and as a consequence initiate the crystallization of the perovskite film. Several studies have reported the optimal conditions for this step, and it has been shown that antisolvent-solvent interactions, such as dipoledipole interactions, modulate the dynamics of the process.<sup>31</sup> The film morphology is affected by composition-dependent liquid-crystal dynamics and competing crystallization routes that occur during the crucial stages of film formation. To optimize the process, a broad variety of solvents was examined, and it was found that the type of antisolvent used limits the window of operation for morphology and power conversion efficiency (PCE).<sup>32–35</sup> Therefore, the solvent-engineering technique is critically important for this process. We tried different solvents along with the use of diverse antisolvents to control the crystallization dynamics and nucleation of the







Figure 3. (a) XRD patterns of the MAPbI<sub>3</sub> perovskite films deposited from various precursor concentrations. (b) XRD patterns of ultrathin perovskite films. (c) Calculated microstrain and average crystallite size were determined from XRD patterns by performing a Willamson–Hall analysis.

perovskite film. We found that toluene as an antisolvent, together with the DMF/DMSO solvent system allowed us to achieve highly reproducible protocol resulting in extremely uniform, pinhole-free films exhibiting low surface roughness as determined using profilometer and AFM. It is worth emphasizing that these characteristics were obtained for concentrations in the range of 0.008–2.5 M (Figure S5). As we further investigated the thicknesses of thin films using both profilometer and ellipsometry measurements, we observed that the relationship between the concentration of precursor ink and thickness of the perovskite film is linear, following the equation:

$$= 260 \times [\text{concentration of ink (M)}]$$
(1)

We further explored the limits of the applicability of the method with the preparation of more and more diluted inks. This led us to conclude that using additive-free precursors in DMF:DMSO-toluene solvent-antisolvent system, it is possible to control the thickness in the range of 3-625 nm. The upper limit results from the solubility of MAPbI<sub>3</sub> in the investigated solvent system (2.5M), beyond which attempting to create a more concentrated ink immediately resulted in ink failure. Importantly, the linear correlation was preserved throughout the entire concentration range (Figure S6). Importantly, the linear correlation of the ultrathin MAPbI<sub>3 films</sub> (below 50 nm), we performed atomic force microscopy (AFM), X-ray diffraction (XRD), and scanning electron microscope (SEM) studies. The SEM and AFM

images of the resultant spin-coated below 3 nm MAPbI<sub>3</sub> films on glass substrates are shown in Figure 2a-c.

The AFM and SEM images both illustrate that the MAPbI<sub>3</sub> layers possess a uniform morphology with a smooth surface, exhibiting a low root-mean-square (RMS) roughness value of less than 1 nm (additionally, analysis of the thickness and topography of the 3 nm film was presented in the Supporting Information, see Figures S17 and S18). However, for thinner films, islands were observed, which can increase the roughness. These fluctuations in thickness can be attributed to various factors, particularly during the formation of the initial layers. Considering that our film thickness is only a few times larger than the lattice constant of MAPbI<sub>3</sub>, that the early stages of crystallization play a significant role in shaping the topography and morphology of the final layer. In these initial stages, perovskite islands begin to grow on the surface. These islands may exhibit a greater affinity for connecting with other perovskite islands rather than the substrate, leading to potential aggregation based on lattice matching. This process likely results in the presence of protruding grains on the surface, thereby contributing to the observed thickness variations. The absorbance spectra of the 30, 20, 10, and 3 nm-thick films are shown in Figure 2d. Due to its higher thickness, the 30 and 20 nm perovskite films absorb more light than 10 and 3 nm. For 10 and 3 nm films the absorption coefficient changes substantially. The XRD patterns of the spin-coated MAPbI3 films on glass substrates are shown in Figure 3a. Despite their thicknesses, all the deposited perovskite layers showed high crystallinity reaching an almost excellent tetragonal cell (space group I4cm). In XRD patterns, regardless of the film's thickness, the presence of (110), (220), (310), (224) and (314) diffraction peaks confirm the formation of the tetragonal perovskite structure. Interestingly, we noticed variations in the relative intensity of the (110) peak among the films (Figures 3a and S8), indicating differences in crystallinity. Table S1 shows the peak intensity and the peak full-width half-maximum (fwhm) of individual crystallite of MAPbI<sub>3</sub> perovskite films measured by the spectral fitting of XRD measurement data as well as the individual crystallite dimensions of the perovskite films, which have been calculated using the Debye-Scherrer equation (Equation S2). The peak intensity and individual crystallite dimensions of the perovskite films have been reported in Table S1. Notably, an intriguing trend emerges: as the film thickness falls below 200 nm, the crystallite size consistently grows with the film's thickness. However, once the thickness exceeds 200 nm, saturation sets in, leading to a stable crystallite size.

In parallel, we performed microstrain analysis on the same XRD patterns (Figure 3c) to assess lattice imperfections and structural defects such as dislocations, stacking faults, and grain boundaries. Line broadening, quantified by fwhm values of diffraction peaks, was employed to estimate both crystallite size and microstrain. This analysis has shown that, in addition to the reduction in crystallite size, there is an increase in microstrain as the film thickness decreases. The microstrain reaches 0.1% for 40 nm, indicating lattice distortion. For films with a thickness of up to 100 nm, the lattice relaxation is observed. The opposite, for the ultrathin layer below 40 nm microstrain reached 2%. That value can be overestimated, it is essential to note that the below 40 nm film exhibited weak peak intensity, which could introduce relatively large errors into the final microstrain value compared to the other samples. This comprehensive characterization sheds light on the

crystallinity and microstructural properties of our  $MAPbI_3$  perovskite films, providing valuable insights into their performance and potential applications.

These results are of significant importance as they represent the first-ever structural investigation of ultrathin MAPbI<sub>3</sub> films, ranging from below 30 nm down to just a few nanometers in thickness. The reduction in thickness aimed at achieving a high average visible transmittance (AVT) value comes with a tradeoff: reduction of effective conversion light to photocurrent. Additionally, we confirmed that this reduction introduces substantial lattice strains in the MAPbI<sub>3</sub> film. These lattice strains can be attributed to reduced stability and hindered charge transport, as carrier mobility closely correlates with lattice strain.  $^{36,37}$  This, in turn, affects the efficiency of carrier collection and may contribute to the formation of defect centers, which can adversely impact the performance of solar cells.<sup>38</sup> Recognizing the potential for overestimating lattice strain in films below 40 nm, we decided to conduct further investigations on solar cell fabrication with two different thicknesses of MAPbI<sub>3</sub>. One thickness corresponds to 30 nm, where lattice strains increase dramatically; photovoltaic performance parameters of devices show whether we overestimated lattice strain or not. The second thickness is 10 nm; this aims to explore the feasibility of fabricating functional solar junctions with a photoactive layer at the nanometer scale.

Moreover, for comprehensive and fundamental optical characterization of the spin-coated layers, we measured PL using a continuous wave green laser (532 nm, 2.33 eV) as an excitation source. To demonstrate that our fabrication method is reproducible, we measured at least 7 spin-coated samples of each thickness in exactly the same measurement conditions (50  $\mu$ W exc. power, 300 K, under vacuum).

The representative spectra are shown in Figure 4. The shape of PL and peak position ( $\sim$ 1.6 eV) for samples thicker than



**Figure 4.** Normalized PL spectra recorded for the samples of different thickness.

225 nm is typical for those reported for  $MAPbI_3$  previously.<sup>39,40</sup> Interestingly, we observed that the behavior of the PL peak was significantly affected by thin film thickness. First of all, the PL is shifted to higher energy with decreasing thickness (Figure S7). Of course, one could expect such a shift in the case of very thin samples (as it can be related to quantum confinement and built-in strain), but here it was clearly observed in the whole investigated thickness range. Another possible explanation is related to the hypothesis that emission in HOIPs such as MAPbI<sub>3</sub> is governed by bistable amphoteric native defects (BANDs), i.e., defects whose nature



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Figure 5. (a) XPS spectra of MAPbI<sub>3</sub> 5 and 30 nm films: I 3d. (b) XPS spectra of MAPbI<sub>3</sub> 5 and 30 nm films: Pb 4f. (c) XRD patterns of ultrathin perovskite films.

(donor/acceptor) and formation energy are controlled by the location of Fermi energy.<sup>41,42</sup> Assuming that due to the increased surface-to-volume ratio in thinner films, the concentration of BANDs is higher, one can expect such a behavior of the PL peak. A further interesting feature in PL spectra is related to the thickness range between 50 and 225 nm. Here, the peak is undeniably accompanied by a lowenergetic shoulder. The existence of multiple peaks/shoulders in MAPbI<sub>3</sub> spectra was usually reported below phase transition temperature (i.e., 160 K; tetragonal  $\rightarrow$  orthorhombic) and it was often ascribed to the presence of tetragonal domains in the orthorhombic lattice. Nevertheless, our process does not involve the use of low temperatures. Moreover, XRD patterns did not reveal any signs of different phases and we performed measurements at RT so it is unlikely that the low-energetic shoulder originates from the different phase inclusions. However, this emission may be also related to the contribution of BANDs or different defect states within the bandgap. This hypothesis is quite plausible since we were able to observe PL using below bandgap excitation (787 nm, 1.57 eV). As there was a clear risk that ultrathin MAPbI<sub>3</sub> layers may be more prone to degradation (eventually resulting in the formation of  $PbI_2$ ) when exposed to ambient air.

That effect was reported in the XRD of the ultrathin layer at ambient conditions (Figure 5c). That reason, why we used X-ray photoelectron spectroscopy (XPS) to verify if the material is chemically uniform. The spectra shown in Figure 5a,b clearly indicate the formation of pure MAPbI<sub>3</sub> for both evaluated ultrathin films (5 and 30 nm). The Pb 4f peaks of the 5 nm\_MAPbI<sub>3</sub> film exhibit higher binding energy compared with 30 nm\_MAPbI<sub>3</sub>. To be specific, Figure 5a shows distinguished Pb 4f<sub>7/2</sub> and Pb 4f<sub>5/2</sub> peaks for 30 nm\_MAPbI<sub>3</sub> at 137.7 and 142.7 eV, respectively. The corresponding Pb peaks of 5 nm\_MAPbI<sub>3</sub> were shifted to a higher binding energy of 138.6 eV for Pb 4f<sub>7/2</sub> and 143.5 eV for Pb 4f<sub>5/2</sub>, which could be

attributed to the changed chemical environment. Note that both the distinguished  $1 \, 3d_{5/2} \, (619.9 \, \text{eV})$  and  $13_{d_{3/2}} \, (631.5 \, \text{eV})$  peaks for 5 nm\_MAPbI<sub>3</sub> are also shifted toward higher binding energy compared to those of the 30 nm\_MAPbI<sub>3</sub> film (617.5 and 627.1 eV) (Figure 5b). This shift suggests a change in the chemical environment of the  $[\text{PbI}_6]^{4-}$  octahedron, probably a deformation of the complex arrangement with decreasing dimensionality.

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Finally, encouraged by the results obtained for ultrathin films, we fabricated flexible semitransparent PSCs with planar architecture and inverted configuration (p-i-n), (active area of 1 cm<sup>2</sup>) using the diluted, additive-free inks on flex substrate with the following structure PET/indium zinc oxide (IZO)/ PEDOT:PSS/MAPbI<sub>3</sub>/C60/bathocuproine (BCP)/Ag (Figure 7a). Here, it is worth noting that in general fabrication of top electrodes for semitransparent PSCs is a separate, yet very important, issue being the subject of numerous studies. Among many approaches, the most common are direct deposition of transparent conductive oxides-based top electrodes without protective buffer layers, fabrication of threedimensional amorphous ITO (a-ITO)/Ag mesh directly on semitransparent perovskite solar cells, and using a dielectric/ metal/dielectric (DMD) multilayer film as the top transparent electrode.43 Continuing the idea of a simple approach, we decided to deposit just 10 nm of silver layer without any additional antireflective coatings. AVT (between 300 and 900 nm spectral region) for the evaluated PSCs was calculated using the formula<sup>4</sup>

$$AVT = \frac{\int_{300}^{900} I(\lambda) T(\lambda) d\lambda}{\int_{300}^{900} I(\lambda) d\lambda}$$
(2)

where  $I(\lambda)$  is the photon flux under AM 1.5G illumination and  $T(\lambda)$  is the photopic response of the human eyes. We achieved a current density  $(J_{sc})$  of 8.68 mA/cm<sup>2</sup> and combined with an



Figure 6. (a) Device configuration of PET/IZO-based semitransparent PSCs fabricated in this work. (b) J-V curves for the optimized perovskite solar cells fabricated with 10 and 30 nm of MAPbI<sub>3</sub> layer. (c) Transmittance spectra of the active layer of such cells. (d) Photograph through a typical flexible semitransparent perovskite solar cell with 30 nm of MAPbI<sub>3</sub> layer and 10 nm silver electrode, demonstrating neutral color and semitransparency.



Figure 7. (a) Statistic of the photovoltaic performance measured for the perovskite solar cells with different  $MAPbI_3$  thicknesses: 10 (red) and 30 nm (black). (b) Typical stabilized PCE of PSC is determined by measuring the photocurrent at the maximum power point (MPP) under continuous AM 1.5G irradiation. (c) FIB-SEM image of the best-performing ultrathin solar cells.

open-circuit voltage ( $V_{oc}$ ) of 0.92 V, and fill-factor (FF) of 71.5% this resulted in a PCE of 5.7% for the champion device under AM 1.5G irradiation (Figures 6b, 7a and S19). The champion device combining high performance and good transparency (AVT of 21.5%) was obtained for the PSC consisting of a 30 nm MAPbI<sub>3</sub> layer and 10 nm of Ag (Figure 6c). The digital photograph of the corresponding device in Figure 6d depicts the overall optical transparency and color neutrality. We also tried to fabricate a PSC with the thinnest ever MAPbI<sub>3</sub> layer, 10 nm. An impressive PSC with PCE of 1.9% and AVT of 41.1% (62.9% without Ag electrode) is achieved when the active layer reaches only 10 nm of thickness (Figure 6b,c). These devices also demonstrate high reproducibility with an average efficiency of 1.8  $\pm$  0.1%, as shown in Figure 6b.

As a common trend in all of these devices, a gradual decrease in the  $J_{sc}$  with decreasing perovskite layer thickness is observed due to reduced photon absorption, especially when the active layer was reduced to 10 nm. This trend is also reflected in the overall PCEs of the completed devices. Notably, the decrease is

more rapid for the 10 nm\_MAPbI<sub>3</sub> devices than that of the 30 nm MAPbI<sub>3</sub> ones as a combined result of a significant decrease in FF,  $V_{oc}$  and  $J_{sc}$ . This is consistent with the fact that the fabrication of perovskite films below 10 nm of thickness formed a film with high lattice strain (up to 2%). Probably, fabrication of that type of ultrathin film on a more thick PEDOT:PSS with high roughness of the surface leads to more defects at the PEDOT:PSS/MAPbI<sub>3</sub> interlayer. Nevertheless, the PEDOT:PSS layer has good uniformity without any pinholes as seen in the SEM images (Figure 7c). In summary, the 30 nm\_MAPbI<sub>3</sub> PSC is the technical limit for minimizing the thickness of the active layer. Further decreasing thickness affected with increasing lattice strains and decrease of absorption coefficient, so drastically dropped all device performance parameters. To ensure the reliability and performance of the manufactured perovskite solar cells (PSCs), we conducted stability assessments by measuring the stabilized power output in proximity to the maximum power point (MPP). When measuring the photocurrent precisely at the MPP under continuous AM 1.5G illumination, the performance of the fabricated semitransparent PSCs exhibited excellent stability.

#### CONCLUSIONS

We developed a simple, yet elegant, protocol using solvent engineering for the deposition of extremely uniform and ultrathin perovskite layers. Probably, the high reproducibility and the ability to control a wide range of molar concentrations were made possible through the stabilization of an intermediate phase using a precisely formulated precursor solution realized via a chemistry precursor solution. Starting from high-purity additive-free materials, we were able to control the thickness of uniform MAPbI<sub>3</sub> film in a range of 3-625 nm. These results will provide an effective strategy for the fabrication of uniform semitransparent perovskite solar cells based on ultrathin MAPbI<sub>3</sub>, demonstrated 5.7% PCE under standard conditions (AM 1.5 G radiation, 100 mW cm<sup>-2</sup>) for 30 nm\_MaPbI<sub>3</sub>-based cells. Remarkably, we achieved 1.9% PCE for 10 nm\_MAPbI<sub>3</sub>. These results represent a key advancement for producing ultralightweight, highly transparent devices with reduced lead content-a significant leap toward sustainability. Our findings also illuminate a promising path for continued research in this field, promising further innovation and development in the future.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.4c00517.

Experimental details, NMR spectra of MAI, optical absorption spectra for samples of different thickness, relationship between ink concentration and film thickness, PL peak position as a function of film thickness, Scherrer and Williamson–Hall analyses of XRD patterns, SEM images, additional J-V curves, and EQE for 10 and 30 nm MAPbI<sub>3</sub> layers (PDF)

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#### Author Contributions

 $^{\nabla}$ Ł.P. and W.Ż. contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. *Science* (1979) **2013**, 342 (6156), 341–344.

(2) Zhumekenov, A. A.; Saidaminov, M. I.; Haque, M. A.; Alarousu, E.; Sarmah, S. P.; Murali, B.; Dursun, I.; Miao, X. H.; Abdelhady, A. L.; Wu, T.; Mohammed, O. F.; Bakr, O. M. Formamidinium Lead Halide Perovskite Crystals with Unprecedented Long Carrier Dynamics and Diffusion Length. ACS Energy Lett. **2016**, 1 (1), 32–37.

(3) Chang, Y. H.; Park, C. H. First-Principles Study of the Structural and the Electronic Properties of the Lead-Halide-Based Inorganic-Organic Perovskites (CH3NH3)PbX3 and CsPbX3 (X = Cl, Br, I). *J. Korean Phys. Soc.* **2004**, 44 (4), 889–893.

(4) Kulkarni, S. A.; Baikie, T.; Boix, P. P.; Yantara, N.; Mathews, N.; Mhaisalkar, S. Band-Gap Tuning of Lead Halide Perovskites Using a Sequential Deposition Process. *J. Mater. Chem. A Mater.* **2014**, *2* (24), 9221–9225.

(5) Żuraw, W.; Vinocour Pacheco, F. A.; Sánchez-Diaz, J.; Przypis, Ł.; Mejia Escobar, M. A.; Almosni, S.; Vescio, G.; Martínez-Pastor, J. P.; Garrido, B.; Kudrawiec, R.; Mora-Seró, I.; Öz, S. Large-Area, Flexible, Lead-Free Sn-Perovskite Solar Modules. *ACS Energy Lett.* **2023**, *8* (11), 4885–4887.

www.acsaem.org

(6) https://www.nrel.gov/pv/assets/pdfs/best-research-celleFFiciencies-rev211214.pdf (accessed: May 2023).

(7) Yue, W.; Yang, H.; Cai, H.; Xiong, Y.; Zhou, T.; Liu, Y.; Zhao, J.; Huang, F.; Cheng, Y.; Zhong, J. Printable High-efficiency and Stable FAPbBr 3 Perovskite Solar Cells for Multifunctional Buildingintegrated Photovoltaics. *Adv. Mater.* **2023**, *35* (36), No. 2301548.

(8) Hörantner, M. T.; Nayak, P. K.; Mukhopadhyay, S.; Wojciechowski, K.; Beck, C.; McMeekin, D.; Kamino, B.; Eperon, G. E.; Snaith, H. J. Shunt-Blocking Layers for Semitransparent Perovskite Solar Cells. *Adv. Mater. Interfaces* **2016**, 3 (10), 1–7.

(9) Cannavale, A.; Eperon, G. E.; Cossari, P.; Abate, A.; Snaith, H. J.; Gigli, G. Perovskite Photovoltachromic Cells for Building Integration. *Energy Environ. Sci.* **2015**, *8* (5), 1578–1584.

(10) Martín-Chivelet, N.; Kapsis, K.; Wilson, H. R.; Delisle, V.; Yang, R.; Olivieri, L.; Polo, J.; Eisenlohr, J.; Roy, B.; Maturi, L.; Otnes, G.; Dallapiccola, M.; Upalakshi Wijeratne, W. M. P. Building-Integrated Photovoltaic (BIPV) Products and Systems: A Review of Energy-Related Behavior. *Energy Build* **2022**, *262*, No. 111998.

(11) Huang, J.; Yuan, Y.; Shao, Y.; Yan, Y. Understanding the Physical Properties of Hybrid Perovskites for Photovoltaic Applications. *Nat. Rev. Mater.* **2017**, *2*, 17042 DOI: 10.1038/natrev-mats.2017.42.

(12) Bag, S.; Durstock, M. F. Efficient Semi-Transparent Planar Perovskite Solar Cells Using a 'Molecular Glue'. *Nano Energy* **2016**, *30*, 542–548.

(13) Marques, A. S.; Faria, R. M.; Freitas, J. N.; Nogueira, A. F. Low-Temperature Blade-Coated Perovskite Solar Cells. *Ind. Eng. Chem. Res.* **2021**, *60* (19), 7145–7154.

