



Controlling crystal growth by chloride-assisted synthesis: Towards optimized charge transport in hybrid halide perovskites



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ABSTRACT

Understanding the charge carrier dynamics and charge transport in metal halide perovskites and their correlation with the synthesis procedure is crucial for the fabrication of competitive thin film photovoltaic devices and their further improvement. In this work we investigate two $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPI) films both deposited by a two-step protocol and only differing in the optional addition of a chloride containing salt to the precursor solution. Although being highly akin from a chemical and structural point of view, these films show substantial differences in their optoelectronic characteristics. For chloride-treated perovskite films we find an enhanced average power conversion efficiency of 10.3% and charge carrier mobility of $\mu=2.16 \text{ cm}^2/\text{Vs}$ in comparison to 5.3% and $\mu=1.62 \text{ cm}^2/\text{Vs}$ for untreated MAPI films, respectively. Moreover, we observe different light-soaking behavior and increased photoluminescence lifetimes of 70 ns in the case of chloride-treated MAPI and 100 ns for pure MAPI. From in-situ photoluminescence lifetime measurements during the crystallization process we conclude that the chloride addition during film deposition results in slower crystal growth, leading to fewer defects and higher crystalline order.

1. Introduction

Organic-inorganic hybrid perovskites have experienced an unexpected scientific boost rendering them the fastest advancing solar technology the community has ever observed [1–4]. Highly advantageous physical properties such as tunable electronic properties [5,6] or strong optical absorption over the visible regime of light [4,7] are considered to be some of the key features for becoming competitive with the presently used commercial technologies such as silicon and CIGS [8–10] and other emerging materials such as CuO_2 [11]. A great effort has been spent to improve and optimize different synthesis approaches with cheap bulk materials [12–15], allowing for the substantial increase of power conversion efficiencies (PCE) in perovskite-based photovoltaic devices, ranging from 3.8% [1] to 6.5% [16] in 2009 to values currently exceeding 21% [17]. Several device engineering protocols are reported to optimize the respective material properties to boost device efficiencies. Amongst others the addition of chloride-containing compounds to the methylammonium iodide pre-

cursor solution for the synthesis of methylammonium lead triiodide (MAPI) films in a two-step solution deposition route became very interesting due to the improved PCE values by this synthesis protocol [18–21]. Although an incorporation of chloride ions into the final crystal structure has not been detected yet by any analytical procedure, the function of chloride for the control of the resulting optoelectronic properties seems to be crucial, but still remains unclear.

Aiming to provide an explanation for the effect of chloride addition during film synthesis we investigated the properties of chloride-treated MAPI thin films and compared them to the results obtained for untreated MAPI films. We first determined the morphology and crystalline structure of the materials by means of scanning electron microscopy and X-ray diffraction together with the optoelectronic properties of the respective films. We then studied the charge carrier mobility and dynamics in the two films using the Time-of-Flight (ToF) technique and time-resolved photoluminescence (PL), both ex-situ as well as in-situ during the crystallization processes. From these in-situ photoluminescence lifetime measurements we conclude that the chlor-

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2. Experimental part

2.1. Perovskite thin film preparation and solar cell fabrication

Preparation of the precursor solutions and perovskite thin film deposition was done following a previously published synthesis route [18,19]. A detailed description of the synthesis procedures as well as solar cell fabrication can be found in the [Supporting information](#).

2.2. In-plane gold electrodes on glass

Laterally arranged gold contacts were fabricated in a cleanroom facility via optical lithography. The individual steps including the fabrication of the structures as well as the deposition of the metallic contacts on the glass substrate are specified in the [Supporting information](#).

2.3. Time-of-Flight measurements

Charge carrier mobilities in perovskite thin films were extracted from Time-of-Flight (ToF) experiments (see [Supporting information](#), [Fig. S2](#)). Laterally contacted perovskite films were illuminated from the semi-transparent glass/gold side ([Fig. 3a](#)) using pulsed laser excitation at 540 nm and a pulse length of 7 ns. By applying a constant external electric field at the electrodes only for the short measurement interval of roughly 1 s to avoid effects due to ion migration [22–24], a current flow is created, leading to the respective ToF transient as seen in [Fig. 3b](#).

2.4. Laser scanning confocal microscopy

Time-resolved photoluminescence (PL) studies [25] were carried out by confocal microscopy in combination with time-correlated single photon counting (TCSPC) and utilized to extract the PL lifetime and intensity of the different films using the software Fluofit (Picoquant). Further information about the configuration of the corresponding setup and the instrument response function (IRF) can be found in the [Supporting information](#), [Figs. S3 and S4](#).