(14) Bae, I. G.; Park, B. All-Self-Metered Solution-Coating Process in Ambient Air for the Fabrication of Efficient, Large-Area, and Semitransparent Perovskite Solar Cells. *Sustain Energy Fuels* **2020**, *4* (6), 3115–3128.

(15) Rahmany, S.; Etgar, L. Semitransparent Perovskite Solar Cells. ACS Energy Lett. **2020**, *5*, 1519–1531.

(16) Eperon, G. E.; Burlakov, V. M.; Goriely, A.; Snaith, H. J. Neutral Color Semitransparent Microstructured Perovskite Solar Cells. *ACS Nano* **2014**, *8* (1), 591–598.

(17) Eperon, G. E.; Bryant, D.; Troughton, J.; Stranks, S. D.; Johnston, M. B.; Watson, T.; Worsley, D. A.; Snaith, H. J. Efficient, Semitransparent Neutral-Colored Solar Cells Based on Microstructured Formamidinium Lead Trihalide Perovskite. *J. Phys. Chem. Lett.* **2015**, *6* (1), 129–138.

(18) Rahmany, S.; Layani, M.; Magdassi, S.; Etgar, L. Fully Functional Semi-Transparent Perovskite Solar Cell Fabricated in Ambient Air. *Sustain Energy Fuels* **2017**, *1* (10), 2120–2127.

(19) Aharon, S.; Layani, M.; Cohen, B. El; Shukrun, E.; Magdassi, S.; Etgar, L. Self-Assembly of Perovskite for Fabrication of Semitransparent Perovskite Solar Cells. *Adv. Mater. Interfaces* **2015**, 2 (12), 1–6.

(20) Zhang, Z.; Ji, R.; Jia, X.; Wang, S. J.; Deconinck, M.; Siliavka, E.; Vaynzof, Y. Semitransparent Perovskite Solar Cells with an Evaporated Ultra-Thin Perovskite Absorber. *Adv. Funct Mater.* **2023**, No. 2307471.

(21) Kwon, H. C.; Kim, A.; Lee, H.; Lee, D.; Jeong, S.; Moon, J. Parallelized Nanopillar Perovskites for Semitransparent Solar Cells Using an Anodized Aluminum Oxide Scaffold. *Adv. Energy Mater.* **2016**, *6* (20), No. 1601055.

(22) Della Gaspera, E.; Peng, Y.; Hou, Q.; Spiccia, L.; Bach, U.; Jasieniak, J. J.; Cheng, Y. B. Ultra-Thin High Efficiency Semitransparent Perovskite Solar Cells. *Nano Energy* **2015**, *13*, 249–257.

(23) Paliwal, A.; Mardegan, L.; Roldan-Carmona, C.; Palazon, F.; Liu, T. Y.; Bolink, H. J. Efficient Semitransparent Perovskite Solar Cells Based on Thin Compact Vacuum Deposited CH3NH3PbI3 Films. *Adv. Mater. Interfaces* **2022**, *9* (29), No. 2201222.

(24) Roldán-Carmona, C.; Malinkiewicz, O.; Betancur, R.; Longo, G.; Momblona, C.; Jaramillo, F.; Camacho, L.; Bolink, H. J. High Efficiency Single-Junction Semitransparent Perovskite Solar Cells. *Energy Environ. Sci.* **2014**, *7* (9), 2968–2973.

(25) Tisdale, J. T.; Smith, T.; Salasin, J. R.; Ahmadi, M.; Johnson, N.; Ievlev, A. V.; Koehler, M.; Rawn, C. J.; Lukosi, E.; Hu, B. Precursor Purity Effects on Solution-Based Growth of MAPbBr3 Single Crystals towards Efficient Radiation Sensing. *CrystEngComm* **2018**, 20 (48), 7818–7825.

(26) Dasgupta, S.; Misztal, K.; Fuentes Pineda, R.; Mróz, W.; Pawlaczyk, Ł.; Serafińczuk, J.; Barker, A. J.; Ahmad, T.; Herman, A. P.; Sahayaraj, S.; Kudrawiec, R.; Petrozza, A.; Dudkowiak, A.; Wojciechowski, K. New Synthetic Route of Ultra-Pure Alkylammonium Iodides for Perovskite Thin Films of Superior Optoelectronic Properties. *Energy Technology* **2020**, *8* (10), No. 2000478.

(27) Mcmeekin, D. P.; Wang, Z.; Rehman, W.; Pulvirenti, F.; Patel, J. B.; Noel, N. K.; Johnston, M. B.; Marder, S. R.; Herz, L. M.; Snaith, H. J. Crystallization Kinetics and Morphology Control of Formamidinium – Cesium Mixed-Cation Lead Mixed-Halide Perovskite via Tunability of the Colloidal Precursor Solution. *Adv. Mater.* **2017**, *29* (29), No. 1607039.

(28) Ran, C.; Gao, W.; Li, N.; Xia, Y.; Li, Q.; Wu, Z.; Zhou, H.; Chen, Y.; Wang, M.; Huang, W. Facet-Dependent Control of PbI 2 Colloids for over 20% Efficient Perovskite Solar Cells. *ACS Energy Lett.* **2019**, 4 (1), 358–367.

(29) Li, B.; Li, M.; Fei, C.; Cao, G.; Tian, J. Colloidal Engineering for Monolayer CH3NH3Pb13 Films toward High Performance Perovskite Solar Cells. *J. Mater. Chem. A Mater.* **2017**, 5 (46), 24168–24177.

(30) Yang, J.; Hu, J.; Zhang, W.; Han, H.; Chen, Y.; Hu, Y. The Opportunities and Challenges of Ionic Liquids in Perovskite Solar Cells. *Journal of Energy Chemistry* **2023**, *77*, 157–171.

(31) Bautista-quijano, J. R.; Vaynzof, Y.; Telschow, O.; Paulus, F.; Bautista, J. R. Solvent – Antisolvent Interactions in Metal Halide Perovskites. *Chem. Commun.* **2023**, *59*, 10588–10603, DOI: 10.1039/ d3cc02090h.

(32) Taylor, A. D.; Sun, Q.; Goetz, K. P.; An, Q.; Schramm, T.; Hofstetter, Y.; Litterst, M.; Paulus, F.; Vaynzof, Y. A General Approach to High-Efficiency Perovskite Solar Cells by Any Antisolvent. *Nat. Commun.* **2021**, *12* (1), 1–11.

(33) Jeon, N. J.; Noh, J. H.; Kim, Y. C.; Yang, W. S.; Ryu, S.; Seok, S. Il. Solvent Engineering for High-Performance Inorganic-Organic Hybrid Perovskite Solar Cells. *Nat. Mater.* **2014**, *13* (9), 897–903.

(34) Zhang, W.; Li, Y.; Liu, X.; Tang, D.; Li, X.; Yuan, X. Ethyl Acetate Green Antisolvent Process for High-Performance Planar Low-Temperature SnO2-Based Perovskite Solar Cells Made in Ambient Air. Chem. Eng. J. 2020, 379, No. 122298.

(35) Yang, F.; Kapil, G.; Zhang, P.; Hu, Z.; Kamarudin, M. A.; Ma, T.; Hayase, S. Dependence of Acetate-Based Antisolvents for High Humidity Fabrication of CH3NH3PbI3 Perovskite Devices in Ambient Atmosphere. *ACS Appl. Mater. Interfaces* **2018**, *10* (19), 16482–16489.

(36) Nishimura, K.; Hirotani, D.; Kamarudin, M. A.; Shen, Q.; Toyoda, T.; Iikubo, S.; Minemoto, T.; Yoshino, K.; Hayase, S. Relationship between Lattice Strain and Efficiency for Sn-Perovskite Solar Cells. ACS Appl. Mater. Interfaces **2019**, *11* (34), 31105–31110. (37) Zhu, C.; Niu, X.; Fu, Y.; Li, N.; Hu, C.; Chen, Y.; He, X.; Na, G.; Liu, P.; Zai, H.; Ge, Y.; Lu, Y.; Ke, X.; Bai, Y.; Yang, S.; Chen, P.; Li, Y.; Sui, M.; Zhang, L.; Zhou, H.; Chen, Q. Strain Engineering in Perovskite Solar Cells and Its Impacts on Carrier Dynamics. Nat. Commun. **2019**, *10* (1), 815.

(38) Fang, J.; Ding, Z.; Chang, X.; Lu, J.; Yang, T.; Wen, J.; Fan, Y.; Zhang, Y.; Luo, T.; Chen, Y.; Liu, S. F.; Zhao, K. Microstructure and Lattice Strain Control towards High-Performance Ambient Green-Printed Perovskite Solar Cells. *J. Mater. Chem. A* **2021**, *9* (22), 13297–13305.

(39) D'Innocenzo, V.; Srimath Kandada, A. R.; De Bastiani, M.; Gandini, M.; Petrozza, A. Tuning the Light Emission Properties by Band Gap Engineering in Hybrid Lead Halide Perovskite. J. Am. Chem. Soc. 2014, 136 (51), 17730–17733.

(40) Staub, F.; Anusca, I.; Lupascu, D. C.; Rau, U.; Kirchartz, T. Effect of Reabsorption and Photon Recycling on Photoluminescence

https://doi.org/10.1021/acsaem.4c00517 ACS Appl. Energy Mater. 2024, 7, 4803–4812

Article

Spectra and Transients in Lead-Halide Perovskite Crystals. JPhys. Materials 2020, 3 (2), No. 025003.

(41) Walukiewicz, W.; Wang, S.; Wu, X.; Sherburne, M. P.; Ager, J. W.; Asta, M. D. Photophysics of Localized Deep Defect States in Hybrid Organic-Inorganic Perovskites. *J. Phys. Chem. C* **2021**, *125* (12), 6975–6982.

(42) Walukiewicz, W.; Wang, S.; Wu, X.; Li, R.; Sherburne, M. P.; Wu, B.; Sum, T. C.; Ager, J. W.; Asta, M. D. The Bright Side and Dark Side of Hybrid Organic-Inorganic Perovskites. *J. Phys. Chem. C* 2020, 124 (50), 27340–27355.

(43) Zanoni, K. P. S.; Paliwal, A.; Hernández-Fenollosa, M. A.; Repecaud, P. A.; Morales-Masis, M.; Bolink, H. J. ITO Top-Electrodes via Industrial-Scale PLD for Efficient Buffer-Layer-Free Semitransparent Perovskite Solar Cells. *Adv. Mater. Technol.* **2022**, 7 (10), No. 2101747.

(44) Yang, C.; Liu, D.; Bates, M.; Barr, M. C.; Lunt, R. R. How to Accurately Report Transparent Solar Cells. *Joule* **2019**, *3*, 1803–1809. Cell Press August 21,

# **Supporting Information**

# Facile Preparation of Large-Area, Ultrathin, Flexible Semi-Transparent Perovskite Solar Cells via Spin-Coating

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## **Experimental Section**

## **Materials** :

The substrate consisted of a 210  $\mu$ m thick PET substrate covered with a layer of Indium Zinc Oxide (IZO;  $\approx$ 270 nm) with a sheet resistance of 15–20  $\Omega$  sq<sup>-1</sup> and a transparency of 80% was purchased from Eastman. (Shenzhen, China). MAI was synthesised using previously reported method<sup>1</sup>. PbI<sub>2</sub> was purchased from Solaveni GmbH, *N*, *N*-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99,9%), toluene (99% anhydrous), bathocuproine (BCP, 99% HPLC), C<sub>60</sub> (99.9%) were purchased from Sigma Aldrich. PEDOT:PSS A14083 dispersion

was purchased from Ossila. All of the above materials are commercial products and can be used directly without further processing.

# **Device fabrication:**

Solution preparation: Additive-free MAI powder synthesised<sup>1</sup> (1 equiv.) and PbI<sub>2</sub> (1 equiv.) were sequentially added to 1 mL of a mixture of DMF:DMSO (9.0:1.1, v/v) stirred at room temperature for 6 h to form the perovskite precursor solution of the desired concentration.

*Device fabrication:* PET/IZO substrates ( $18 \times 13 \text{ mm}^2 \text{ pieces}$ ) were patterned by dipping one side in the HCl solution (15 wt% in deionized water). The etched substrates were cleaned by ultrasonication in deionized water and isopropanol for 7 minutes in each solvent and dried by nitrogen flow. Before layer processing, substrates were treated with oxygen plasma for 2 minutes. The PEDOT:PSS dispersion was spin-coated at 5000 rpm for 40 seconds, followed by annealing at 120°C for 30 minutes. The perovskite solution was spin-coated on the top of PEDOT:PSS with 6000 rpm for 30 seconds (2 seconds of acceleration). Anhydrous toluene (100  $\mu$ L) was dispensed on the sample 20 seconds before the end of the spinning program. After drying at room temperature (RT) for 2 minutes, the as-prepared structure was transferred to a hotplate and annealed at 100°C for 30 minutes. A 25 nm layer of C<sub>60</sub> was thermally evaporated on top of the perovskite layer as the electron transport layer, followed by 5 nm of BCP as a buffer layer and 10 nm of Ag as a top electrode.

# Material and device characterization and measurement

## Dynamic light scattering

The dynamic light scattering (DLS) was recorded by 90Plus PALS (Brookhaven Instruments Corporation).

## Fourier transform infrared spectroscopy

The Fourier transform infrared spectroscopy (FTIR) was measured by a Bruker Vertex 80v spectrometer, the concentration of perovskite precursors was 0.25 M, 0.50 M, and 1.00 M.

## Profilometer measurements

Samples had their thickness and roughness measured using a Veeco Dektak 150 Profilometer.

### AFM measurements

Atomic force microscopy (AFM) topographic images were performed using A Park Systems Atomic Force Microscope

## Scanning electron microscopy

Top-view morphology images of samples were obtained with a field emission SEM (Phenom ProX), which had an accelerating voltage of 5 kV with a working distance of 8.0 mm. Cross-section images were developed by deploying a focus ion beam scanning electron microscope, FIB-SEM (FEI Helios 600), which had an accelerating voltage of 2 kV. The samples for measurement were prepared by depositing carbon and platinum films on the top side.

### X-ray diffraction measurements

X-ray diffraction (XRD) patterns were collected with Rigaku MiniFlex600 (Cu K $\alpha$  radiation,  $\lambda$ =1.5406 Å) diffractometer. The samples were measured using  $\theta$ -2 $\theta$  scans. The set-up was equipped with a copper anode and a graphite monochromator to select Cu K $\alpha$  radiation (2 $\theta$  5– 50 deg; the diffractograms were scanned using 0.1 deg steps and a counting time of 1 s per step).

## Optical characterization

Transmission spectra were measured in a spectrophotometer (Edinburgh Instruments FS5), using an Xe lamp light source (spectral range 300-900 nm), an integration time of 0.2 seconds, and a spectral spacing between points of 5 nm. Ellipsometry data were collected in a Semilab

SE-2000 ellipsometer, using an illumination angle of 70 degrees, and a spectral range 300-2500 nm.

## Photoluminescence measurements

Steady-state photoluminescence (PL) spectra were measured using an experimental setup equipped with a Peltier-cooled Avantes CCD spectrometer (AvaSpec-ULS2048x64TEC-EVO) and appropriate optics. The samples were excited with a 532 nm semiconductor laser.

## X-ray Photoelectron Spectroscopy measurements

The XPS (X-ray Photoelectron Spectroscopy) measurements were performed under UHV (Ultrahigh vacuum) conditions. The base pressure in the analysis chamber was  $\leq 2 \cdot 10 - 10$  mbar. The photoemission process was initiated using an AlK $\alpha$  radiation source (1486.6 eV) oriented at 55° to the normal of the samples. The energy of the photoelectrons was determined with the VGScienta R3000 spectrometer. The energy step was set to  $\Delta E = 0.1$  eV.

## Current-voltage measurements

For the device operation measurements at simulated AM1.5G irradiation (100 mA cm<sup>-2</sup>), an AAA-rated solar simulator (Abet Technologies, sun 2000) was used, calibrated against an RR-208-KG5 silicon reference cell (Abet Technologies). Solar cells were masked with a 0.64 cm<sup>2</sup> shadow mask. The stabilized power conversion efficiency (SPO) was measured at the maximum power point voltage for 30 s.

## Additional discussion – ink chemistry

An in-depth understanding of the precursor ink chemistry is essential for the wet fabrication methods of PSCs as it directly affects thin film quality and, as a consequence, the device's performance. Even the most common method involving direct mixing of raw materials (i.e. monovalent halide and lead(II) halide) can result in the formation of various lead polyhalide coordination complexes such as  $[PbI_3]^-$ ,  $[PbI_4]^{2-}$ ,  $[PbI_5]^{3-}$ ,  $[PbI_6]^{4-}$ . Moreover, it should be kept in mind that solvent molecules may compete with iodide anions as ligands for the Pb<sup>2+</sup>. The presence of lead polyiodides and lead-solvent coordination complexes, as well as the formation of the so-called intermediate phase, and/or introduction of impurities to the film adversely impacts the nucleation and crystal growth of the HOIPs, which brings a great deal of uncertainty in terms of reproducibility of physiochemical (in particular optoelectronic) properties of the resultant perovskite thin films. The MHP precursor ink is usually colloidal, and the interactions between perovskite particles and solvent critically affect the deposition process. During spincoating the sol-precursors undergo transformation to wet gel films upon the removal of solvent. The size and concentration of the colloids clearly impact the crystal quality as well as the morphology of the perovskite thin film. The above-mentioned lead polyhalide networks which may be present in the precursor solution can offer preferential sites for heterogeneous nucleation, which in turn affects the rate of crystallization and final film properties. An in-depth understanding of these complexities remains not fully resolved. One of the major factors for colloid formation/stabilization is affected by the purity of the perovskite precursor in the solution. Several studies have concluded that defects and grain boundaries in perovskite films are the main cause of performance losses or hysteresis. The fabrication of HOIP thin films by the so-called wet methods is known to introduce impurities in the film. Impurities themselves have a dramatic effect on controlling and regulating the deposition rate of MAI. The impurities of MAI play an important role in the fabrication process and have a significant impact on the performance of perovskite solar cells. Hypophosphorous acid (HPA) present in hydroiodic acid (HI) as a reactant to synthesize MAI by reacting with methylamine has been performed by Zhang et al, MA<sub>2</sub>HPA. This in turn could lead to the formation of insoluble Pb(H<sub>2</sub>PO<sub>2</sub>)<sub>2</sub> nanoparticles during the perovskite precursor solution preparation. It was suggested that these nanoparticles could act as nucleation centers during perovskite thin-film crystallization and support large domain formation. Similarly, other impurities (unreacted acid, amines, halogens) can affect the colloidal chemistry occurring in the perovskite precursor solution, which in turn would have an impact on the nucleation process and perovskite thin-film morphology. The quality of the second component of MAPbI<sub>3</sub> also plays a pivotal role in the photovoltaic performance of perovskite solar cells. The experimental studies suggest that the use of PbI<sub>2</sub> precursor with high purity is important for the photovoltaic performance of perovskite solar cells. The impact of PbI<sub>2</sub> purity has been illustrated by a comparison of the material of 98.0% purity and highly pure (99.999%) showing that the former results in low crystallinity of HOIP thin film and a significant drop in charge carrier lifetime and diffusion length. The impurities originating from PbI<sub>2</sub> (i.e. Pb(OH)<sub>2</sub>, PbO(OH), Pb(OH)I. Pb(OH)I) introduce traps in the bulk film which in turn act as non-radiative recombination centres, reducing device's performance.



Figure S1. Two years old synthesized MAI without any evidence of aging.



Figure S2. Solubility test of PbI<sub>2</sub> in DMF/DMSO system (9.0:1.1).



Figure S3. <sup>1</sup>H NMR of MAI.



Figure S4. <sup>13</sup>C NMR of MAI.



Figure S5. FTIR spectra of perovskite precursors with different concentrations: blue -1.00M, green -0.050M, red -0.037M.



Figure S6. The relationship between the concentration of precursor ink and thickness of the perovskite film.



Figure S7. Optical absorption coefficient versus photon Energy for 3-150 nm thick MAPbI<sub>3</sub> films.



Figure S8. Photoluminescence (PL) peak positions as a function of film thickness MAPbI<sub>3</sub>.

# **XRD Analysis**

The X-ray diffraction patterns are shown in Figure 3a.

The d-spacing for each thickness was found from the angle of the perovskite (110) and (220) peaks using Braggs law:

$$2dsin\theta = n\lambda$$
 (Equation S1)

# **Scherrer Equation**

Smaller grains lead to larger FWHM since there are fewer aligned crystal planes to contribute to diffraction. The grain size can therefore be found from the full width at half maximum (FWHM) of the perovskite peaks, using the Scherrer equation:

$$D = \frac{\kappa\lambda}{\beta\cos\theta} \qquad (\text{Equation S2})$$

where D is the crystallite size,  $\beta$  is the FWHM in radians,  $\lambda = 0.15406$  nm is the wavelength of the X-rays,  $\theta$  is the Bragg angle, and K is known as the shape factor which is determined by the definition of the peak breadth and the shape of the crystallite, K = 0.8859.

# Williamson-Hall Plot

The Scherrer formula is only valid when the crystallite size is the main contribution and broadening due to micro-strain (i.e. the distribution of lattice plane spacing in the sample) can be neglected. When microstrain is included, the formula is given by

$$\beta = \frac{\kappa\lambda}{D\cos\theta} + 4\varepsilon tan\theta \quad (\text{Equation S3})$$

This expression can be rearranged to give

$$\beta = \frac{\kappa\lambda}{D\cos\theta} + 4\varepsilon tan\theta \quad (\text{Equation S4})$$

Plotting a graph with  $y = \beta \cos \theta$  and  $x = 4 \sin \theta$  allows us to determine the strain from the gradient and the crystallite size from the intercept.

Thickness	20	Intensity	FWHM	D	Microstrains
nm	deg.	a.u.	deg.	nm	%
10	13,82	3817	1,1912	6,9	2,07393
20	13,75	7167	0,8573	9,6	1,49799
40	13,89	22404	0,3070	26,1	1,09972
93	13,84	15850	0,1959	40,8	0,07045
128	13,67	56275	0,1602	49,9	0,05832
200	13,75	121767	0,1642	48,7	0,05944
250	13,82	119167	0,1669	48,0	0,06007
315	13,74	100883	0,1722	46,5	0,06238
400	13,68	137825	0,1521	52,6	0,05532
500	13,72	219883	0,1502	53,3	0,05447
625	13,69	359017	0,1302	61,4	0,04734

Tabel S1. Tetragonal lattice parameters, strains, and XRD Peak (110) parameters for MAPbI3Thin-Film Samples.



Figure S9. XRD of MAPbI $_3$  for 10-625 nm films at peak 110.



Figure S10. The crystallite height (blue rhombus) is calculated from the full width at half maximum of the peak (orange circles) using the Scherrer equation.



Figure S11. The lattice parameter (red circles, in Ångstrom) is the mean of the lattice parameter (blue rhombus) for the (100) and (200) peaks.



Figure S12. Williamson-Hall plot for the MAPbI3 sample 625 nm.



Figure S13. Microstrain comparison - direct equation (black rhombus) versus Williamson-Hall (WH) Plot (red squares).



Figure S14. a-i) SEM images of MAPbI<sub>3</sub> layer with different thickness.



Figure S15. SEM images and grain size distribution of the perovskite thin films – 250 nm and 128 nm.



Figure S16. AFM images and statistical analysis of surface topography of the perovskite thin films 10 nm.



Figure S17. AFM images and analysis of surface topography of the perovskite thin films 3 nm.



Figure S18. Thickness determination of ultrathin MAPbI3 film using AFM microscopy.



Figure S19. J-V parameters of semitransparent solar cells fabricated for different thicknesses - 30 nm and 10nm.



Figure S20. EQE spectra for different different thickness perovskite active layer - 30nm and 10nm.

# **References:**

 S. Dasgupta, K. Misztal, R. Fuentes Pineda, W. Mróz, Ł. Pawlaczyk, J. Serafińczuk, A. J. Barker, T. Ahmad, A. P. Herman, S. Sahayaraj, R. Kudrawiec, A. Petrozza, A. Dudkowiak and K. Wojciechowski, *Energy Technology*, , DOI:10.1002/ente.202000478.

# 6 Carboxylic Acid-Assisted Synthesis of Tin(II) Iodide: Key for Stable Large-Area Lead-Free Perovskite Solar Cells

# 6.1 Overview

The second publication outlines a key development strategy to accelerate the complete replacement of lead-based PSCs with tin-based ones. As mentioned in Chapter 2, tin-based perovskites are a promising alternative due to their lower toxicity, but they are inherently affected by stability issues due to the p-doping behavior of the tin perovskite precursors, which accelerates degradation. This study addresses this fundamental problem by introducing a novel method for the synthesis of SnI<sub>2</sub> using elemental tin and iodine, catalyzed by carboxylic acid. The proposed method offers a simple and efficient approach for synthesizing high-purity SnI<sub>2</sub> under mild conditions. Additionally, the synthesis can be performed directly in solvents suitable for the preparation of perovskite inks, streamlining the production process. The resulting perovskite ink and fabricated layers demonstrated significantly improved performance and enhanced resistance to oxidation compared to commercial precursors. Using this processing philosophy, flexible tin-based PSCs with an active area of 1 cm<sup>2</sup> were fabricated, achieving a remarkable power conversion efficiency. The presented work shows a significant step forward in the development of lead-free perovskite technology.

# 6.2 Author's contribution

Wiktor Żuraw performed and optimized the fabrication process of tin-based perovskite solar cells presented in the article, carried out their current-voltage characteristics, external quantum efficiency measurements, and participated in the preparation of the original manuscript text. The author also performed structural, morphological, and optical characterization (scanning electron microscopy, X-ray diffraction, and photoluminescence measurements) with the analysis and interpretation of the obtained results. Wiktor Żuraw and Łukasz Przypis (co-supervisor) contributed equally to this work.

# 6.3 Publication



TPSCs with significant improvement in open-circuit voltage leading to the champion device showing a power conversion efficiency of 8.35%.

etal-halide perovskites have emerged as gamechanging materials for energy conversion. Their unique optoelectronic properties and straightforward fabrication processes hold great promise. These lightweight and cost-effective materials can be manufactured at high throughput using inexpensive raw materials and minimal energy inputs. Among solution-processable solar cells, leadbased perovskite solar cells are on the top with an impressive power conversion efficiency (PCE) of 26.1% for single-junction opaque solar cells.<sup>1</sup> However, Pb toxicity poses a significant challenge for practical life applications. To address this problem, the most likely substitute is tin (Sn), which like Pb, is also a group 14 metal. In addition, Sn-based perovskites display similar or superior electronic and optical properties compared to Pb-based perovskites, such as higher charge carrier mobilities and long-lived hot carriers.<sup>2</sup> The organicinorganic tin-based perovskites show good semiconducting behavior with an optical bandgap in the range of 1.2-1.4 eV.<sup>3-5</sup> The first investigation about their application in optoelectronic devices was reported in 2012 for CsSnI<sub>3</sub>. Since then, the development of tin perovskites has expanded to various optoelectronic fields, including photovoltaics, lightemitting devices, and photosensors.<sup>7-10</sup> Despite these favorable optoelectronic properties, tin-based perovskite solar cells (TPSCs) still show PCEs that are much lower than those

of their Pb counterparts. This is mainly attributed to the propensity of the metastable  $Sn^{2+}$  in the perovskite lattice to be oxidized to p-type Sn<sup>4+</sup> defects in the presence of oxygen during the device fabrication (self-doping), or spontaneously through disproportionation in tin-poor environments.<sup>11</sup> Therefore, stopping or controlling this oxidation pathway is one of the requirements to achieve efficient and stable TPSCs. For this reason, several strategies have been employed to tackle the oxidation of Sn<sup>2+</sup>. These include purifying or synthesizing highpurity SnI<sub>2</sub> to minimize SnI<sub>4</sub> content in the precursor,<sup>1</sup> adding bulky A-site cations to stabilize the resulting films, or the use of new solvent systems to avoid oxidation by dimethyl sulfoxide (DMSO). $^{14-17}$  To mitigate Sn<sup>2+</sup> oxidation during fabrication processes, reducing agents or antioxidants are used. Several reducing agents have been implemented, including metallic Sn powder,<sup>18</sup> hypophosphate,<sup>19</sup> sodium borohy-dride,<sup>20</sup> and various organic compounds.<sup>21–24</sup> As for the antioxidants, the most extensively described is SnF<sub>2</sub>.<sup>25</sup>

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Additionally, various sulfur organic derivatives have been used for this purpose.<sup>26,27</sup> Most of these approaches are increasingly used simultaneously to fabricate high-performing TPSCs (Figure 1).



Figure 1. Advancing TPSCs: strategies for enhanced performance.

In this work, we present a novel approach for the synthesis of ultrapure  $\mbox{tin}(II\bar{J})$  iodide, a critical component in the fabrication of TPSCs. Our methodology involves the surface functionalization of tin nanoparticles (NPs) with carboxylic acid ligands, dubbed carboxylic acid-assisted synthesis (CAAS). This method is not only aimed at synthesizing tin(II) iodide but also at hindering the oxidation process. The incorporation of carboxylic acid ligands serves a dual purpose. We expect a synergistic effect wherein these ligands positively interact with the tin-based perovskite compound during the crystallization stage. This interaction is pivotal for the formation of a stable perovskite structure. To study the influence of CAAS on the device performance, we fabricated flexible perovskite solar cells with an active area of >1 cm<sup>2</sup>. The champion device exhibits a PCE of 8.35%, with an open-circuit voltage  $(V_{oc})$  of 0.59 V, a short-circuit current density  $(J_{sc})$  of 21.60 mA/cm<sup>2</sup>, and a fill factor (FF) of 66.5%.

The synthesis of  $SnI_2$  from elements has been reported in the literature,<sup>28</sup> and the use of tin NPs to improve tin-based perovskite ink has also been demonstrated.<sup>24</sup> In our study, by

combining these methodologies, we have proposed a novel approach to synthesize SnI2 in order to obtain a stable tinbased perovskite ink that is not only more resistant to oxidation but also exhibits high device efficiencies. We start by inspecting the key stage of the SnI<sub>2</sub> in situ synthesis, the solidliquid interface interaction of metallic tin and the I2 DMSO complex. This interface is the limiting factor for the reaction. Therefore, to fully control this reaction, it is important to optimize this step. To achieve this, we focused on customizing that interface by increasing the surface area to volume ratio. This approach aimed to overcome limitations and facilitate faster and more efficient synthesis of pure and stable SnI<sub>2</sub>. Metal NPs exhibit highly reduced sizes, resulting in significantly enhanced reactivity, ideal for promoting the desired reaction pathway. To achieve this goal, we applied grafted tin NPs for SnI2 synthesis. By combining the advantages of SnI<sub>2</sub> synthesis from elements and in situ Snnanoparticle generation, we anticipate significant enhancement in the performance of tin-based perovskite inks. Moreover, due to the boosted reaction rate, this method enables the production of SnI<sub>2</sub> in a variety of solvent systems and provides the possibility to work in noninert atmospheres. This opens doors to improved lead-free perovskite solar cell technologies.

The most comprehensive methodology for the preparation of metal NPs involves treatment assisted with ligands.<sup>29–31</sup> We chose to use carboxylic acids as ligands capable of modifying the tin surface. Moreover, carboxylic acids were reported in the literature as effective additives that aid in the formation and crystallization of perovskites.<sup>32–36</sup> Therefore, in our concept, carboxylic acid serves not only as an agent for the formation of Sn-NPs for the synthesis of tin(II) iodide but also can positively affect perovskite formation.

We started the verification of the hypothesis about the key role of nanoparticles by looking for an approach that would involve the formation of Sn-NPs. In general, carboxylic acid can form stabilizing interactions with tin in three different ways.<sup>37</sup> The first is dipole attraction (I), where the –OH group from a carboxylic acid interacts with metallic tin, which being a strong Lewis acid, has a strong affinity for groups containing



Figure 2. (a) Grafting of tin NPs with carboxylic acid—potential interactions. (b) Comparison of reactions with tin powder vs CAAS-SnI<sub>2</sub>. (c) Plausible mechanism of tin(II) iodide formation catalyzed by carboxylic acid.
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Figure 3. Images of SnI<sub>2</sub> precursor solution in DMF:DMSO for different times of exposure to the air: control (on the left) and CAAS-SnI<sub>2</sub> (on the right).

oxygen. Another configuration is carboxylic acid acting as a pincer ligand (II), where the negative dipole moment is shared between two oxygen atoms. The last option combines the first two, forming a bridge-type interaction (III) where one carboxylic unit interacts with two tin centers (Figure 2a).

In the CAAS approach, interactions of the carboxylic acid with tin are enough to form Sn-NPs and recrystallize the surface of tin powder (Figure 2b and Figure S2). Additionally, the anchored carboxylic acid units on the reaction surface can interact positively with iodine molecules, further enhancing the progress of the reaction. In light of the above facts, the natural choice was formic acid, the simplest carboxylic acid. Many preparation protocols for metallic nanoclusters using formic acid were reported in the literature.<sup>38-40</sup> In further experiments, we focus on this acid to develop the perovskite ink preparation procedure. However, for a broader evaluation, we showed that the synthesis of SnI<sub>2</sub> based on the CAAS approach is possible using different carboxylic acids (typical reducing agents or with additional functional groups), which opens the door to introducing additives tailored to the desired composition (Supplementary Discussion 1).

Based on these observations, we propose a plausible pathway for SnI<sub>2</sub> formation in the CAAS process (Figure 2c). In the first step, carboxylic acid coordinates with metallic tin, forming a carboxylic acid-tin complex. In Figure 2a, we present three possible interactions for the carboxylic acid to the tin atom: dipole, pincer, and bridged interaction. However, it is more likely that the carbonyl oxygen of the carboxylic acid coordinates with the tin atom due to its higher nucleophilicity, making the pincer form of the complex the most probable. In the next step, an iodine molecule coordinates with the tincarboxylic acid complex. The carboxylic acid facilitates the oxidative addition of iodine to the tin atom, forming  $\mathrm{SnI}_2$  and regenerating the carboxylic acid for the next catalytic cycle. This proposed stabilization mechanism would explain the observed faster and more efficient reaction under carboxylic acid treatment. We expect that carboxylic acid will have a positive effect on perovskite crystallization. Moreover, the metallic tin NPs suppress the formation of Sn<sup>4+</sup> ions through the reaction  $\operatorname{Sn}^0 + \operatorname{Sn}^{4+} \rightarrow 2\operatorname{Sn}^{2+}$ .

In our approach, we observed that the reaction proceeded at a faster rate compared to the protocol previously reported in the literature (standard synthesis)  $^{28}$  – in our method, the formation of SnI<sub>2</sub> happened immediately. The comparison of the reaction rates between these methods is shown in Figure S3. The enhanced reaction facilitated by Sn-NPs offers numerous advantages for tin-based perovskite ink preparation, including easy scalability for large-scale production and the preparation of  $SnI_2$  in a variety of solvents (Figure S4). Moreover, our method does not require highly restrictive conditions (Figure S5), making it more practical for large-scale production. To evaluate the stability of our ink, we conducted an aging test under controlled conditions (Figure 3). After 2 h, the CAAS-SnI<sub>2</sub> solution maintained its vibrant yellow color without any signs of aging, in contrast to the control (commercial  $SnI_2$ ) sample which promptly turned red. Based on these results, we conclude that, in line with our initial assumptions, the CAAS ink is more resistant to oxidation. Remarkably, these perovskite inks show no signs of aging after 2 years of storage in an  $N_2\mbox{-filled}$  glovebox (Figure S6).

Next, we investigated how CAAS influences perovskite film formation. We prepared perovskite precursor solutions by mixing CAAS-SnI<sub>2</sub> (target) and commercial SnI<sub>2</sub> (control) in DMF:DMSO with FAI and SnF<sub>2</sub> in a 1:1:0.1 molar ratio. Using the spin-coating technique with antisolvent approach, we fabricated highly reproducible uniform perovskite films. We analyzed the composition of perovskite layers using X-ray diffraction (XRD) and did not observe peaks corresponding to the 2D perovskite structure or additive (Figure S7). In the next step, we characterized the morphology of films using a scanning electron microscope (SEM). We confirmed a large grain size that was tightly packed in the film (Figure S8). The photoluminescence (PL) spectrum shown in Figure S9 displays higher emission for the CAAS-FASnI<sub>3</sub> layer than for control FASnI<sub>3</sub>. These results indicate that the CAAS method enables the formation of high-quality perovskite films.

We next study the atomic-level structure of the material using solid-state NMR. <sup>119</sup>Sn Magic Angle Spinning (MAS) NMR has been shown to be highly sensitive to the Sn oxidation state in halide perovskites in solution<sup>41</sup> and the solid state.<sup>42</sup> Notably, the solid-state spectrum of the Sn<sup>2+</sup> perovskite species is sensitive to disproportionation (self-doping) with materials prepared under reducing conditions giving rise to narrow signals and the signal substantially broadening when



Figure 4. <sup>119</sup>Sn solid-state MAS NMR spectra of (a) reference materials, metallic tin, FASnI<sub>3</sub> prepared without a reducing agent, MASnI<sub>3</sub> prepared with a reducing agent ( $H_3PO_2$ ), FA<sub>2</sub>SnI<sub>6</sub> (data adapted from refs 42, red, and 43, blue), and (b) FASnI<sub>3</sub> based on CAAS-SnI<sub>2</sub>. The T<sub>1</sub> of this species is 0.45 s. (c) <sup>13</sup>C solid-state MAS NMR spectra of FASnI<sub>3</sub> based on CAAS-SnI<sub>2</sub>. (Data in panels b and c recorded at 11.7 T, 20 kHz MAS and 298 K.)



Figure 5. (a) J-V parameters and (b) EQE spectra of TPSCs for CAAS-SnI<sub>2</sub> and commercial SnI<sub>2</sub> (control). (c) J-V reverse scan for fresh and aged champion device (inset: picture of the flexible TPSC).

the material is exposed to air (Figure 4a, middle spectra).<sup>43</sup> Figure 4b shows <sup>119</sup>Sn MAS NMR spectra of a sample fabricated using the one-step antisolvent CAAS approach. The spectra show only the presence of FASnI<sub>3</sub> whose signal is narrow ( $85.2 \pm 0.8 \text{ ppm}$ ) and comparable to that previously reported for MASnI<sub>3</sub> prepared in the presence of strongly reducing H<sub>3</sub>PO<sub>2</sub>. There are no detectable signals of metallic tin and FA<sub>2</sub>SnI<sub>6</sub>. These results indicate that the material is fully in its Sn<sup>2+</sup>, unoxidized form. <sup>13</sup>C MAS NMR spectra of the material show the presence of the formate (C=O) and ethylenediammonium signals (Figure 4c), used as additives in

the fabrication process, and residual DMSO, indicating that these species are preserved in the solid material after thin film fabrication. Cross-polarization (CP) and echo spectra are qualitatively similar to CP preferentially enhancing rigid local environments of the sample.

To study the influence of CAAS-SnI<sub>2</sub> on device performance, we fabricated large-area (active area of 1 cm<sup>2</sup>) flexible perovskite solar cells with the simple perovskite composition and device structure: PET/IZO/PEDOT:PSS/FASnI<sub>3</sub>/C<sub>60</sub>/ BCP/Ag. Ethylenediammonium diiodide (EDAI<sub>2</sub>) was used as an additive in perovskite precursor solution as a commonly

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known compound in TPSCs which improves reproducibility and device performance.<sup>44</sup> We observed a significant increase in  $V_{oc}$  and thus PCE for devices made from CAAS-SnI<sub>2</sub> compared to commercial  $SnI_2$  (Figure 5a). This is consistent with the ssNMR and PL results and is ascribed to a reduced defect density due to a decreased amount of Sn<sup>4+</sup> impurities which play the role of nonradiative recombination centers.<sup>45</sup> We note that many factors can influence  $V_{oc}$  and lower values compared to state-of-the-art can result from the large-area flexible substrate and simple 3D perovskite composition without any passivation layers.<sup>46,47</sup> Short-circuit current was similar for both approaches and was mainly in the range of 18-20 mA/cm<sup>2</sup> (Figure 5a). External quantum efficiency (EQE) spectra did not show considerable differences between both methods. Maximum EQE up to 77% was obtained for 510 nm and integrated  $J_{\rm sc}$  matches with  $J_{\rm sc}$  obtained from current density-voltage (J-V) scan (Figure 5b). The thickness of both perovskite layers was the same and reached 190  $\pm$  10 nm (Figure S10). Additionally, CAAS showed better reproducibility of prepared PSCs with an average PCE of  $7.17 \pm 0.15\%$ , compared to the average PCE of 6.07  $\pm$  0.51% for PSCs made from commercial SnI<sub>2</sub>.

To study the charge carrier transport in prepared TPSCs, we measured dark J-V characteristics shown in Figure S11. The device with the CAAS layer exhibited a lower dark current density which can be attributed to the lower density of bulk or interface defect states. The relationship between reverse saturation dark current density ( $J_0$ ) and  $V_{oc}$  is given by  $V_{oc} = \frac{nkT}{q} \ln \frac{I_{sc}}{J_0}$ , where *n* is an ideality factor, *k* is a Boltzmann's

constant, *T* is an absolute temperature and *q* is an elementary charge. The lower  $J_0$  obtained for CAAS leads to higher  $V_{\rm oc}$  which agrees with the  $V_{\rm oc}$  values obtained from J-V light measurements.

We also assessed the stability of unencapsulated PSCs inside an N2-filled glovebox. In the literature, it was reported that EDAI<sub>2</sub> causes slow relaxation of the perovskite structure resulting in increasing performance in time with maximum PCE after 1-3 months of storage.<sup>49</sup> We expected that effect in our PSCs but to avoid the influence of oxygen and water during J-V measurements in ambient conditions, we remeasured the champion device after 7 months of storage and we obtained PCE of 7.96%. Surprisingly, after 2 weeks PCE increased up to 8.35% which is the highest reported PCE for flexible lead-free PSC with a large active area (Figure 5c). That result also indicates that exposing devices to ambient conditions for a few minutes during J-V measurements can accelerate the passivation and crystal relaxation effect of EDAI<sub>2</sub>. PV parameters for the champion cell and record results from the literature are summarized in Table S1. The stability of the device under ambient conditions is presented in Figure S12. After 2000 h of storage on air (35–40% RH) the prepared device (without any encapsulation or passivation layer) retained 40% of the initial PCE.