2.5. In-situ PL measurements

PL measurements during crystal growth of both perovskites at room temperature were performed using a TCSPC setup. Glass substrates coated with a thin layer of PbI_2 were immersed into a cuvette filled with the methylammonium iodide precursor to initiate the perovskite film formation at room temperature. Laser excitation was provided by the same laser as used for the aforementioned time-resolved PL studies. PL transients were recorded over a time frame of 1000 min by means of a photomultiplier detector assembly.

3. Results and discussion

3.1. Morphology, structure and optical properties

Methylammonium lead triiodide (MAPI) thin films investigated in this work were fabricated via a two-step solution deposition conversion protocol [18,19], representing one of the state-of-the-art synthesis techniques. From this procedure, either MAPI films, in the following referred to as “pure MAPI”, or “chloride-treated MAPI” films are obtained. When comparing these films by different analytical techniques including scanning electron microscopy (SEM) ([Fig. 1a and b](#)) and UV-Vis spectroscopy ([Fig. 1d](#)), no significant differences could be observed. In particular, the X-ray diffraction (XRD) patterns obtained

for the two materials ([Fig. 1c](#)) are virtually identical indicating that the same crystal structure is formed and that the addition of the chloride salt during film synthesis does not lead to an incorporation of chloride anions into the final film structure. This is in agreement with our previous experiments [19] and experiments conducted by other groups suggesting that MACl sublimes in the course of the film fabrication [26]. We further note that a range of other analytical techniques, including energy dispersive X-ray spectroscopy (EDX), electron diffraction and electron energy loss spectroscopy (EELS), have been used before on the same sample materials confirming their very similar chemical and structural properties [19].

3.2. J-V characteristics of perovskite solar cells

When incorporating these compounds in planar photovoltaic devices (see SEM cross sections shown in the [Supporting information](#), [Fig. S1](#)) substantial differences in their performance are observed [18–21]. Solar cells based on chloride-treated MAPI reveal a significantly improved power conversion efficiency (PCE) yielding 10.3% on average and a peak around 13% compared to the system comprising pure MAPI with an average PCE value of 5.3% and a maximum around 9%, similar to reports of other groups [18–21]. The corresponding *J-V* performance data ([Fig. 2a](#)) and the extracted statistical distribution of the resulting PCE are shown in [Fig. 2b](#).

3.3. Time-of-Flight mobility studies on contacted perovskite films

To gain further insights into these enhancement effects of chloride addition during synthesis on the resulting films’ optoelectronic properties, we carried out Time-of-Flight (ToF) mobility studies on individual laterally contacted layers of the two films with inter-electrode distances ranging from 7 to 13 μm . A scheme of the employed sample layout and the principle of the transient photocurrent measurement is depicted in [Fig. 3a](#). Further information about the experimental setup and the measurement procedure can be found in the [Supporting information](#), [Fig. S2](#).

The generated charge carriers are separated by applying a constant external DC field of approximately 7 kV/cm and thus start moving in lateral direction across the film towards the opposite electrode. Note that mobile ionic species strongly affect the material’s properties and are discussed to be the origin of the anomalous hysteretic *J-V* behavior of perovskite-based solar cells [22–24,27–29]. To minimize the influence of ionic drift on the obtained ToF data, the DC electric field is switched on only during the measurement (for less than 1 s), since ion migration is known to occur on minute timescales [28,30]. The obtained photocurrent transients for different electrode distances ([Fig. 3b](#)) point out that larger distances between the lateral metallic contacts result in longer charge carrier transport times. The shape of these photocurrent transients indicates dispersive transport that presumably results from spatially varying hopping rates due to energetic heterogeneities and electric field variations caused by trapped space charges [31].

The average carrier mobility μ in pure and chloride-treated $\text{CH}_3\text{NH}_3\text{PbI}_3$ films can then be approximated by the following equation:

$$\mu = \frac{d}{E \cdot t_{tr}} \quad (1)$$

with d being the inter-electrode distance, $E = U_{bias}/d$ the constant applied electric field and t_{tr} the transit time charge carriers need to travel from the spot where they were generated to the opposite contact. The determination of t_{tr} follows a procedure adapted from literature [31] and was performed via linear fit functions (see [Fig. 3c](#)). For higher reproducibility an automatic fit routine was programmed based on an iterative fitting of linear function modeling of the slope close to the point of interest of the measured photocurrent transient. Plotting the

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