In summary, we have introduced a novel method for the synthesis of ultrapure and stable  $SnI_2$ , using a nanoparticlebased approach with carboxylic acid ligands (CAAS-SnI<sub>2</sub>). This innovative method involves nanoparticle surface functionalization, which we have demonstrated using various carboxylic acids, with formic acid showing the most promising results. The absence of Sn<sup>4+</sup> species and the long-term stability of the SnI<sub>2</sub> ink were confirmed through aging tests. <sup>119</sup>Sn solidstate MAS NMR analysis revealed that this approach effectively eliminates self-doping, with the FASnI<sub>3</sub> prepared in this way being free of Sn<sup>4+</sup>. This method serves as a versatile platform for the *in situ* preparation of tin-based perovskite ink. The fabricated large-area (1 cm<sup>2</sup>) flexible TPSCs achieved a remarkable PCE of 8.35%. These findings not only advance lead-free perovskite solar cell technology but also pave the way for scalable production of high-performance devices.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.4c02027.

Experimental details including materials, synthesis, solar cells fabrication, characterization data (XRD patterns, SEM images, PL spectra), photographs of synthesized SnI<sub>2</sub> and FASnI<sub>3</sub> perovskite inks, additional discussion about interaction and reaction progress with different carboxylic acids, and JV parameters of state-of-the-art large-area spin-coated tin-based perovskite solar cells (PDF)

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#### REFERENCES

(1) National Renewable Energy Laboratory (NREL). Best Research-Cell Efficiency Chart. https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.pdf (accessed: 2024-05-08).

(2) Fang, H. H.; Adjokatse, S.; Shao, S.; Even, J.; Loi, M. A. Long-Lived Hot-Carrier Light Emission and Large Blue Shift in Formamidinium Tin Triiodide Perovskites. *Nat. Commun.* **2018**, 9 (1), DOI: 10.1038/s41467-017-02684-w.

(3) Pitaro, M.; Tekelenburg, E. K.; Shao, S.; Loi, M. A. Tin Halide Perovskites: From Fundamental Properties to Solar Cells. *Adv. Mater.* **2022**, DOI: 10.1002/adma.202105844.

(4) Filippetti, A.; Kahmann, S.; Caddeo, C.; Mattoni, A.; Saba, M.; Bosin, A.; Loi, M. A. Fundamentals of Tin Iodide Perovskites: A Promising Route to Highly Efficient, Lead-Free Solar Cells. *J. Mater. Chem. A Mater.* **2021**, *9* (19), 11812–11826.

(5) Hao, F.; Stoumpos, C. C.; Cao, D. H.; Chang, R. P. H.; Kanatzidis, M. G. Lead-Free Solid-State Organic-Inorganic Halide Perovskite Solar Cells. *Nat. Photonics* **2014**, *8* (6), 489–494.

(6) Chung, I.; Song, J. H.; Im, J.; Androulakis, J.; Malliakas, C. D.; Li, H.; Freeman, A. J.; Kenney, J. T.; Kanatzidis, M. G. CsSnI 3: Semiconductor or Metal? High Electrical Conductivity and Strong near-Infrared Photoluminescence from a Single Material. High Hole Mobility and Phase-Transitions. J. Am. Chem. Soc. **2012**, 134 (20), 8579–8587.

(7) Żuraw, W.; Vinocour Pacheco, F. A.; Sánchez-Diaz, J.; Przypis,
Ł.; Mejia Escobar, M. A.; Almosni, S.; Vescio, G.; Martínez-Pastor, J.
P.; Garrido, B.; Kudrawiec, R.; Mora-Seró, I.; Öz, S. Large-Area,
Flexible, Lead-Free Sn-Perovskite Solar Modules. ACS Energy Lett.
2023, 8 (11), 4885–4887.

(8) Adl, H. P.; Sánchez-Díaz, J.; Vescio, G.; Cirera, A.; Garrido, B.; Pacheco, F. A. V.; Żuraw, W.; Przypis, Ł.; Öz, S.; Mora-Seró, I.; Martínez-Pastor, J. P.; Suárez, I. Tailoring Single-Mode Random Lasing of Tin Halide Perovskites Integrated in a Vertical Cavity. *Adv. Mater.* **2024**, DOI: 10.1002/adma.202313252.

(9) Vescio, G.; Dirin, D. N.; González-Torres, S.; Sanchez-Diaz, J.; Vidal, R.; Franco, I. P.; Das Adhikari, S.; Chirvony, V. S.; Martínez-Pastor, J. P.; Vinocour Pacheco, F. A.; Przypis, L.; Öz, S.; Hernández, S.; Cirera, A.; Mora-Seró, I.; Kovalenko, M. V.; Garrido, B. Inkjet-Printed Red-Emitting Flexible LEDs Based on Sustainable Inks of Layered Tin Iodide Perovskite. *Adv. Sustain Syst* **2024**, DOI: 10.1002/ adsu.202400060.

(10) Noel, N. K.; Stranks, S. D.; Abate, A.; Wehrenfennig, C.; Guarnera, S.; Haghighirad, A. A.; Sadhanala, A.; Eperon, G. E.; Pathak, S. K.; Johnston, M. B.; Petrozza, A.; Herz, L. M.; Snaith, H. J. Lead-Free Organic-Inorganic Tin Halide Perovskites for Photovoltaic Applications. *Energy Environ. Sci.* **2014**, *7* (9), 3061–3068.

(11) Ricciarelli, D.; Meggiolaro, D.; Ambrosio, F.; De Angelis, F. Instability of Tin Iodide Perovskites: Bulk p-Doping versus Surface Tin Oxidation. *ACS Energy Lett.* **2020**, *5* (9), 2787–2795.

(12) Ozaki, M.; Katsuki, Y.; Liu, J.; Handa, T.; Nishikubo, R.; Yakumaru, S.; Hashikawa, Y.; Murata, Y.; Saito, T.; Shimakawa, Y.; Kanemitsu, Y.; Saeki, A.; Wakamiya, A. Solvent-Coordinated Tin Halide Complexes as Purified Precursors for Tin-Based Perovskites. *ACS Omega* **2017**, *2* (10), 7016–7021.

(13) Zeng, G.; Pu, D.; Huang, L.; Guan, H.; Zhou, S.; Zhou, J.; Shen, W.; Li, G.; Fang, G.; Ke, W. Enhancing the Performance of Tin-Based Perovskite Solar Cells through Solvent Purification of Tin Iodide. *J. Mater. Chem. A Mater.* **2023**, *11* (21), 11245–11253.

(14) Pascual, J.; Nasti, G.; Aldamasy, M. H.; Smith, J. A.; Flatken, M.; Phung, N.; Di Girolamo, D.; Turren-Cruz, S. H.; Li, M.; Dallmann, A.; Avolio, R.; Abate, A. Origin of Sn(Ii) Oxidation in Tin Halide Perovskites. *Mater. Adv.* **2020**, *1* (5), 1066–1070.

(15) Di Girolamo, D.; Pascual, J.; Aldamasy, M. H.; Iqbal, Z.; Li, G.; Radicchi, E.; Li, M.; Turren-Cruz, S. H.; Nasti, G.; Dallmann, A.; De Angelis, F.; Abate, A. Solvents for Processing Stable Tin Halide Perovskites. *ACS Energy Lett.* **2021**, *6* (3), 959–968.

(16) Zhang, Z.; Liang, J.; Wang, J.; Zheng, Y.; Wu, X.; Tian, C.; Sun, A.; Huang, Y.; Zhou, Z.; Yang, Y.; Liu, Y.; Tang, C.; Chen, C. C. DMSO-Free Solvent Strategy for Stable and Efficient Methylammonium-Free Sn-Pb Alloyed Perovskite Solar Cells. *Adv. Energy Mater.* **2023**, *13* (17), DOI: 10.1002/aenm.202300181.

(17) Saidaminov, M. I.; Spanopoulos, I.; Abed, J.; Ke, W.; Wicks, J.; Kanatzidis, M. G.; Sargent, E. H. Conventional Solvent Oxidizes Sn(II) in Perovskite Inks. ACS Energy Lett. 2020, 1153–1155. DOI: 10.1021/acsenergylett.0c00402.

(18) Gu, F.; Ye, S.; Zhao, Z.; Rao, H.; Liu, Z.; Bian, Z.; Huang, C. Improving Performance of Lead-Free Formamidinium Tin Triiodide Perovskite Solar Cells by Tin Source Purification. *Solar RRL* **2018**, 2 (10), DOI: 10.1002/solr.201800136.

(19) Liang, H.; Yuan, F.; Johnston, A.; Gao, C.; Choubisa, H.; Gao, Y.; Wang, Y. K.; Sagar, L. K.; Sun, B.; Li, P.; Bappi, G.; Chen, B.; Li, J.; Wang, Y.; Dong, Y.; Ma, D.; Gao, Y.; Liu, Y.; Yuan, M.; Saidaminov, M. I.; Hoogland, S.; Lu, Z. H.; Sargent, E. H. High Color Purity Lead-Free Perovskite Light-Emitting Diodes via Sn Stabilization. *Advanced Science* **2020**, *7* (8), DOI: 10.1002/advs.201903213.

(20) Sanchez-Diaz, J.; Sánchez, R. S.; Masi, S.; Kreĉmarová, M.; Alvarez, A. O.; Barea, E. M.; Rodriguez-Romero, J.; Chirvony, V. S.; Sánchez-Royo, J. F.; Martinez-Pastor, J. P.; Mora-Seró, I. Tin Perovskite Solar Cells with > 1,300 h of Operational Stability in N2 through a Synergistic Chemical Engineering Approach. *Joule* 2022, 6 (4), 861–883.

(21) Dai, X.; Chen, S.; Jiao, H.; Zhao, L.; Wang, K.; Ni, Z.; Yu, Z.; Chen, B.; Gao, Y.; Huang, J. Efficient Monolithic All-Perovskite Tandem Solar Modules with Small Cell-to-Module Derate. *Nat. Energy* **2022**, *7* (10), 923–931.

(22) Gong, J.; Li, X.; Huang, W.; Guo, P.; Marks, T. J.; Schaller, R. D.; Xu, T. Suppressed Oxidation and Photodarkening of Hybrid Tin Iodide Perovskite Achieved with Reductive Organic Small Molecule. *ACS Appl. Energy Mater.* **2021**, *4* (5), 4704–4710.

(23) Wang, C.; Gu, F.; Zhao, Z.; Rao, H.; Qiu, Y.; Cai, Z.; Zhan, G.; Li, X.; Sun, B.; Yu, X.; Zhao, B.; Liu, Z.; Bian, Z.; Huang, C. Self-Repairing Tin-Based Perovskite Solar Cells with a Breakthrough Efficiency Over 11%. *Adv. Mater.* **2020**, *32* (31), DOI: 10.1002/ adma.201907623.

(24) Nakamura, T.; Yakumaru, S.; Truong, M. A.; Kim, K.; Liu, J.; Hu, S.; Otsuka, K.; Hashimoto, R.; Murdey, R.; Sasamori, T.; Kim, H. Do; Ohkita, H.; Handa, T.; Kanemitsu, Y.; Wakamiya, A. Sn(IV)-Free Tin Perovskite Films Realized by in Situ Sn(0) Nanoparticle Treatment of the Precursor Solution. *Nat. Commun.* **2020**, *11* (1), DOI: 10.1038/s41467-020-16726-3.

(25) Zillner, J.; Boyen, H. G.; Schulz, P.; Hanisch, J.; Gauquelin, N.; Verbeeck, J.; Küffner, J.; Desta, D.; Eisele, L.; Ahlswede, E.; Powalla, M. The Role of  $SnF_2$  Additive on Interface Formation in All Lead-Free FASnI<sub>3</sub> Perovskite Solar Cells. *Adv. Funct Mater.* **2022**, *32* (28), DOI: 10.1002/adfm.202109649.

(26) Tai, Q.; Guo, X.; Tang, G.; You, P.; Ng, T.; Shen, D.; Cao, J.; Liu, C.; Wang, N.; Zhu, Y.; Lee, C.; Yan, F. Antioxidant Grain Passivation for Air-Stable Tin-Based Perovskite Solar Cells. *Angew. Chem.* **2019**, *131* (3), 816–820.

(27) Abdel-Shakour, M.; Matsuishi, K.; Chowdhury, T. H.; Islam, A. Regulated Oxidation and Moisture Permeation via Sulfinic Acid Based Additive Enables Highly Efficient and Stable Tin-Based Perovskite Solar Cells. *Sol. Energy Mater. Sol. Cells* **2023**, *254*, 112241.

(28) Jiang, X.; Li, H.; Zhou, Q.; Wei, Q.; Wei, M.; Jiang, L.; Wang, Z.; Peng, Z.; Wang, F.; Zang, Z.; Xu, K.; Hou, Y.; Teale, S.; Zhou, W.; Si, R.; Gao, X.; Sargent, E. H.; Ning, Z. One-Step Synthesis of SnI2-(DMSO)XAdducts for High-Performance Tin Perovskite Solar Cells. J. Am. Chem. Soc. **2021**, 143 (29), 10970–10976.

(29) Heuer-Jungemann, A.; Feliu, N.; Bakaimi, I.; Hamaly, M.; Alkilany, A.; Chakraborty, I.; Masood, A.; Casula, M. F.; Kostopoulou, A.; Oh, E.; Susumu, K.; Stewart, M. H.; Medintz, I. L.; Stratakis, E.; Parak, W. J.; Kanaras, A. G. The Role of Ligands in the Chemical Synthesis and Applications of Inorganic Nanoparticles. *Chem. Rev.* **2019**, 4819–4880. DOI: 10.1021/acs.chemrev.8b00733.

(30) Barth, B. E. K.; Leusmann, E.; Harms, K.; Dehnen, S. Towards the Installation of Transition Metal Ions on Donor Ligand Decorated Tin Sulfide Clusters. *Chem. Commun.* **2013**, *49* (59), 6590–6592.

(31) Sarkar, A.; Kapoor, S.; Mukherjee, T. Synthesis of Silver Nanoprisms in Formamide. *J. Colloid Interface Sci.* **2005**, 287 (2), 496–500.

(32) Wang, T.; Tai, Q.; Guo, X.; Cao, J.; Liu, C. K.; Wang, N.; Shen, D.; Zhu, Y.; Lee, C. S.; Yan, F. Highly Air-Stable Tin-Based Perovskite

https://doi.org/10.1021/acsenergylett.4c02027 ACS Energy Lett. 2024, 9, 4509–4515 Solar Cells through Grain-Surface Protection by Gallic Acid. ACS Energy Lett. 2020, 5 (6), 1741–1749.

(33) Meng, X.; Wu, T.; Liu, X.; He, X.; Noda, T.; Wang, Y.; Segawa, H.; Han, L. Highly Reproducible and Efficient FASnI3 Perovskite Solar Cells Fabricated with Volatilizable Reducing Solvent. *J. Phys. Chem. Lett.* **2020**, *11* (8), 2965–2971.

(34) Su, Y.; Yang, J.; Liu, G.; Sheng, W.; Zhang, J.; Zhong, Y.; Tan, L.; Chen, Y. Acetic Acid-Assisted Synergistic Modulation of Crystallization Kinetics and Inhibition of Sn<sup>2+</sup> Oxidation in Tin-Based Perovskite Solar Cells. *Adv. Funct Mater.* **2022**, *32* (12), DOI: 10.1002/adfm.202109631.

(35) Li, P.; Cao, X.; Li, J.; Jiao, B.; Hou, X.; Hao, F.; Ning, Z.; Bian, Z.; Xi, J.; Ding, L.; Wu, Z.; Dong, H. Ligand Engineering in Tin-Based Perovskite Solar Cells. *Nano-Micro Letters* **2023**, *15* (167), DOI: 10.1007/s40820-023-01143-0.

(36) Wang, S.; Bidinakis, K.; Haese, C.; Hasenburg, F. H.; Yildiz, O.; Ling, Z.; Frisch, S.; Kivala, M.; Graf, R.; Blom, P. W. M.; Weber, S. A. L.; Pisula, W.; Marszalek, T. Modification of Two-Dimensional Tim-Based Perovskites by Pentanoic Acid for Improved Performance of Field-Effect Transistors. *Small* **2023**, *19* (23), DOI: 10.1002/ smll.202207426.

(37) Galoppini, E. Linkers for Anchoring Sensitizers to Semiconductor Nanoparticles. *Coord. Chem. Rev.* 2004, 248, 1283–1297.
(38) Shi, Q.; Vitchuli, N.; Nowak, J.; Noar, J.; Caldwell, J. M.;

Breidt, F.; Bourham, M.; McCord, M.; Zhang, X. One-Step Synthesis of Silver Nanoparticle-Filled Nylon 6 Nanofibers and Their Antibacterial Properties. *J. Mater. Chem.* **2011**, *21* (28), 10330–10335.

(39) Corradini, P. G.; Antolini, E.; Perez, J. Structural and Electrochemical Characterization of Carbon Supported Pt-Pr Catalysts for Direct Ethanol Fuel Cells Prepared Using a Modified Formic Acid Method in a CO Atmosphere. *Phys. Chem. Chem. Phys.* **2013**, *15* (28), 11730–11739.

(40) Wang, Q.; Wang, Y.; Guo, P.; Li, Q.; Ding, R.; Wang, B.; Li, H.; Liu, J.; Zhao, X. S. Formic Acid-Assisted Synthesis of Palladium Nanocrystals and Their Electrocatalytic Properties. *Langmuir* **2014**, 30 (1), 440–446.

(41) Pascual, J.; Nasti, G.; Aldamasy, M. H.; Smith, J. A.; Flatken, M.; Phung, N.; Di Girolamo, D.; Turren-Cruz, S. H.; Li, M.; Dallmann, A.; Avolio, R.; Abate, A. Origin of Sn(Ii) Oxidation in Tin Halide Perovskites. *Mater. Adv.* **2020**, *1* (5), 1066–1070.

(42) Kubicki, D. J.; Prochowicz, D.; Salager, E.; Rakhmatullin, A.; Grey, C. P.; Emsley, L.; Stranks, S. D. Local Structure and Dynamics in Methylammonium, Formamidinium, and Cesium Tin(II) Mixed-Halide Perovskites from 119Sn Solid-State NMR. *J. Am. Chem. Soc.* **2020**, *142* (17), 7813–7826.

(43) Ha, M.; Karmakar, A.; Bernard, G. M.; Basilio, E.; Krishnamurthy, A.; Askar, A. M.; Shankar, K.; Kroeker, S.; Michaelis, V. K. Phase Evolution in Methylammonium Tin Halide Perovskites with Variable Temperature Solid-State 119Sn NMR Spectroscopy. J. Phys. Chem. C 2020, 124 (28), 15015–15027.

(44) Jokar, E.; Chien, C. H.; Fathi, A.; Rameez, M.; Chang, Y. H.; Diau, E. W. G. Slow Surface Passivation and Crystal Relaxation with Additives to Improve Device Performance and Durability for Tin-Based Perovskite Solar Cells. *Energy Environ. Sci.* **2018**, *11* (9), 2353– 2362.

(45) Zhang, X.; Wang, S.; Zhu, W.; Cao, Z.; Wang, A.; Hao, F. The Voltage Loss in Tin Halide Perovskite Solar Cells: Origins and Perspectives. *Advanced Functional Materials*. John Wiley and Sons Inc., 2022. DOI: 10.1002/adfm.202108832.

(46) Chen, M.; Dong, Q.; Xiao, C.; Zheng, X.; Dai, Z.; Shi, Y.; Luther, J. M.; Padture, N. P. Lead-Free Flexible Perovskite Solar Cells with Interfacial Native Oxide Have > 10% Efficiency and Simultaneously Enhanced Stability and Reliability. ACS Energy Lett. 2022, 7 (7), 2256–2264.

(47) Hou, E.; Chen, J.; Luo, J.; Fan, Y.; Sun, C.; Ding, Y.; Xu, P.; Zhang, H.; Cheng, S.; Zhao, X.; Xie, L.; Yan, J.; Tian, C.; Wei, Z. Cross-Linkable Fullerene Enables Elastic and Conductive Grain Boundaries for Efficient and Wearable Tin-Based Perovskite Solar Cells. Angewandte Chemie - International Edition 2024, 63 (20), DOI: 10.1002/anie.202402775.

(48) Meyer, E. L. Extraction of Saturation Current and Ideality Factor from Measuring  $V_{oc}$  and  $I_{sc}$  of Photovoltaic Modules. International Journal of Photoenergy **2017**, 2017, 1.

(49) Jokar, E.; Chuang, H. S.; Kuan, C. H.; Wu, H. P.; Hou, C. H.; Shyue, J. J.; Wei-Guang Diau, E. Slow Passivation and Inverted Hysteresis for Hybrid Tin Perovskite Solar Cells Attaining 13.5% via Sequential Deposition. J. Phys. Chem. Lett. **2021**, 12 (41), 10106– 10111.

# Supporting information:

# Carboxylic Acid-Assisted Synthesis of Tin(II) Iodide: Key for Stable Large-Area Lead-Free Perovskite Solar Cells

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# **Experimental Section**

## Materials:

Tin powder (99.8%, Thermo Scientific, 325 mesh), iodine 99.5% (Sigma-Aldrich), formic acid 99% (Thermo Scientific), tin(II) iodide (anhydroBeads<sup>TM</sup> 10 mesh, 99.99% trace metals basis, Sigma-Aldrich), formamidinium iodide (FAI, 99.9%, Ajay North America), tin(II) fluoride (SnF<sub>2</sub>, 99%, Sigma-Aldrich), ethylenediammonium diiodide (EDAI<sub>2</sub>, >98.0%, Sigma-Aldrich), poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS, Clevios Al 4083 dispersion), fullerene-C<sub>60</sub> (99.9%, Sigma-Aldrich), bathocuproine (BCP, 99.99%, Sigma-Aldrich), silver (99.99%, Kurt. J. Lesker), N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), dimethyl sulfoxide (DMSO, 99.9%, Sigma-Aldrich), toluene (99.8%, Sigma-Aldrich) were used without further purification. Indium zinc oxide (IZO)-coated polyethylene

terephthalate (PET) substrates (sheet resistance of 15  $\Omega \cdot \Box^{-1}$ ) were bought from Eastman Chemical Company.

#### **Perovskite film fabrication:**

Under a nitrogen atmosphere, the tin powder was suspended in 1 mL of DMF:DMSO 4:1 (v/v). Subsequently, 15  $\mu$ l of formic acid was added, resulting in a greyish-dense dispersion. The dispersion was stirred for 4 hours. The 0.8 mmol of iodine was added gradually to the dispersion under vigorous stirring. The mixture was further agitated for 15 minutes and Snl<sub>2</sub> solution was obtained. The precursor solution for the FASnI<sub>3</sub> perovskite film was prepared by mixing Snl<sub>2</sub> ink with 0.8 mmol of FAI and 0.08 mmol of SnF<sub>2</sub>. For solar cells fabrication, additionally, 2 mol% of EDAI<sub>2</sub> was added to the perovskite precursor solution. For comparison with commercial SnI<sub>2</sub>, a "Control" solution was made by mixing SnI<sub>2</sub>, FAI, SnF<sub>2</sub>, formic acid, and tin powder (additionally EDAI<sub>2</sub> for solar cells) with the same molar ratio to form 0.8 M perovskite solution. Before deposition, the solution was filtered by a 0.22  $\mu$ m PTFE filter. The perovskite precursor solution was dropped onto the surface at the 10<sup>th</sup> second. The resulting film was annealed at 50 °C for 1 minute and at 100 °C for 10 minutes.

#### Solar cell fabrication:

Perovskite solar cells were fabricated on flexible polyethylene terephthalate (PET) foil. IZOcoated PET substrates were etched by dipping one side in the HCl solution (15 wt% in deionized water) and then cleaned by ultrasonication in deionized water and isopropanol for 10 minutes in each solvent and dried by nitrogen flow. After that, substrates were treated with oxygen plasma for 2 minutes. The PEDOT:PSS dispersion was spin-coated at 5000 rpm for 45 seconds, followed by annealing at 120 °C for 30 minutes. The perovskite films were deposited as mentioned above. Then 30 nm of fullerene C<sub>60</sub> and 5 nm of BCP were sequentially evaporated on the perovskite layer. Finally, 100 nm of silver electrode was deposited on top of devices by thermal evaporation through a shadow mask resulting in an active area of >1 cm<sup>2</sup>.

#### **Characterization:**

#### Solid-state NMR

Solid-state MAS NMR spectra of <sup>119</sup>Sn (186.5 MHz) were recorded on a Bruker Avance Neo 11.7 T spectrometer equipped with a 3.2 mm MAS probe using 154 kHz (<sup>119</sup>Sn) and 62.5 kHz (<sup>13</sup>C) RF strength. The recycle delays were as follows: for <sup>119</sup>Sn, 5 ms for the metallic tin and FA<sub>2</sub>SnI<sub>6</sub> regions, and 1 s for the FASnI<sub>3</sub> region, in accordance with reference<sup>1</sup>; for <sup>13</sup>C echo, 10 s, for <sup>1</sup>H-<sup>13</sup>C CP, 15 s. Number of scans: for <sup>119</sup>Sn, 30000 (metallic tin region), 25600 (FA<sub>2</sub>SnI<sub>6</sub> region), 1664 for the FASnI<sub>3</sub> region; for <sup>13</sup>C, 4096 (echo), 2712 (CP). <sup>119</sup>Sn chemical shifts were referenced to neat SnO<sub>2</sub> at -604 ppm. <sup>13</sup>C chemical shifts were referenced to the CH carbon (38.48 ppm) of neat adamantane.

#### Current-voltage measurements

Current density-voltage measurements were carried out by a Keithley 2461 source measure unit. The solar cells were illuminated under ambient conditions with a simulated AM1.5G irradiation of 100 mW·cm<sup>-2</sup> using an AAA-rated solar simulator obtained from Abet Technologies, sun 2000 which was calibrated against an RR-208-KG5 silicon reference cell also procured from Abet Technologies.

#### X-ray diffraction measurements

X-ray diffraction (XRD) patterns were collected with Rigaku MiniFlex600 (Cu K $\alpha$  radiation,  $\lambda$ =1.5406 Å) diffractometer. The samples were measured using  $\theta$ -2 $\theta$  scans. The setup was equipped with a copper anode and a graphite monochromator to select Cu K $\alpha$  radiation (2 $\theta$  5–50 deg; the diffractograms were scanned using 0.1 deg steps and a counting time of 1 s per step).

#### Scanning electron microscopy

Top-view morphology images of samples were obtained with a field emission SEM (Phenom ProX), which had an accelerating voltage of 10 kV with a working distance of 8.0 mm. Cross-section images were developed by deploying a focus ion beam scanning electron microscope, FIB-SEM (FEI Helios 600), which had an accelerating voltage of 2 kV.

#### Photoluminescence measurements

Photoluminescence measurements were performed with the Photon Etc IMA-VIS setup. A green laser (wavelength: 532 nm) was used as the excitation source.

#### External quantum efficiency

External quantum efficiency measurements were obtained with the Bentham PVE300 photovoltaic QE system.

#### **Supplementary Discussion 1:**

In addition to the simple formic acid (ForA), we also tested oxalic acid (OxA, closely resembling ForA), citric acid (featuring additional oxygen atoms, CitA), 2,3pyrazinedicarboxylic acid (with nitrogen atoms, PDCA), and 2,5-thiophenedicarboxylic acid (incorporating an extra sulfur atom, TDCA). Heteroatoms in those acids (such as O, N, S) act as Lewis bases, conceivably leading to additional interactions with the tin metal surface. These interactions have the potential to influence the formation of SnI2 and the properties of the final perovskite ink. Furthermore, our selected additives can be classified into two categories: reducing agents and compounds with strong coordination abilities to metals (Figure S1a). This distinction was crucial as we aimed to discern which factor plays a more significant role in the formation of SnI<sub>2</sub>. Firstly, we suspended the tin powder in DMF:DMSO 4:1 (v/v) solution and then we added carboxylic acid (Figure S1b). Except PDCA, for other dispersions we got greymilky color. The tin powder appeared to be uniformly distributed within the solvent mixture. For the PDCA, we obtained a yellow dispersion which we attribute to the oxidation of Sn<sup>0</sup> to Sn<sup>2+</sup> ions by this acid. PDCA can also strongly coordinate with metal ions resulting in a polymeric structure.<sup>2</sup> In the next step, tin powder activated in this way was reacted with iodine beads (Figure S1c). The reaction was fastest for ForA, and also immediate effects were observed for TDCA and CitA - we obtained yellow solutions indicating that all of the iodine has reacted. The reaction was slower with OxA and PDCA. However, with OxA, tin was in the end converted to SnI2. The observation of the orange-red color in the PDCA system indicated potential further evolution to Sn<sup>4+</sup>, which can strongly interact with PDCA.<sup>2</sup> To confirm the identity of the compound formed in this case, a simple test was conducted by adding formamidinium iodide (FAI) to the ink. If SnI2 was indeed formed, perovskite-complex should have occurred in the presence of the organic component. However, no change in color to yellow was observed even after adding an equal volume of the organic component. The ink retained its intense red color for at least 24 hours. We concluded that the production of perovskite ink was not achievable in this system. In summary, the synthesis of SnI<sub>2</sub> based on CAAS is possible using the versatile nature of carboxylic acids. However, competitive complexation may occur if the carboxylic acid interacts too strongly with the tin ions, as observed with PDCA.



**Figure S1.** (a) Structures of tested carboxylic acids with highlighted additional functionalities; (b) Interaction of different carboxylic acids with tin powder; c) Reaction progress after adding iodine (after 5 minutes).



Figure S2. Tin metallic flakes collected after SnI<sub>2</sub> ink preparation.



**Figure S3**. Comparison of SnI<sub>2</sub> synthesis progress over time a) 30 minutes; b) 2 hours - standard synthesis vs. CAAS method in DMSO.



Figure S4. 20 ml of FASnI<sub>3</sub> ink prepared using the CAAS method.



Figure S5. Comparison of SnI<sub>2</sub> synthesis progress over time under ambient conditions a) 5 minutes; b) 24 hours - standard synthesis vs. CAAS method in DMSO.



Figure S6. Two years old FASnI<sup>3</sup> ink stored in the glove-box.



Figure S7. XRD of FASnI<sub>3</sub> films based on commercial SnI<sub>2</sub> (Control) and CAAS method.



Figure S8. SEM images of FASnI3 films based on commercial SnI2 (Control) and CAAS method.



Figure S9. Photoluminescence spectra for control and CAAS-SnI<sub>2</sub> FASnI<sub>3</sub> layers.



Figure S10. FIB-SEM image of the CAAS-SnI<sub>2</sub> TPSC.



Figure S11. Dark J-V scans for control and CAAS-SnI<sub>2</sub> TPSCs.



Figure S12. Stability of prepared TPSCs exposed to an ambient atmosphere (35-40% RH).

Substrate	Active area (cm²)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF (%)	PCE (%)	Strategy	
Rigid	1.02	19.59	0.53	61	6.33	MACl vapor annealing <sup>3</sup>	
Rigid	1	17.57	0.56	72.0	7.08	Conjugated organic cation additive <sup>4</sup>	
Rigid	1	20.25	0.63	61.2	7.8	CsSnI₃ stabilizer⁵	
Rigid	1	19.80	0.68	66.2	8.9	N-type additive <sup>6</sup>	
Rigid	1.02	19.96	0.77	65.7	10.09	2-step deposition method <sup>7</sup>	
Rigid	1.02	22.69	0.775	68.6	12.05	Modification of	
						NiOx/perovskite interface <sup>8</sup>	
Flexible	1	19.98	0.56	58.8	6.6	CsSnI₃ stabilizer⁵	
Flexible	1	21.60	0.59	65.5	8.35	This work	

Table S1. State-of-the-art large-area spin-coated tin-based perovskite solar cells.

## **References:**

- Kubicki, D. J.; Prochowicz, D.; Salager, E.; Rakhmatullin, A.; Grey, C. P.; Emsley, L.; Stranks, S. D. Local Structure and Dynamics in Methylammonium, Formamidinium, and Cesium Tin(II) Mixed-Halide Perovskites from 119Sn Solid-State NMR. *J Am Chem Soc* 2020, *142* (17), 7813–7826. https://doi.org/10.1021/jacs.0c00647.
- (2) Yin, H. D.; Li, F. H.; Wang, C. H. Syntheses, Characterization and Crystal Structure of Diorganotin and Triorganotin Heterocyclicdicarboxylates with Monomeric, 2D Network and 3D Framework Structures. *Inorganica Chim Acta* 2007, *360* (8), 2797–2808. https://doi.org/10.1016/j.ica.2006.12.012.
- (3) Chowdhury, T. H.; Kayesh, M. E.; Lee, J. J.; Matsushita, Y.; Kazaoui, S.; Islam, A. Post-Deposition Vapor Annealing Enables Fabrication of 1 Cm2 Lead-Free Perovskite Solar Cells. *Solar RRL* 2019, 3 (12). https://doi.org/10.1002/solr.201900245.
- (4) Ran, C.; Gao, W.; Li, J.; Xi, J.; Li, L.; Dai, J.; Yang, Y.; Gao, X.; Dong, H.; Jiao, B.; Spanopoulos, I.; Malliakas, C. D.; Hou, X.; Kanatzidis, M. G.; Wu, Z. Conjugated Organic Cations Enable Efficient Self-Healing FASnI3 Solar Cells. *Joule* 2019, *3* (12), 3072–3087. https://doi.org/10.1016/j.joule.2019.08.023.
- (5) Ye, T.; Wang, X.; Wang, K.; Ma, S.; Yang, D.; Hou, Y.; Yoon, J.; Wang, K.; Priya, S. Localized Electron Density Engineering for Stabilized B-ΓCsSnI3-Based Perovskite Solar Cells with Efficiencies >10%. ACS Energy Lett 2021, 6 (4), 1480–1489. https://doi.org/10.1021/acsenergylett.1c00342.
- (6) Zhang, Z.; Su, Z.; Li, G.; Li, J.; Aldamasy, M. H.; Wu, J.; Wang, C.; Li, Z.; Gao, X.; Li, M.; Abate, A. Improved Air Stability of Tin Halide Perovskite Solar Cells by an N-Type Active Moisture Barrier. *Adv Funct Mater* 2024, *34* (2). https://doi.org/10.1002/adfm.202306458.

- Liu, X.; Wu, T.; Luo, X.; Wang, H.; Furue, M.; Bessho, T.; Zhang, Y.; Nakazaki, J.; Segawa, H.; Han, L. Lead-Free Perovskite Solar Cells with Over 10% Efficiency and Size 1 Cm2 Enabled by Solvent–Crystallization Regulation in a Two-Step Deposition Method. *ACS Energy Lett* 2022, 7 (1), 425–431. https://doi.org/10.1021/acsenergylett.1c02651.
- (8) Li, B.; Zhang, C.; Gao, D.; Sun, X.; Zhang, S.; Li, Z.; Gong, J.; Li, S.; Zhu, Z. Suppressing Oxidation at Perovskite–NiOx Interface for Efficient and Stable Tin Perovskite Solar Cells. *Advanced Materials* 2023. https://doi.org/10.1002/adma.202309768.

# 7 Large-Area, Flexible, Lead-Free Sn-Perovskite Solar Modules

# 7.1 Overview

The publication presents the fabrication of the first-ever tin-based perovskite solar module using a scalable blade-coating technique, marking a significant milestone in the development of lead-free perovskite technology. This achievement is the result of several interlinked innovations. Firstly, a 3D/2D perovskite composition was designed, combining the structural stability of 2D layers with the excellent optoelectronic properties of 3D perovskite. This hybrid composition addressed the inherent instability of tin-based perovskites, which has been a major obstacle in the field. Secondly, additive engineering has further stabilized the tin-based perovskite structure by mitigating the effects of p-doping and oxidation. A key element of this success was the novel synthesis of high-purity tin(II) iodide, described in Chapter 6. In addition to material innovation, attention was given to optimizing the perovskite interface with the hole transport layer and adjusting the laser scribing process. This work represents a crucial step towards the commercialization of tin-based perovskite solar cells, offering a sustainable and environmentally friendly alternative to lead-based systems. The successful realization of this module demonstrates the potential of lead-free perovskites for industrial-scale production.

# 7.2 Author's contribution

Wiktor Żuraw performed and optimized the fabrication of tin-based perovskite solar modules presented in the article, carried out their current-voltage characteristics, analyzed and interpreted all measurements included in the publication, and prepared the original manuscript text. Additionally, Wiktor Żuraw is the corresponding author of this publication.

# 7.3 Publication



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**EXERNENCE AND MENDE** 

# Large-Area, Flexible, Lead-Free Sn-Perovskite Solar Modules

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the past decade due to their promise in optoelectronic and photovoltaic applications. Perovskite solar cells (PSCs) have achieved up to 26% power conversion efficiency (PCE) for single-junction devices.<sup>1</sup> Despite their excellent properties, Pb-based perovskites can be problematic in real-life applications due to concerns about their toxicity.<sup>2</sup> Recently, much attention has been paid to Sn-based PSCs, with a reported PCE close to 15%.<sup>3</sup> However, all the reports available in the literature refer to small-area cells made with non-scalable techniques such as spin-coating. Therefore, the development of methods that allow the fabrication of uniform, large-area thin films is a key step toward the commercialization of lead-free perovskite photovoltaics.

The main reason for the rather slow development of Snbased perovskites is the easy oxidation of  $\text{Sn}^{2+}$  into  $\text{Sn}^{4+}$ , which induces several degradation mechanisms and device performance losses.<sup>4</sup> Another challenge is obtaining uniform layers, as the crystallization kinetics of Sn-based perovskites is faster compared to Pb analogues, producing non-uniform and pinhole-containing films.<sup>5</sup> These facts could be addressed by using additives to reduce  $\text{Sn}^{2+}$  oxidation and to delay the crystallization, or by changing the solvent system, for example, increasing the dimethyl sulfoxide (DMSO) content.<sup>6</sup> However, DMSO is known as a solvent that can accelerate  $\text{Sn}^{2+}$ oxidation. Even though alternative solvent systems have been proposed in the literature, the highest efficiencies have been obtained using DMSO mixed with dimethylformamide (DMF) or pure DMSO compositions.<sup>7</sup> Moreover, these challenges are exacerbated when making large-area devices, as the antisolvent process cannot be used to promote crystallization, in contrast to small-area devices made by spin-coating.

Very recently we have successfully deposited FASnI<sub>3</sub> Pb-free perovskite via a blade-coating technique for the first time. *N*-Butylammonium acetate (BAAc) was used as an additive to control the crystallization dynamics, allowing the fabrication of solar cells with an active area of 1 cm<sup>2</sup> and a PCE of 3.7%.<sup>8</sup> However, further scaling up requires module preparation with solar cells interconnected in series, and more material research is needed to improve the performance.

Here, we present the first report of blade-coated flexible, lead-free perovskite solar modules. We also illustrate how proper 3D/2D perovskite composition can help in the crystallization of the film, as well as how the choice of hole transport material (HTM) can drastically affect the final efficiency of the fabricated mini module. Finally, we demonstrate the potential of Sn-based perovskite solar devices

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https://doi.org/10.1021/acsenergylett.3c02066 ACS Energy Lett. 2023, 8, 4885–4887 with an achieved 5.7% PCE on a 25  $\text{cm}^2$  flexible module for 1000 W/m<sup>2</sup> irradiance (AM 1.5G) and 9.4% PCE for 2000 lx.

Experimental details are provided in the Supporting Information. Briefly, we aimed for a hybrid 3D/2D perovskite composition  $((BA_{0.5}PEA_{0.5})_2FA_3Sn_4I_{13})$  with the addition of an ionic liquid (BAAc) and a reducing agent  $(NaBH_4)$ .<sup>9–11</sup> Figure 1a,b shows the structural and morphological characterization



Figure 1. (a) X-ray diffraction pattern and (b) top-view scanning electron microscopy image of a blade-coated  $(BA_{0.5}PEA_{0.5})_2$ -FA<sub>3</sub>Sn<sub>4</sub>I<sub>13</sub> layer. (c) Normalized photoluminescence and (d) UV-vis absorbance spectra of the corresponding film.

of the blade-coated perovskite layer. The XRD pattern shows the typical diffraction peaks for the (100) and (200) planes around 14° and 28° and additional signals below 5° representative of low-dimensional perovskite phases.<sup>12</sup> Similarly, the photoluminescence spectrum displays not only the expected peak for 3D FASnI<sub>3</sub> around 850 nm but also peaks at lower wavelengths that can be assigned to contributions from the quasi-2D phases, see Figure 1c.<sup>12</sup> These emission bands are correlated with exciton resonances in the absorbance spectrum shown in Figure 1d.<sup>12</sup>

Modules were fabricated in a p-i-n configuration with the following structure: polyethylene terephthalate (PET)/indium tin oxide (ITO)/HTM/(BA<sub>0.5</sub>PEA<sub>0.5</sub>)<sub>2</sub>FA<sub>3</sub>Sn<sub>4</sub>I<sub>13</sub>/C<sub>60</sub>/bathocuproine (BCP)/Ag. As HTM we used (1) an aqueous poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) dispersion, (2) a PEDOT dispersion in toluene, and (3) a nickel oxide dispersion (NiO<sub>x</sub>). For every HTM, we investigated the optimal P2 line processing conditions. P2 processing parameters are presented in Tables S1 and S2. Although PEDOT:PSS is the most widely used HTM in the fabrication of Sn-based PSCs, in our case, the maximum obtained efficiency was 1%. Despite using different laser powers during the P2 process, the short-circuit current density  $(J_{sc})$  obtained for each variant was very low, see Figure S1. We suspect that this is related to the re-absorption of water by the PEDOT:PSS during the P2 process, which was conducted in ambient conditions (25% RH).<sup>13</sup> Current density-voltage (J-V) parameters for NiO<sub>x</sub> are shown in Figure S2. We observed a significant increase in  $J_{sc}$  and fill factor (FF) compared to modules with PEDOT:PSS, but it is known that  $NiO_x$  can promote the oxidation of Sn-based perovskites and is also more prone to mechanical damage from bending, which is a significant parameter for the application of flexible solar cells.<sup>14</sup>

Recently, Di Girolamo et al. successfully employed a nonaqueous HTM source for Sn-based PSCs.<sup>15</sup> With the PEDOT/ Al<sub>2</sub>O<sub>3</sub> bilayer we achieved a  $J_{sc}$  of 16.04 mA/cm<sup>2</sup>, and combined with an open-circuit voltage ( $V_{oc}$ ) of 4.85 V, this resulted in a PCE of 5.7% for the champion module under AM 1.5G illumination. A photograph of the fabricated module and forward scans for champion devices with varying HTMs are displayed in Figure 2a,b, and dark scans are plotted in Figure S3. The J-V parameters and J-V scans for the champion module are shown in Figures S4 and S5.



Figure 2. (a) Picture of the module, (b) J-V forward scans for different HTMs, (c) shelf-stability in N<sub>2</sub> for the champion (19.6 A) and a module fabricated with higher P2 laser power (19.8 A), and (d) J-V forward scans for the champion module for 1000 and 2000 lx illuminance.

We also assessed the stability of our modules over time, see Figure 2c. Non-encapsulated samples were kept inside an N<sub>2</sub>filled glovebox under dark conditions and were exposed to ambient conditions for J-V measurements periodically (30%) RH). The laser power applied during the P2 patterning had a large impact on the module performance but did not play a significant role in the long-term durability. The difference in stability in the first 1600 h might relate to the air exposure time during P2 processing, but most modules achieved 80% of the initial efficiency  $(T_{80})$  after 2000 h, and after 3300 h they obtained similar values in the range of 70-80% of the initial PCE. The evolution of J-V parameters over time for the rest of the modules fabricated on PEDOT/Al<sub>2</sub>O<sub>3</sub> is shown in Figure S6. A significant obstacle during the module fabrication is the degradation of the perovskite layer, which is exposed to the ambient atmosphere during the P2 process. Performing all the steps in an N2 atmosphere could improve the module's final performance and stability even further, but this would be problematic for mass production, and a trade-off would be needed. Our results prove that, despite performing most of the steps in an ambient atmosphere—except for perovskite,  $C_{60}/$ BCP, and Ag deposition-we were still able to obtain satisfactory module performance and stability, see Figure S7.

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Finally, we tested the module behavior at low illuminance conditions, since recently there has been a growing interest in using PSCs for indoor applications.<sup>16</sup> We achieved 7.0% and 9.4% PCE for 1000 and 2000 lx (366 and 738  $\mu$ W/cm<sup>2</sup>), respectively, see Figure 2d. The measurement setup and absolute spectrum for each illuminance are shown in Figures S8 and S9. This result represents a significant milestone for indoor applications of flexible Sn-based perovskite modules and shows a path forward for further research on this topic.

In summary, we present the first report on Pb-free perovskite modules, formed by blade-coating on flexible substrates, demonstrating that Sn-based perovskite photovoltaic modules can be successfully prepared using scalable techniques. After optimization of the HTM/perovskite interface with a PEDOT/Al<sub>2</sub>O<sub>3</sub> bilayer, the champion module achieved a power conversion efficiency of 5.7% under AM 1.5G 1 sun illumination and 9.4% under low light conditions.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.3c02066.

Experimental methods, P2 process parameters, additional data, and characterization measurements (PDF)

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

 Best Research-Cell Efficiency Chart | Photovoltaic Research | NREL. https://www.nrel.gov/pv/cell-efficiency.html (accessed 2023-08-07).
 Ren, M.; Qian, X.; Chen, Y.; et al. Potential Lead Toxicity and Leakage Issues on Lead Halide Perovskite Photovoltaics. J. Hazard. Mater. 2022, 426, 127848.

(3) Jiang, X.; Zang, Z.; Ma, M.; et al. Highly Efficient Tin Perovskite Solar Cells Based on a Triple Reactant Strategy. *ACS Photonics* **2023**, *10*, 1992.

(4) Lanzetta, L.; Webb, T.; Zibouche, N.; et al. Degradation Mechanism of Hybrid Tin-Based Perovskite Solar Cells and the Critical Role of Tin (IV) Iodide. *Nat. Commun.* **2021**, *12*, 2853.

(5) Wang, J.; Gao, Z.; Yang, J.; et al. Controlling the Crystallization Kinetics of Lead-Free Tin Halide Perovskites for High Performance Green Photovoltaics. *Adv. Energy Mater.* **2021**, *11*, 02131.

(6) Sanchez-Diaz, J.; Sánchez, R. S.; Masi, S.; et al. Tin Perovskite Solar Cells with > 1,300 h of Operational Stability in N2 through a Synergistic Chemical Engineering Approach. *Joule* **2022**, *6*, 861.

(7) Nasti, G.; Aldamasy, M. H.; Flatken, M. A.; et al. Pyridine Controlled Tin Perovskite Crystallization. *ACS Energy Lett.* 2022, 7, 3197.

(8) Sanchez-Diaz, J.; Vinocour-Pacheco, F.; Żuraw, W. Ink Engineering and Additive Strategy for Upscaling Deposition of Pb-Free FASnI3 Perovskite Solar Cells on Flexible Substrates via Blade-Coating. Submitted 2023.

(9) Qiu, J.; Xia, Y.; Zheng, Y.; et al. 2D Intermediate Suppression for Efficient Ruddlesden-Popper (RP) Phase Lead-Free Perovskite Solar Cells. *ACS Energy Lett.* **2019**, *4*, 1513.

(10) Li, G.; Su, Z.; Li, M.; et al. Ionic Liquid Stabilizing High-Efficiency Tin Halide Perovskite Solar Cells. *Adv. Energy Mater.* **2021**, *11*, 01539.

(11) Vescio, G.; Sanchez-Diaz, J.; Frieiro, J. L.; et al. 2D PEA 2 SnI 4 Inkjet-Printed Halide Perovskite LEDs on Rigid and Flexible Substrates. *ACS Energy Lett.* **2022**, *7*, 3653.

(12) Yu, B.-B.; Chen, Z.; Zhu, Y.; et al. Heterogeneous 2D/3D Tin-Halides Perovskite Solar Cells with Certified Conversion Efficiency Breaking 14%. *Adv. Mater.* **2021**, *33*, 02055.

(13) Zhanshayeva, L.; Favaron, V.; Lubineau, G. Macroscopic Modeling of Water Uptake Behavior of PEDOT:PSS Films. ACS Omega **2019**, *4*, 21883.

(14) Chen, M.; Dong, Q.; Xiao, C.; et al. Lead-Free Flexible Perovskite Solar Cells with Interfacial Native Oxide Have >10% Efficiency and Simultaneously Enhanced Stability and Reliability. *ACS Energy Lett.* **2022**, *7*, 2256.

(15) Di Girolamo, D.; Aktas, E.; Ponti, C.; et al. Enabling Water-Free PEDOT as Hole Selective Layer in Lead-Free Tin Perovskite Solar Cells. *Mater. Adv.* **2022**, *3*, 9083.

(16) Wojciechowski, K.; Forgács, D. Commercial Applications of Indoor Photovoltaics Based on Flexible Perovskite Solar Cells. ACS Energy Lett. **2022**, *7*, 3729.

# Supporting information:

# Large-area flexible lead-free Sn-perovskite solar modules

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## Materials

Unless otherwise stated, all the materials were purchased from Sigma-Aldrich and used as received. Indium tin oxide (ITO)-coated polyethylene terephthalate (PET) substrates were bought from Eastman Chemical Company. PEDOT:PSS Al 4083 aqueous dispersion and PEDOT:complex HTL Solar 3 dispersion in toluene were purchased from Ossila. Tin(II) iodine (SnI<sub>2</sub>, >99.99%) ink was received from Solaveni. Silver (Ag, 99.99%) was purchased from Kurt. J. Lesker. Formamidinium iodide (FAI) was purchased from Ajay North America. Phenethylammonium iodide (PEAI), and butylammonium iodide (BAI) were purchased from Greatcell Solar Materials.

## Butylammonium acetate (BAAc) synthesis

Acetic acid and butylamine were mixed in a molar ratio of 1:1. First, butylamine was put into stirring in a round bottom flask in an ice bath, and then a diluted solution of acetic acid in ethanol (1:1, v/v) was dropwise added to the flask under vigorous stirring. After the addition of acetic acid, the reaction was left in the ice bath and continuous steering for 2 hours. After that, the mixture was rotary evaporated at 60 °C for 1 h. The resultant liquid product was put into a fridge for 2 hours to crystallize, and then washed with diethyl ether and recrystallized three to five times. The resultant product was dissolved in absolute ethanol and was rotary evaporated at 60 °C for 1 h. Finally, it was cooled down to room temperature to obtain the final liquid product of BAAc.

#### Nickel oxide dispersion preparation

Nickel oxide nanoparticles were prepared from a 5 mol L<sup>-1</sup> aqueous solution of nickel(II) nitrate hexahydrate, tetramethylammonium hydroxide was added to achieve a pH of 10; the precipitated Ni(OH)<sub>2</sub> was washed with deionized water five times, then dried at 80 °C and calcinated at 270 °C for 2 h, after which a black fine powder was collected. The suspension was prepared with nanoparticles concentration of 20 mg mL<sup>-1</sup> in a H<sub>2</sub>O:EtOH (85:15 v/v%) mixture.

## (BA0.5PEA0.5)2FA3Sn4I13 precursor solution formulation

First, 3% molar concentration of sodium borohydride NaBH<sub>4</sub>, 10% molar concentration of SnF<sub>2</sub>, and 60 mg mL<sup>-1</sup> BAAc were added to a 0.6 mol L<sup>-1</sup> ink of SnI<sub>2</sub> precursor in DMF:DMSO (4:1). Then FAI, BAI, PEAI were added in a (3:1:1) molar ratio and stirred at room temperature until a clear yellow solution was obtained. Before use the solutions were passed through a 0.22  $\mu$ m PTFE filter.

#### Module fabrication

ITO-coated PET sheets were patterned using a near-infrared laser (1064 nm wavelength), followed by a washing process with isopropanol. Then, the sheets were dried with N<sub>2</sub> flow and subsequently introduced in an oxygen-plasma chamber for 3 min. The PEDOT:PSS dispersion diluted in ethanol (6:1, v/v), nickel oxide dispersion, or PEDOT:complex dispersion was filtered with a 0.45  $\mu$ m filter. Then, every dispersion were deposited through a blade-coating technique using an effective gap of 125  $\mu$ m at a velocity of 2.5 mm·s<sup>-1</sup> for PEDOT:PSS and nickel oxide dispersions and at a velocity of 5 mm·s<sup>-1</sup> for the PEDOT:complex dispersion. The obtained films were annealed at 100 °C for 30 min. Additionally, for PEDOT:complex layer a Al<sub>2</sub>O<sub>3</sub> wetting layer was deposited using 1 wt% Al<sub>2</sub>O<sub>3</sub> dispersion in isopropanol, 250  $\mu$ m effective gap and 5 mm·s<sup>-1</sup> velocity. The perovskite deposition was done in N<sub>2</sub> filled glovebox by blade-coating

with an effective gap of 150  $\mu$ m and a velocity of 0.7 mm s<sup>-1</sup>. During the coating, the film was dried with a nitrogen flow through an air knife. Then, the sheets were annealed at 80 °C for 10 minutes and at 100 °C for 20 min. A 30 nm layer of C<sub>60</sub> was thermally evaporated on top of the perovskite layer as the electron transport layer, followed by 5 nm of BCP as a buffer layer. All layers except ITO were patterned (P2) in an ambient atmosphere (~30 min exposure) for the interconnection between cells. Then, 100 nm of Ag was deposited through a shadow mask to obtain the electrical insulation between electrodes of adjacent cells.

## Film/module characterization

## Scanning electron microscopy

Top-view morphology images of samples were obtained with a field emission SEM (Phenom ProX), which had an accelerating voltage of 10 kV.

## X-ray diffraction measurements

X-ray diffraction (XRD) patterns were collected with Rigaku MiniFlex600 (Cu K<sub> $\alpha$ </sub> radiation,  $\lambda$ =1.5406 Å) diffractometer.

## Current-voltage measurements

J-V measurements were carried out by a Keithley 2461 source measure unit. The solar cells were illuminated with a simulated AM1.5G irradiation of 100 mW/cm<sup>2</sup> using an AAA-rated solar simulator obtained from Abet Technologies, sun 2000, which was calibrated against an RR-208-KG5 silicon reference cell also procured from Abet Technologies. Measurements in low-light conditions were performed under a warm white LED (CLU028-1201C4-303H7M5-F1, Citizen Electronics, ~3280 K). The spectrum of 1000 and 2000 lx illuminance was measured with the spectrometer SEKONIC C-800 Spectromaster and then, proper irradiance was calculated.

## Absorption and photoluminescence measurements

Absorption spectra, and steady-state photoluminescence measurements were performed with the Edinburgh Instruments FS5 Spectrofluorometer. Samples were excited with a 405 nm laser diode.

Current	18.8 – 19.8 A
Frequency	3000 Hz
Speed	600 mm/s
Line width	80 µm
Pulse width	1.6 μs

Table S1. P2 processing parameters.

 Table S2. Laser power versus output power dependence.

Laser current (A)	18.8	18.9	19.0	19.1	19.2	19.3	19.4	19.5	19.6	19.7	19.8
Output power (W)	0.796	0.835	0.875	0.923	0.971	1.019	1.067	1.115	1.164	1.212	1.260



Figure S1. J-V parameters of solar modules fabricated on PEDOT:PSS for different laser operating currents.



Figure S2. J-V parameters of solar modules fabricated on NiO<sub>x</sub> for different laser operating currents.



Figure S3. J-V forward scans for different HTMs (filled symbols) and dark scans (unfilled symbols).



Figure S4. J-V parameters of solar modules fabricated on PEDOT/Al<sub>2</sub>O<sub>3</sub> for different laser operating currents.



Figure S5. Forward and reverse J-V scan for the champion module.



Figure S6. Shelf-stability of modules fabricated on PEDOT/Al<sub>2</sub>O<sub>3</sub> for different laser operating currents.



Figure S7. Stabilized power output at maximum power point for the champion module after 3300 hours of storage time (3.94% PCE from J-V scan).



Figure S8. The experimental setup for J-V measurements in low illuminance conditions.



Figure S9. Spectrum of the warm white LED (~3280 K) at 1000 and 2000 lx.

# 8 Patent application

Title: A METHOD FOR SYNTHESIZING HALIDE SALTS, A HALIDE SALT BASED PEROVSKITE INK AND POWDER AND A HALIDE SALT BASED PEROVSKITE International application number: PCT/EP2024/061436

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Inventors: Przypis Łukasz, Żuraw Wiktor

Abstract: A method for synthesizing halide salts of a Formula  $Me^{y+}X_{y}^{-}$ , wherein  $Me^{y+}$  represents a cation of a metal having a valency y, and X<sup>-</sup> represents an anion of a halogen (X<sub>2</sub>). The method comprises reacting a first reactant comprising the metal at a zero oxidation degree (Me<sup>0</sup>) in a powder form and an organic acid (A) in a solvent (S), wherein the molar ratio of the metal (Me<sup>0</sup>) to the organic acid (A) is in the range of 0.1:1.0 to 2.0:1.0 with a second reactant being a diatom halogen: X<sub>2</sub>.

# 8.1 Background of the invention

Thin-film perovskite solar cells feature good efficiency and substantially low production costs. Unlike traditional silicon solar cells, thin-film perovskite solar cells can be deposited on flexible substrates, which makes them suitable for use in applications such as flexible and portable electronics, building-integrated photovoltaics, vehicles, etc. Perovskites for perovskite solar cells, such as ABX<sub>3</sub>-type perovskites, can be produced from suitable precursor compounds, including metal halide salts (MeX<sub>y</sub>), such as SnI<sub>2</sub> and SnBr<sub>2</sub>, PbI<sub>2</sub>, or PbBr<sub>2</sub>. The presence of impurities in the perovskite precursors, including metal halide salts MeX<sub>y</sub>, where X typically represents I, Br, or Cl, is highly undesired because the impurities can cause defects in formed perovskite material as well as influence perovskite film morphology, and contribute to forming recombination centers for charge carriers, thereby, reducing both efficiency and stability of PSCs. Among the impurities typically detected in the perovskite precursors, Sn(IV) cations  $(Sn^{4+})$ , being a result of oxidation of tin perovskite precursors  $(SnX_2)$ , are considered an inevitable severe drawback. For instance, even highly pure SnI<sub>2</sub>, such as that commercially available from Sigma-Aldrich or Alfa Aesar, may contain a substantial amount of Sn<sup>4+</sup>. Moreover, batches of SnI<sub>2</sub> from the same provider can vary in purity, resulting in big differences in photovoltaic efficiency of the PSCs comprising the perovskite formed using these precursors.

Thereby, the oxidation of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  can occur during both the preparation of perovskite precursor solutions and perovskite film fabrication, leading to inferior device reproducibility. Certain impurities may be created further, for example, due to the oxidative action of ambient oxygen molecules on the perovskite material in the PSC.

For the reasons mentioned above, perovskite materials - including those based on metal halides - are prone to accelerated material degradation and reduced light absorption over a substantially short time in PSCs. From the patent literature, there are known various attempts aiming at minimizing the presence of defects and impurities, such as tin(IV) cations, in the perovskite material and methods for preparing metal halides of improved purity to be used as perovskite precursors. However, the known methods for synthesizing metal halides as well as forming perovskites from inks comprising these metal halide salts do not provide a satisfactory effect of purity of the synthesized metal halide salts, inks, powders, and perovskites.

# 8.2 Description of the invention

The aim of the present disclosure is to provide a method for synthesizing metal halide salts, as well as preparing perovskite precursor inks, powders, and perovskites based on these metal halide salts that can be devoid of at least one of the above inconveniences, particularly, to minimize the presence of defects and impurities in both the metal halide salts serving as perovskite precursors as well as perovskites themselves, thereby, optimizing perovskite solar cells performance.

In one aspect of the present disclosure, there is provided a method for synthesizing halide salts of a formula  $Me^{y+}X_{y}^{-}$ , wherein  $Me^{y+}$  represents a cation of a metal having a valency y, and X<sup>-</sup> represents an anion of a halogen (X<sub>2</sub>). The method comprises reacting a first reactant comprising the metal at a zero oxidation degree (Me<sup>0</sup>) in a powder form and an organic acid (A) in a solvent (S), wherein the molar ratio of the metal (Me<sup>0</sup>) to the organic acid (A) is in the range of 0.1:1.0 to 2.0:1.0 with a second reactant being a diatom halogen: X<sub>2</sub>.

The method may comprise obtaining the first reactant by preparing a mixture of components: the metal ( $Me^0$ ) in a powder form comprising particles of the metal ( $Me^0$ ), the organic acid, and the solvent, and mixing components for 5 minutes to 24 hours whilst heating components to the temperature from the range of 20 to 100°C.

Said, reacting the first reactant with the second reactant can be carried out directly after obtaining the first reactant.

The metal (Me<sup>0</sup>) can be selected from the group consisting of Al, Ag, Bi, Cd, Co, Cu, Fe, Ga, Ge, Hf, Hg, Mn, Nb, Ni, Pb, Sc, Sn, Ta, Ti, Tl, V, Y, Zn, and Zr.

The cation (Me<sup>y+</sup>) of the metal can be selected from the group consisting of Ag<sup>+</sup>, Bi<sup>3+</sup>, Cs<sup>+</sup>, Cu<sup>+</sup>, Ge<sup>2+</sup>, Mn<sup>2+</sup>, Pb<sup>2+</sup>, Sn<sup>2+</sup>, and Zn<sup>2+</sup>.

The diatom halogen  $(X_2)$  can be selected from the group consisting of Br<sub>2</sub>, and I<sub>2</sub>,

The organic acid can be at least one acid selected from the group consisting of formic acid, propanoic acid, hexanoic acid, myristic acid, oxalic acid, maleic acid, tartaric acid, 1,4-cyclohexanodicarboxylic acid, sebacic acid, japanic acid, phtalic acid, isophtalic acid, terephtalic acid, 2,5-furandicarboxylic acid, tricarboxylic acid, citric acid, agaric acid, gallic acid, 1,2,3,4-butanetetracarboxylic acid, and pyromellitic acid, or any mixture of two or more thereof.

The solvent can be selected from polar protic solvents selected from water, methanol, ethanol, isopropanol, n-butanol, ethylene glycol, glycerol, or a mixture of two or more thereof being miscible to each other, or aprotic polar solvents selected from ethyl acetate, acetonitrile, dimethylformamide, dimethyl sulfoxide, dioxane, gamma-butyrolactone, tetrahydrofuran, or a mixture of two or more thereof being miscible to each other, or said nonpolar solvents selected from chloroform, chlorobenzene, toluene, or a mixture of two or more thereof being miscible to each other, and wherein the weight ratio of the metal ( $Me^0$ ) to the solvent (S) in the mixture is in the range of 2:1 to 25:1

The method may comprise, whilst reacting, heating reactants to a temperature from the range of 20 to 100°C till obtaining a post-reaction system comprising the halide salt.

The method may further comprise obtaining a perovskite precursor in the form of ink or powder by introducing to said post-reaction system, a second component (AX) selected from the group consisting of methyl ammonium iodide (MAI), formamidinium iodide (FAI), noctylammonium iodide (OAI), phenylethylammonium bromide (PEABr), or metal halide (MeX<sub>y</sub>), such as CsI, CsBr, in an amount effective for the perovskite precursor synthesis.

The method may further comprise forming a photoactive perovskite (AMeX<sub>3</sub>) from the perovskite precursor by coating a substrate with said perovskite precursor, and annealing the perovskite precursor coat to a temperature suitable for crystallizing the photoactive perovskite. In another aspect, the invention relates to a halide salt obtained by the method as described herein.

In yet another aspect, the invention relates to a perovskite precursor in the form of ink or powder, obtained by reacting the halide salt as described herein with a second reagent (AX) for the perovskite precursor synthesis.

The invention further relates to a photoactive perovskite layer (AMeX<sub>3</sub>) prepared from the perovskite precursor as described herein.

These and other features of the invention are schematically shown in Figure 17 and Figure 18.



Figure 17. A schema of the process of preparing a first reactant for metal halide synthesis.



Figure 18. A schema of the method for preparing an ink or powder, followed by preparing a perovskite (AMeX<sub>3</sub>), using synthesized metal halides.

# 8.3 Summary

The main aspect of the method, according to the present disclosure, is the use of elemental halides  $(X_2)$  and metals at zero oxidation degree  $(Me^0)$  such that the first reactant and the second reactant can show improved purity. Further, due to the simple composition of the obtained post-reaction system, preparation of the ink (serving as a perovskite precursor) or powder can be carried out *in situ* – at the place of metal halide synthesis, no further isolation or purification steps of the obtained metal halide salt is needed since all post-reaction components can become ink components or powder. Thereby, the risk of further contamination of the perovskite

precursors obtained therefrom is reduced. Furthermore, the metal halides, inks, and powders based on the synthesized metal halide salts show a considerably reduced tendency to generate impurities in them. Therefore, the level of impurities in the perovskite precursors, prepared according to the present disclosure, originating from both external sources and intrinsically generated, is considerably decreased.

The metal halides synthesized according to the present disclosure, as well as inks, powders, and perovskites prepared therefrom, exhibit improved purity (having no or reduced amount of impurities). Therefore, the lifespan and efficiency of the perovskite photoactive materials based on the metal halides synthesized according to the present disclosure are improved. This is especially noticeable for the tin(II) halides (SnX<sub>2</sub>) such as SnI<sub>2</sub> and SnBr<sub>2</sub>, since standard compounds of tin(II) - synthesized according to standard methods - are prone to contamination with  $Sn^{4+}$  (being the product of  $Sn^{2+}$  oxidation). Unlike the standard tin(II) halides, the tin(II) halides prepared according to the present disclosure lack or have a reduced amount of Sn<sup>4+</sup> compared to conventional synthesis or commercially available ones. The same applies to inks, powders, and perovskites prepared therefrom, which have shown no or considerably reduced concentration of Sn<sup>4+</sup> ions. The metal halides serving as the perovskite precursors can show substantially improved purity, whereas said purity can be maintained at a constant level within one production batch and from one batch to another. This enables one to achieve minor or no differences in photovoltaic efficiency of the PCSs comprising the perovskites based on inks or powders according to the present disclosure, leading to increased device reproducibility and therefore reliable quality.

# 9 Conclusions

This dissertation focuses on the development of lead-reduced perovskite solar cells, emphasizing the fabrication of flexible perovskite devices that demonstrate direct implementation and application potential. The presented results confirm that it is possible to fabricate large-area lead-reduced PSCs by engineering the composition of the perovskite ink.

The experimental section explores different possible approaches to fabricating lead-reduced perovskite solar cells. First, the approach of reducing lead content by minimizing the amount of perovskite material used in the cell was demonstrated. By engineering perovskite ink with highly pure precursors, uniform and ultrathin perovskite layers with thickness controlled between 3-625 nm were successfully fabricated. These results represent a significant advancement in the production of lightweight, semi-transparent PSCs based on ultrathin MAPbI<sub>3</sub>, offering a path towards sustainable and highly transparent devices with reduced lead content.

The next step towards lead-reduced PSCs involves the complete replacement of lead with tin. However, this introduces challenges related to the low performance and stability of the devices. The second publication presented in this thesis demonstrates an innovative approach to the synthesis of the crucial precursor for tin-based perovskites - tin(II) iodide. The developed method allows the synthesis of ultrapure and stable SnI<sub>2</sub>, using a nanoparticle-based approach with carboxylic acid ligands. Additionally, this method not only ensures the absence of Sn<sup>4+</sup> impurities but also serves as a versatile platform for the *in situ* preparation of a tin-based perovskite ink. The fabricated large-area flexible tin-based PSCs have achieved remarkable performance and long-term stability, highlighting the potential of lead-free perovskite technology for scalable and sustainable solar energy solutions.

An important aspect of the commercialization of lead-free perovskite photovoltaics is the development of fabrication methods for large-area perovskite solar modules. The third publication presented in this dissertation is the first report on lead-free perovskite modules fabricated by the blade-coating technique on flexible substrates, demonstrating that tin-based perovskite devices can be successfully prepared using scalable deposition methods. This was achieved by optimizing the composition of the perovskite ink and modifying the solvent system for the hole transport layer deposition. Furthermore, the results demonstrate that lead-free perovskite devices can be fabricated using scalable methods, setting a milestone for indoor

applications of flexible tin-based perovskite modules, pointing the way to further progress in this field.

The last part of the experimental work presents a patented method for synthesizing perovskite precursor inks and powders. These inks can be used directly without any further purification steps, which significantly reduces the introduction of impurities into the perovskite precursor system. The perovskite inks and powders exhibit superior purity compared to inks prepared from commercially available precursors, leading to improved power conversion efficiency of PSCs fabricated using this method.

In summary, the research presented in this thesis confirms the hypothesis that, with appropriate engineering of perovskite ink, it is possible to fabricate large-area perovskite solar cells and modules with significantly reduced lead content. The findings underscore the potential of lead-reduced and lead-free photovoltaics in real-world applications, offering a sustainable and scalable alternative for next-generation solar energy solutions.
## Appendix: List of scientific articles

## Publications included in this thesis:

- Ł. Przypis,<sup>‡</sup> W. Żuraw,<sup>‡</sup> M. Grodzicki, M. Ścigaj, R. Kudrawiec, & A. P. Herman, Facile Preparation of Large-Area, Ultrathin, Flexible Semi-Transparent Perovskite Solar Cells via Spin-Coating. ACS Applied Energy Materials, 7 (2024) 4803–4812. https://doi.org/10.1021/acsaem.4c00517.
- W. Żuraw,<sup>‡</sup> D. Kubicki, R. Kudrawiec, & Ł. Przypis,<sup>‡</sup> Carboxylic Acid-Assisted Synthesis of Tin(II) Iodide: Key for Stable Large-Area Lead-Free Perovskite Solar Cells. ACS Energy Letters, 9 (2024) 4509–4515. https://doi.org/10.1021/acsenergylett.4c02027.
- W. Żuraw, F. A. Vinocour Pacheco, J. Sánchez-Diaz, Ł. Przypis, M. A. Mejia Escobar, S. Almosni, G. Vescio, J. P. Martínez-Pastor, B. Garrido, R. Kudrawiec, I. Mora-Seró, & S. Öz, Large-Area, Flexible, Lead-Free Sn-Perovskite Solar Modules. ACS Energy Letters, 8 (2023) 4885–4887. <u>https://doi.org/10.1021/acsenergylett.3c02066</u>.

<sup>‡</sup>These authors made equal contributions to the work.

## Publications not included in this thesis:

- W. Żuraw, W. M. Linhart, J. Occena, T. Jen, J. W. Mitchell, R. S. Goldman, & R. Kudrawiec, Temperature-dependent study of GaAs<sub>1-x-y</sub>N<sub>x</sub>Bi<sub>y</sub> alloys for band-gap engineering: photoreflectance and k · p modeling. *Applied Physics Express*, 13 (2020) 091005. <u>https://doi.org/10.35848/1882-0786/ABB286</u>.
- J. Kopaczek, F. Dybała, S. J. Zelewski, N. Sokołowski, W. Żuraw, K. M. McNicholas, R. H. El-Jaroudi, R. C. White, S. R. Bank, & R. Kudrawiec, Photoreflectance studies of temperature and hydrostatic pressure dependencies of direct optical transitions in BGaAs alloys grown on GaP. *Journal of Physics D: Applied Physics*, 55 (2021) 015107. <u>https://doi.org/10.1088/1361-6463/AC2643</u>.
- G. S. Perez, S. Dasgupta, W. Żuraw, R. F. Pineda, K. Wojciechowski, L. K. Jagadamma, I. Samuel, & N. Robertson, Solution-processable perylene diimide-based electron transport materials as non-fullerene alternatives for inverted perovskite solar cells. *Journal of Materials Chemistry A*, 10 (2022) 11046–11053. https://doi.org/10.1039/D2TA01321E.
- S. Dasgupta, W. Żuraw, T. Ahmad, L. A. Castriotta, E. Radicchi, W. Mróz, M. Ścigaj, Ł. Pawlaczyk, M. Tamulewicz-Szwajkowska, M. Trzciński, J. Serafińczuk, E. Mosconi, A. Di Carlo, F. De Angelis, A. Dudkowiak, & K. Wojciechowski, Modification of a Buried Interface with Bulky Organic Cations for Highly Stable Flexible Perovskite Solar Cells. *ACS Applied Energy Materials*, 5 (2022) 15114–15124. <u>https://doi.org/10.1021/acsaem.2c02780</u>.
- G. Vescio, G. Mathiazhagan, S. González-Torres, J. Sanchez-Diaz, A. Villaueva-Antolí, R. S. Sánchez, A. F. Gualdrón–Reyes, M. Oszajca, F. Linardi, A. Hauser, F. A. Vinocour-Pacheco, W. Żuraw, S. Öz, S. Hernández, I. Mora-Seró, A. Cirera, & B.

Garrido, Fully Inkjet-Printed Green-Emitting PEDOT:PSS/NiO/Colloidal CsPbBr<sub>3</sub>/SnO<sub>2</sub> Perovskite Light-Emitting Diode on Rigid and Flexible Substrates. *Advanced Engineering Materials*, 25 (2023) 2300927. https://doi.org/10.1002/adem.202300927.

- H. P. Adl, J. Sánchez-Díaz, G. Vescio, A. Cirera, B. Garrido, F. A. V. Pacheco, W. Żuraw, Ł. Przypis, S. Öz, I. Mora-Seró, J. P. Martínez-Pastor, & I. Suárez, Tailoring Single-Mode Random Lasing of Tin Halide Perovskites Integrated in a Vertical Cavity. *Advanced Materials*, 36 (2024) 2313252. <u>https://doi.org/10.1002/adma.202313252</u>.
- E. Zdanowicz, Ł. Przypis, W. Żuraw, M. Grodzicki, M. Chlipała, C. Skierbiszewski, A. P. Herman, & R. Kudrawiec, Revealing the TMA<sub>2</sub>SnI<sub>4</sub>/GaN band alignment and carrier transfer across the interface. *Journal of Materials Chemistry C*, 12 (2024) 18356–18362. <u>https://doi.org/10.1039/D4TC03203A</u>.
- A. Wąsiak-Maciejak, Ł. Przypis, W. Żuraw, K. Rycek, P. Janicka, M. Ścigaj, K. Dyk, H. Lai, A. Piejko, D. Pucicki, F. Fu, V. Kinzhybalo, & K. Wojciechowski, Compositional and interfacial engineering for improved light stability of flexible widebandgap perovskite solar cells. *Journal of Materials Chemistry A*, 13 (2025) 7335–7346. <u>https://doi.org/10.1039/D4TA07266A</u>.

## References

- D. Kweku, O. Bismark, A. Maxwell, K. Desmond, K. Danso, E. Oti-Mensah, A. Quachie, & B. Adormaa, Greenhouse Effect: Greenhouse Gases and Their Impact on Global Warming. *Journal of Scientific Research and Reports*, **17** (2017) 1–9. https://doi.org/10.9734/jsrr/2017/39630.
- [2] Climate Action Tracker, Glasgow's 2030 credibility gap: net zero's lip service to climate action (2021). <u>https://climateactiontracker.org/publications/glasgows-2030-credibility-gap-net-zeros-lip-service-to-climate-action/</u> (accessed 2025-02-05).
- [3] International Energy Agency, World Energy Outlook 2023. https://www.iea.org/reports/world-energy-outlook-2023 (accessed 2025-02-05).
- [4] National Renewable Energy Laboratory, Best Research-Cell Efficiency Chart. https://www.nrel.gov/pv/cell-efficiency.html (accessed 2025-02-05).
- [5] Fraunhofer ISE, Photovoltaics Report (2024). <u>https://www.ise.fraunhofer.de/en/publications/studies/photovoltaics-report.html</u> (accessed 2025-02-05).
- [6] O. Vigil-Galán, M. Courel, J. A. Andrade-Arvizu, Y. Sánchez, M. Espíndola-Rodríguez, E. Saucedo, D. Seuret-Jiménez, & M. Titsworth, Route towards low cost-high efficiency second generation solar cells: current status and perspectives. *Journal of Materials Science: Materials in Electronics*, **26** (2015) 5562–5573. https://doi.org/10.1007/s10854-014-2196-4.
- B. G. Akinoglu, B. Tuncel, & V. Badescu, Beyond 3rd generation solar cells and the full spectrum project. Recent advances and new emerging solar cells. *Sustainable Energy Technologies and Assessments*, 46 (2021) 101287. https://doi.org/10.1016/j.seta.2021.101287.
- [8] P. Wang, L. Yang, H. Wu, Y. Cao, J. Zhang, N. Xu, S. Chen, J. D. Decoppet, S. M. Zakeeruddin, & M. Grätzel, Stable and Efficient Organic Dye-Sensitized Solar Cell Based on Ionic Liquid Electrolyte. *Joule*, 2 (2018) 2145–2153. https://doi.org/10.1016/j.joule.2018.07.023.
- [9] L. Zhu, K. H. Lee, M. Yamaguchi, H. Akiyama, Y. Kanemitsu, K. Araki, & N. Kojima, Analysis of nonradiative recombination in quantum dot solar cells and materials. *Progress in Photovoltaics: Research and Applications*, 27 (2019) 971–977. <u>https://doi.org/10.1002/pip.3110</u>.
- [10] S. Kim, H. Van Quy, & C. W. Bark, Photovoltaic technologies for flexible solar cells: beyond silicon. *Materials Today Energy*, **19** (2021) 100583. <u>https://doi.org/10.1016/j.mtener.2020.100583</u>.
- [11] K. Wojciechowski & D. Forgács, Commercial Applications of Indoor Photovoltaics Based on Flexible Perovskite Solar Cells. ACS Energy Letters, 7 (2022) 3729–3733. <u>https://doi.org/10.1021/acsenergylett.2c01976</u>.

- [12] H. S. Jung & N. G. Park, Perovskite solar cells: From materials to devices. *Small*, 11 (2015) 10–25. <u>https://doi.org/10.1002/smll.201402767</u>.
- [13] A. S. Bhalla, R. Guo, & R. Roy, The perovskite structure A review of its role in ceramic science and technology. *Materials Research Innovations*, 4 (2000) 3–26. https://doi.org/10.1007/s100190000062.
- [14] M. A. Green, A. Ho-Baillie, & H. J. Snaith, The emergence of perovskite solar cells. *Nature Photonics*, 8 (2014) 506–514. <u>https://doi.org/10.1038/nphoton.2014.134</u>.
- [15] V. M. Goldschmidt, Die Gesetze der Krystallochemie. Die Naturwissenschaften, 14 (1926) 477–485. <u>https://doi.org/10.1007/BF01507527</u>.
- [16] Y. Fu, M. P. Hautzinger, Z. Luo, F. Wang, D. Pan, M. M. Aristov, I. A. Guzei, A. Pan, X. Zhu, & S. Jin, Incorporating Large A Cations into Lead Iodide Perovskite Cages: Relaxed Goldschmidt Tolerance Factor and Impact on Exciton-Phonon Interaction. ACS Central Science, 5 (2019) 1377–1386. <u>https://doi.org/10.1021/acscentsci.9b00367</u>.
- [17] E. T. Hoke, D. J. Slotcavage, E. R. Dohner, A. R. Bowring, H. I. Karunadasa, & M. D. McGehee, Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics. *Chemical Science*, 6 (2015) 613–617. https://doi.org/10.1039/c4sc03141e.
- [18] A. Kojima, K. Teshima, Y. Shirai, & T. Miyasaka, Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society*, 131 (2009) 6050–6051. <u>https://doi.org/10.1021/ja809598r</u>.
- [19] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, & H. J. Snaith, Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. *Science*, 342 (2013) 341–344. <u>https://doi.org/10.1126/science.1243982</u>.
- [20] S. Li, Y. L. Cao, W. H. Li, & Z. S. Bo, A brief review of hole transporting materials commonly used in perovskite solar cells. *Rare Metals*, 40 (2021) 2712–2729. <u>https://doi.org/10.1007/s12598-020-01691-z</u>.
- [21] I. Lee, J. H. Yun, H. J. Son, & T. S. Kim, Accelerated Degradation Due to Weakened Adhesion from Li-TFSI Additives in Perovskite Solar Cells. ACS Applied Materials and Interfaces, 9 (2017) 7029–7035. <u>https://doi.org/10.1021/acsami.6b14089</u>.
- [22] N. B. Kotadiya, A. Mondal, P. W. M. Blom, D. Andrienko, & G. J. A. H. Wetzelaer, A window to trap-free charge transport in organic semiconducting thin films. *Nature Materials*, **18** (2019) 1182–1186. <u>https://doi.org/10.1038/s41563-019-0473-6</u>.
- [23] C. S. Jiang, M. Yang, Y. Zhou, B. To, S. U. Nanayakkara, J. M. Luther, W. Zhou, J. J. Berry, J. Van De Lagemaat, N. P. Padture, K. Zhu, & M. M. Al-Jassim, Carrier separation and transport in perovskite solar cells studied by nanometre-scale profiling of electrical potential. *Nature Communications*, 6 (2015) 8397. https://doi.org/10.1038/ncomms9397.
- [24] W. Shockley & H. J. Queisser, Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *Journal of Applied Physics*, 32 (1961) 510–519. <u>https://doi.org/10.1063/1.1736034</u>.

- [25] T. S. Sherkar, C. Momblona, L. Gil-Escrig, J. Ávila, M. Sessolo, H. J. Bolink, & L. J. A. Koster, Recombination in Perovskite Solar Cells: Significance of Grain Boundaries, Interface Traps, and Defect Ions. ACS Energy Letters, 2 (2017) 1214–1222. https://doi.org/10.1021/acsenergylett.7b00236.
- [26] J. K. W. Ho, H. Yin, & S. K. So, From 33% to 57% an elevated potential of efficiency limit for indoor photovoltaics. *Journal of Materials Chemistry A*, 8 (2020) 1717–1723. <u>https://doi.org/10.1039/c9ta11894b</u>.
- [27] H. Li & W. Zhang, Perovskite Tandem Solar Cells: From Fundamentals to Commercial Deployment. *Chemical Reviews*, **120** (2020) 9835–9950. <u>https://doi.org/10.1021/acs.chemrev.9b00780</u>.
- [28] N. Marinova, S. Valero, & J. L. Delgado, Organic and perovskite solar cells: Working principles, materials and interfaces. *Journal of Colloid and Interface Science*, 488 (2017) 373–389. <u>https://doi.org/10.1016/j.jcis.2016.11.021</u>.
- [29] A. Babayigit, A. Ethirajan, M. Muller, & B. Conings, Toxicity of organometal halide perovskite solar cells. *Nature Materials*, **15** (2016) 247–251. <u>https://doi.org/10.1038/nmat4572</u>.
- [30] J. Li, H. L. Cao, W. Bin Jiao, Q. Wang, M. Wei, I. Cantone, J. Lü, & A. Abate, Biological impact of lead from halide perovskites reveals the risk of introducing a safe threshold. *Nature Communications*, **11** (2020) 310. <u>https://doi.org/10.1038/s41467-019-13910-y</u>.
- [31] C. C. Stoumpos, C. D. Malliakas, & M. G. Kanatzidis, Semiconducting tin and lead iodide perovskites with organic cations: Phase transitions, high mobilities, and nearinfrared photoluminescent properties. *Inorganic Chemistry*, **52** (2013) 9019–9038. <u>https://doi.org/10.1021/ic401215x</u>.
- [32] R. S. Drago, Thermodynamic evaluation of the inert pair effect. *Journal of Physical Chemistry*, **62** (1958) 353–357. <u>https://doi.org/10.1021/j150561a027</u>.
- [33] D. Ricciarelli, D. Meggiolaro, F. Ambrosio, & F. De Angelis, Instability of tin iodide perovskites: Bulk p-doping versus surface tin oxidation. ACS Energy Letters, 5 (2020) 2787–2795. <u>https://doi.org/10.1021/acsenergylett.0c01174</u>.
- [34] L. Lanzetta, T. Webb, N. Zibouche, X. Liang, D. Ding, G. Min, R. J. E. Westbrook, B. Gaggio, T. J. Macdonald, M. S. Islam, & S. A. Haque, Degradation mechanism of hybrid tin-based perovskite solar cells and the critical role of tin(IV) iodide. *Nature Communications*, **12** (2021) 2853. <u>https://doi.org/10.1038/s41467-021-22864-z</u>.
- [35] M. Ozaki, Y. Katsuki, J. Liu, T. Handa, R. Nishikubo, S. Yakumaru, Y. Hashikawa, Y. Murata, T. Saito, Y. Shimakawa, Y. Kanemitsu, A. Saeki, & A. Wakamiya, Solvent-coordinated tin halide complexes as purified precursors for tin-based perovskites. ACS Omega, 2 (2017) 7016–7021. <u>https://doi.org/10.1021/acsomega.7b01292</u>.
- [36] K. J. Savill, A. M. Ulatowski, & L. M. Herz, Optoelectronic Properties of Tin-Lead Halide Perovskites. ACS Energy Letters, 6 (2021) 2413–2426. <u>https://doi.org/10.1021/acsenergylett.1c00776</u>.
- [37] N. Sun, W. Gao, H. Dong, Y. Liu, X. Liu, Z. Wu, L. Song, C. Ran, & Y. Chen, Architecture of p-i-n Sn-based perovskite solar cells: Characteristics, advances, and

perspectives. ACS Energy Letters, 6 (2021) 2863–2875. https://doi.org/10.1021/acsenergylett.1c01170.

- [38] M. H. Kumar, S. Dharani, W. L. Leong, P. P. Boix, R. R. Prabhakar, T. Baikie, C. Shi, H. Ding, R. Ramesh, M. Asta, M. Graetzel, S. G. Mhaisalkar, & N. Mathews, Lead-free halide perovskite solar cells with high photocurrents realized through vacancy modulation. *Advanced Materials*, 26 (2014) 7122–7127. https://doi.org/10.1002/adma.201401991.
- [39] J. Pascual, M. Flatken, R. Félix, G. Li, S. H. Turren-Cruz, M. H. Aldamasy, C. Hartmann, M. Li, D. Di Girolamo, G. Nasti, E. Hüsam, R. G. Wilks, A. Dallmann, M. Bär, A. Hoell, & A. Abate, Fluoride Chemistry in Tin Halide Perovskites. *Angewandte Chemie International Edition*, 60 (2021) 21583–21591. <u>https://doi.org/10.1002/anie.202107599</u>.
- [40] F. Gu, S. Ye, Z. Zhao, H. Rao, Z. Liu, Z. Bian, & C. Huang, Improving Performance of Lead-Free Formamidinium Tin Triiodide Perovskite Solar Cells by Tin Source Purification. *Solar RRL*, 2 (2018) 1800136. <u>https://doi.org/10.1002/solr.201800136</u>.
- [41] H. Liang, F. Yuan, A. Johnston, C. Gao, H. Choubisa, Y. Gao, Y. K. Wang, L. K. Sagar, B. Sun, P. Li, G. Bappi, B. Chen, J. Li, Y. Wang, Y. Dong, D. Ma, Y. Gao, Y. Liu, M. Yuan, M. I. Saidaminov, S. Hoogland, Z. H. Lu, & E. H. Sargent, High Color Purity Lead-Free Perovskite Light-Emitting Diodes via Sn Stabilization. *Advanced Science*, 7 (2020) 1903213. <u>https://doi.org/10.1002/advs.201903213</u>.
- [42] M. E. Kayesh, T. H. Chowdhury, K. Matsuishi, R. Kaneko, S. Kazaoui, J. J. Lee, T. Noda, & A. Islam, Enhanced Photovoltaic Performance of FASnI<sub>3</sub>-Based Perovskite Solar Cells with Hydrazinium Chloride Coadditive. ACS Energy Letters, 3 (2018) 1584–1589. <u>https://doi.org/10.1021/acsenergylett.8b00645</u>.
- [43] Y. Liao, H. Liu, W. Zhou, D. Yang, Y. Shang, Z. Shi, B. Li, X. Jiang, L. Zhang, L. N. Quan, R. Quintero-Bermudez, B. R. Sutherland, Q. Mi, E. H. Sargent, & Z. Ning, Highly Oriented Low-Dimensional Tin Halide Perovskites with Enhanced Stability and Photovoltaic Performance. *Journal of the American Chemical Society*, **139** (2017) 6693–6699. <u>https://doi.org/10.1021/jacs.7b01815</u>.
- [44] E. Jokar, C. H. Chien, A. Fathi, M. Rameez, Y. H. Chang, & E. W. G. Diau, Slow surface passivation and crystal relaxation with additives to improve device performance and durability for tin-based perovskite solar cells. *Energy and Environmental Science*, **11** (2018) 2353–2362. <u>https://doi.org/10.1039/c8ee00956b</u>.
- [45] S. Joy, H. R. Atapattu, S. Sorensen, H. Pruett, A. B. Olivelli, A. J. Huckaba, A. F. Miller, & K. R. Graham, How additives for tin halide perovskites influence the Sn<sup>4+</sup> concentration. *Journal of Materials Chemistry A*, **10** (2022) 13278–13285. <u>https://doi.org/10.1039/d2ta01429g</u>.
- [46] R. A. Kerner, E. D. Christensen, S. P. Harvey, J. Messinger, S. N. Habisreutinger, F. Zhang, G. E. Eperon, L. T. Schelhas, K. Zhu, J. J. Berry, & D. T. Moore, Analytical Evaluation of Lead Iodide Precursor Impurities Affecting Halide Perovskite Device Performance. ACS Applied Energy Materials, 6 (2023) 295–301. https://doi.org/10.1021/acsaem.2c02842.

- [47] P. Zhu, D. Wang, Y. Zhang, Z. Liang, J. Li, J. Zeng, J. Zhang, Y. Xu, S. Wu, Z. Liu, X. Zhou, B. Hu, F. He, L. Zhang, X. Pan, X. Wang, N.-G. Park, & B. Xu, Aqueous synthesis of perovskite precursors for highly efficient perovskite solar cells. *Science*, **383** (2024) 524–531. <u>https://doi.org/10.1126/science.adj7081</u>.
- [48] C. Roldán-Carmona, P. Gratia, I. Zimmermann, G. Grancini, P. Gao, M. Graetzel, & M. K. Nazeeruddin, High efficiency methylammonium lead triiodide perovskite solar cells: The relevance of non-stoichiometric precursors. *Energy and Environmental Science*, 8 (2015) 3550–3556. <u>https://doi.org/10.1039/c5ee02555a</u>.
- [49] J. Chang, H. Zhu, J. Xiao, F. H. Isikgor, Z. Lin, Y. Hao, K. Zeng, Q. H. Xu, & J. Ouyang, Enhancing the planar heterojunction perovskite solar cell performance through tuning the precursor ratio. *Journal of Materials Chemistry A*, 4 (2016) 7943–7949. https://doi.org/10.1039/c6ta00679e.
- [50] D. Bi, W. Tress, M. I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J. P. Correa Baena, J. D. Decoppet, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel, & A. Hagfeldt, Efficient luminescent solar cells based on tailored mixed-cation perovskites. *Science Advances*, 2 (2016). <u>https://doi.org/10.1126/sciadv.1501170</u>.
- [51] S. Shao, M. Nijenhuis, J. Dong, S. Kahmann, G. H. Ten Brink, G. Portale, & M. A. Loi, Influence of the stoichiometry of tin-based 2D/3D perovskite active layers on solar cell performance. *Journal of Materials Chemistry A*, 9 (2021) 10095–10103. <u>https://doi.org/10.1039/d0ta10277f</u>.
- [52] Y. Xu, K. J. Jiang, P. Wang, W. M. Gu, G. H. Yu, X. Zhou, & Y. Song, Highly oriented quasi-2D layered tin halide perovskites with 2-thiopheneethylammonium iodide for efficient and stable tin perovskite solar cells. *New Journal of Chemistry*, 46 (2022) 2259– 2265. <u>https://doi.org/10.1039/d1nj05178d</u>.
- [53] S. G. Kwon & T. Hyeon, Formation mechanisms of uniform nanocrystals via hotinjection and heat-up methods. *Small*, 7 (2011) 2685–2702. <u>https://doi.org/10.1002/smll.201002022</u>.
- [54] K. J. Klabunde & R. M. Richards, Nanoscale materials in chemistry. John Wiley & Sons (2009). <u>https://doi.org/10.1002/9780470523674</u>.
- [55] C. Liu, Y. B. Cheng, & Z. Ge, Understanding of perovskite crystal growth and film formation in scalable deposition processes. *Chemical Society Reviews*, **49** (2020) 1653– 1687. <u>https://doi.org/10.1039/c9cs00711c</u>.
- [56] Z. Lin, Y. Su, R. Dai, G. Liu, J. Yang, W. Sheng, Y. Zhong, L. Tan, & Y. Chen, Ionic Liquid-Induced Ostwald Ripening Effect for Efficient and Stable Tin-Based Perovskite Solar Cells. ACS Applied Materials and Interfaces, 13 (2021) 15420–15428. <u>https://doi.org/10.1021/acsami.1c01408</u>.
- [57] C. A. Johnson, Generalization of the Gibbs-Thomson equation. Surface Science, 3 (1965) 429–444. <u>https://doi.org/10.1016/0039-6028(65)90024-5</u>.
- [58] H. J. V. Tyrrell, The origin and present status of Fick's diffusion law. Journal of Chemical Education, 41 (1964) 397–400. <u>https://doi.org/10.1021/ed041p397</u>.

- [59] A. D. Taylor, Q. Sun, K. P. Goetz, Q. An, T. Schramm, Y. Hofstetter, M. Litterst, F. Paulus, & Y. Vaynzof, A general approach to high-efficiency perovskite solar cells by any antisolvent. *Nature Communications*, **12** (2021) 1878. https://doi.org/10.1038/s41467-021-22049-8.
- [60] J. Yang, E. L. Lim, L. Tan, & Z. Wei, Ink Engineering in Blade-Coating Large-Area Perovskite Solar Cells. Advanced Energy Materials, 12 (2022) 2200975. <u>https://doi.org/10.1002/aenm.202200975</u>.
- [61] Y. Xiao, C. Zuo, J. X. Zhong, W. Q. Wu, L. Shen, & L. Ding, Large-Area Blade-Coated Solar Cells: Advances and Perspectives. *Advanced Energy Materials*, **11** (2021) 2100378. <u>https://doi.org/10.1002/aenm.202100378</u>.
- [62] Y. Deng, C. H. Van Brackle, X. Dai, J. Zhao, B. Chen, & J. Huang, Tailoring solvent coordination for high-speed, room-temperature blading of perovskite photovoltaic films. *Science*, 5 (2019). <u>https://doi.org/10.1126/sciadv.aax7537</u>.
- [63] M. Yin, H. Yao, H. Qiu, C. Wu, M. Zhang, & F. Hao, A Revisit of Crystallization in Tin Halide Perovskite Thin Films: From Nucleation, Intermediate to Crystal Growth. *Advanced Functional Materials*, 34 (2024) 2404792. https://doi.org/10.1002/adfm.202404792.
- [64] P. Caprioglio, M. Stolterfoht, C. M. Wolff, T. Unold, B. Rech, S. Albrecht, & D. Neher, On the Relation between the Open-Circuit Voltage and Quasi-Fermi Level Splitting in Efficient Perovskite Solar Cells. *Advanced Energy Materials*, 9 (2019) 1901631. <u>https://doi.org/10.1002/aenm.201901631</u>.
- [65] M. Stolterfoht, P. Caprioglio, C. M. Wolff, J. A. Márquez, J. Nordmann, S. Zhang, D. Rothhardt, U. Hörmann, Y. Amir, A. Redinger, L. Kegelmann, F. Zu, S. Albrecht, N. Koch, T. Kirchartz, M. Saliba, T. Unold, & D. Neher, The impact of energy alignment and interfacial recombination on the internal and external open-circuit voltage of perovskite solar cells. *Energy and Environmental Science*, **12** (2019) 2778–2788. <u>https://doi.org/10.1039/c9ee02020a</u>.
- [66] I. Lange, J. Kniepert, P. Pingel, I. Dumsch, S. Allard, S. Janietz, U. Scherf, & D. Neher, Correlation between the open circuit voltage and the energetics of organic bulk heterojunction solar cells. *Journal of Physical Chemistry Letters*, 4 (2013) 3865–3871. https://doi.org/10.1021/jz401971e.
- [67] S. Rühle, Tabulated values of the Shockley-Queisser limit for single junction solar cells. *Solar Energy*, **130** (2016) 139–147. <u>https://doi.org/10.1016/j.solener.2016.02.015</u>.
- [68] M. Gruber, J. Wagner, K. Klein, U. Hörmann, A. Opitz, M. Stutzmann, & W. Brütting, Thermodynamic efficiency limit of molecular donor-acceptor solar cells and its application to diindenoperylene/C60-based planar heterojunction devices. *Advanced Energy Materials*, 2 (2012) 1100–1108. https://doi.org/10.1002/aenm.201200077.
- [69] X. Zhang, S. Wang, W. Zhu, Z. Cao, A. Wang, & F. Hao, The Voltage Loss in Tin Halide Perovskite Solar Cells: Origins and Perspectives. *Advanced Functional Materials*, 32 (2022) 2108832. <u>https://doi.org/10.1002/adfm.202108832</u>.

- [70] J. Liu, S. Wang, W. Zhu, Z. Tang, L. Ding, & F. Hao, Highly symmetric Lewis base coordinated with Sn<sup>2+</sup> for reducing voltage loss and retarding oxidation in tin-halide perovskite solar cells. *Chemical Engineering Journal*, **453** (2023) 139975. <u>https://doi.org/10.1016/j.cej.2022.139975</u>.
- [71] M. Stolterfoht, C. M. Wolff, Y. Amir, A. Paulke, L. Perdigón-Toro, P. Caprioglio, & D. Neher, Approaching the fill factor Shockley-Queisser limit in stable, dopant-free triple cation perovskite solar cells. *Energy and Environmental Science*, **10** (2017) 1530–1539. https://doi.org/10.1039/c7ee00899f.
- [72] M. Diantoro, T. Suprayogi, A. Hidayat, A. Taufiq, A. Fuad, & R. Suryana, Shockley's equation fit analyses for solar cell parameters from I-V curves. *International Journal of Photoenergy*, 2018 (2018) 9214820. <u>https://doi.org/10.1155/2018/9214820</u>.
- [73] L. V. Mercaldo, E. Bobeico, A. De Maria, M. Della Noce, M. Ferrara, L. Lancellotti, A. Romano, G. V. Sannino, G. Nasti, A. Abate, & P. Delli Veneri, Procedure Based on External Quantum Efficiency for Reliable Characterization of Perovskite Solar Cells. *Energy Technology*, **10** (2022) 2200748. <u>https://doi.org/10.1002/ente.202200748</u>.
- [74] M. Saliba & L. Etgar, Current density mismatch in Perovskite solar cells. ACS Energy Letters, 5 (2020) 2886–2888. <u>https://doi.org/10.1021/acsenergylett.0c01642</u>.
- [75] R. Carron, C. Andres, E. Avancini, T. Feurer, S. Nishiwaki, S. Pisoni, F. Fu, M. Lingg,
  Y. E. Romanyuk, S. Buecheler, & A. N. Tiwari, Bandgap of thin film solar cell absorbers: A comparison of various determination methods. *Thin Solid Films*, 669 (2019) 482–486. <u>https://doi.org/10.1016/j.tsf.2018.11.017</u>.
- [76] H. Zai, Y. Ma, Q. Chen, & H. Zhou, Ion migration in halide perovskite solar cells: Mechanism, characterization, impact and suppression. *Journal of Energy Chemistry*, 63 (2021) 528–549. <u>https://doi.org/10.1016/j.jechem.2021.08.006</u>.
- [77] S. Ravishankar, C. Aranda, P. P. Boix, J. A. Anta, J. Bisquert, & G. Garcia-Belmonte, Effects of Frequency Dependence of the External Quantum Efficiency of Perovskite Solar Cells. *Journal of Physical Chemistry Letters*, 9 (2018) 3099–3104. <u>https://doi.org/10.1021/acs.jpclett.8b01245</u>.
- [78] T. G. Mayerhöfer, S. Pahlow, & J. Popp, The Bouguer-Beer-Lambert Law: Shining Light on the Obscure. *ChemPhysChem*, **21** (2020) 2029–2046. <u>https://doi.org/10.1002/cphc.202000464</u>.
- [79] J. Tauc, R. Grigorovici, & A. Vancu, Optical Properties and Electronic Structure of Amorphous Germanium. *physica status solidi* (b), **15** (1966) 627–637. <u>https://doi.org/10.1002/pssb.19660150224</u>.
- [80] J. Klein, L. Kampermann, B. Mockenhaupt, M. Behrens, J. Strunk, & G. Bacher, Limitations of the Tauc Plot Method. *Advanced Functional Materials*, 33 (2023) 2304523. <u>https://doi.org/10.1002/adfm.202304523</u>.
- [81] W. H. Bragg & W. L. Bragg, The Reflection of X-rays by Crystals. Proceedings of the Royal Society of London. Series A, 88 (1913) 428–438. <u>https://doi.org/10.1098/rspa.1913.0040</u>.

- [82] W. L. Tan & C. R. McNeill, X-ray diffraction of photovoltaic perovskites: Principles and applications. *Applied Physics Reviews*, 9 (2022) 021310. <u>https://doi.org/10.1063/5.0076665</u>.
- [83] V. K. Pecharsky & P. Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials. Springer (2009). <u>https://doi.org/10.1007/978-0-387-09579-0</u>.
- [84] D. Kriegner, Z. Matěj, R. Kužel, & V. Holý, Powder diffraction in bragg-brentano geometry with straight linear detectors. *Journal of Applied Crystallography*, 48 (2015) 613–618. <u>https://doi.org/10.1107/S1600576715003465</u>.
- [85] B. S. Hulbert & W. M. Kriven, Specimen-displacement correction for powder X-ray diffraction in Debye–Scherrer geometry with a flat area detector. *Journal of Applied Crystallography*, 56 (2023) 576. <u>https://doi.org/10.1107/S160057672300153X</u>.
- [86] A. L. Patterson, The Scherrer Formula for X-Ray Particle Size Determination. *Physical Review*, 56 (1939) 978. <u>https://doi.org/10.1103/PhysRev.56.978</u>.
- [87] A. Monshi, M. R. Foroughi, & M. R. Monshi, Modified Scherrer Equation to Estimate More Accurately Nano-Crystallite Size Using XRD. World Journal of Nano Science and Engineering, 2 (2012) 154–160. <u>https://doi.org/10.4236/wjnse.2012.23020</u>.
- [88] S. N. Danilchenko, O. G. Kukharenko, C. Moseke, I. Y. Protsenko, L. F. Sukhodub, & B. Sulkio-Cleff, Determination of the bone mineral crystallite size and lattice strain from diffraction line broadening. *Crystal Research and Technology*, **37** (2002) 1234–1240. <u>https://doi.org/10.1002/1521-4079(200211)37:11<1234::AID-CRAT1234>3.0.CO;2-X</u>.
- [89] A. R. Stokes & A. J. C. Wilson, The diffraction of X rays by distorted crystal aggregates
  I. *Proceedings of the Physical Society*, 56 (1944) 174. <u>https://doi.org/10.1088/0959-5309/56/3/303</u>.
- [90] G. K. Williamson & W. H. Hall, X-ray line broadening from filed aluminium and wolfram. Acta Metallurgica, 1 (1953) 22–31. <u>https://doi.org/10.1016/0001-6160(53)90006-6</u>.
- [91] K. Nishimura, D. Hirotani, M. A. Kamarudin, Q. Shen, T. Toyoda, S. Iikubo, T. Minemoto, K. Yoshino, & S. Hayase, Relationship between Lattice Strain and Efficiency for Sn-Perovskite Solar Cells. ACS Applied Materials and Interfaces, 11 (2019) 31105–31110. <u>https://doi.org/10.1021/acsami.9b09564</u>.
- [92] S. Yao, H. Li, S. Pang, B. Zhu, X. Zhang, & S. Fatikow, A Review of Computer Microvision-Based Precision Motion Measurement: Principles, Characteristics, and Applications. *IEEE Transactions on Instrumentation and Measurement*, **70** (2021) 5007928. <u>https://doi.org/10.1109/TIM.2021.3065436</u>.
- [93] L. Reimer, Scanning Electron Microscopy. Springer (1998). https://doi.org/10.1007/978-3-540-38967-5.
- [94] H. Williams, SEM for conductive and non-conductive specimens. *Physics Education*, 56 (2021) 055034. <u>https://doi.org/10.1088/1361-6552/AC1503</u>.

- [95] T. J. Shaffner & R. D. Van Veld, "Charging" effects in the scanning electron microscope. Journal of Physics E: Scientific Instruments, 4 (1971) 633. <u>https://doi.org/10.1088/0022-3735/4/9/002</u>.
- [96] Z. L. Wang & J. L. Lee, Electron Microscopy Techniques for Imaging and Analysis of Nanoparticles - Developments in Surface Contamination and Cleaning (Second Edition).
   William Andrew Publishing. (2008) 395–443. <u>https://doi.org/10.1016/B978-0-323-29960-2.00009-5</u>.