Investigations on morphology and photophysical characteristics of CH₃NH₃PbI₃ polycrystalline films

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NANYANG
TECHNOLOGICAL
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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

INVESTIGATIONS ON MORPHOLOGY AND PHOTOPHYSICAL CHARACTERISTICS OF
 $\text{CH}_3\text{NH}_3\text{PbI}_3$ POLYCRYSTALLINE FILMS

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School of Materials Science and Engineering

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POLYCRYSTALLINE FILMS**

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requirement for the degree of Master of Engineering

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Abstract

Mesoscopic superstructured solid state solar cells based on organic-inorganic lead halide perovskites have recently emerged as alternative to dye sensitized solid state solar cells. This work focuses on thorough morphological characterization of solution-processed $\text{CH}_3\text{NH}_3\text{PbI}_3$ and on the identification of factors affecting the morphology of the crystallized product. It is shown that the material can adopt a wide range of morphological habits. The results allow insight into possible electron pathways important for both device optimization and understanding of working principle. Fluorescence Lifetime Imaging allows to spatially resolve emerging fluorescence and correlate differences in lifetimes to morphological features. Cathodoluminescence mapping allows investigating phase distribution in $\text{CH}_3\text{NH}_3\text{PbI}_3$ polycrystalline coatings prepared by different methods and indicates formation of multiple phases exhibiting CL in the visible range. A study on stability of material and devices in local ambient conditions shows rapid degradation of material and device performance under exposure to high relative humidity.

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1 Introduction

1.1 Background

Sunlight has been argued to be the most abundant source of free, clean energy on earth. A multitude of technologies make use of the 1.7×10^5 TW provided by the sun today, ranging from thermal solar power to generation of electricity by solar panels. Governments revising their energy and environmental policies and a general public in many parts of the world growing more conscious of the impact posed to the planet by excessive use of fossil fuels are an indication for research in solar energy conversion systems being a highly promising field. Aside from the various types of silicon solar cells and other technologies, dye sensitized solar cells (DSCs) are a candidate for sustainable energy conversion.¹ Aside from simple manufacturing processes or the possibility for fabrication of colorful as well as translucent solar cells,² it is their short energy payback time that could give them an advantage over the established silicon based technologies. However, to date highest efficiencies with dye sensitized solar cells are achieved in devices incorporating liquid components which present an obstacle to long term device stability under realistic operating conditions.³ This has been a major concern although long-term stability of systems incorporating liquid electrolytes has been demonstrated with modules maintaining an efficiency of 8%.⁴ Aside from dyes⁵⁻⁷ a large variety of semiconductor quantum dots (QDs) have successfully been employed as sensitizers.⁸⁻¹¹

Solid-state dye sensitized solar cells (ssDSCs) relying on a solid polymeric hole-transport material (HTM) replacing the classical liquid electrolytes have emerged as new concept in

order to avoid common problems of electrolyte leaking and chemical instability associated to liquid DSCs.^{12–16} Since the first reports of dye-sensitized solar cells incorporating polypyrrole with LiClO_4 ¹⁷ as solid-state hole conductor efficiencies have improved considerably and a number of HTMs have been introduced. The most common organic molecular HTM to date is 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,99 spirobifluorene (spiro-OMeTAD)^{16,18–20} although polymeric materials such as P3HT^{14,21–24}, inorganic HTMs²⁵ and copper compounds such as CuI ^{26,27} and CuSCN ²⁸ have been successfully employed. One obstacle to high PCE commonly encountered in most types of ssDSCs remains incomplete filling of the mesopores of the semiconductor with the HTM and particular attention has been paid to the design of nanostructures that facilitate pore filling and development of novel infiltration methods.^{14,29–31}

However, despite great efforts on optimization of all components for ssDSCs highest efficiencies today do not exceed 7.2%.³²

Recently solid state solar cells based on device architectures similar to solid-state DSCs incorporating an organic-inorganic perovskite-type material as absorber have emerged and shown great promise with regards to efficiency and ease of fabrication. Their preparation, properties and recent advances in the field will be discussed in detail in section 1.7.

1.2 Motivation

Research involving characterization of layered organic-inorganic plumbobalide perovskites in the last decades has primarily been focussed on optical, electronic and structural properties. While extensive work has been undertaken on these aspects, little is known about the factors dictating the morphology of these materials. With regards to the growing interest in this class of materials for applications in solid state mesoscopic solar cells, morphology, and ways to control it, will become an important aspect. Aside from creating uniform load of material on mesoporous scaffolds it will be important to optimize the coverage in a way that allows for access of the pores of the scaffold. Understanding the effect of the nature of the scaffold on the morphology of the crystallized product on the nanoscale is of particular importance with regards to consequences on possible electron pathways on inert scaffolds.

As many layered hybrid perovskites are known to be sensitive to moisture and/or air long-term material stability is an issue that has to be addressed particularly when the application of such material might involve exposure to harsh environmental conditions. Although tentative results for device performance monitoring have been published, device and material stability in realistic conditions with high humidity have not yet been addressed.

1.3 Objectives

The main objectives of the project are to provide detailed morphological characterization of crystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$ as used in solid-state solar cells, to investigate the effect of substrate and deposition method on the habit of the crystallized product and to investigate relationships between morphology, substrate and photophysical properties as well as device performance. Furthermore, this work aims to study the effect of environmental conditions on material stability. Steps to realization of this project include the following:

1. Investigation of the effect of substrate, deposition method and precursor on morphological characteristics of polycrystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$
 - Investigate effect of variation in mesoporous scaffold and composition of the precursor on crystal habit
 - Assess effect of surface modifications on development of crystal habit and substrate coverage
 - Investigate differences of nanoscale morphology of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and consequences for possible electron pathways
2. Investigation of relationship between photophysical properties, morphology and scaffold¹

¹ In collaboration with Prof ME M-B's group at SPMS, measurements supported/training provided by Dr Mai Thu KHUC and Ms Lin MA

- Fluorescence Lifetime Imaging (FLIM) on confocal microscope to correlate fluorescence phenomena and variation in morphology as well as effect of scaffold band gap on the latter
 - Examination of distribution of phases and assess homogeneity and band structure by cathodoluminescence in realistic device-like configurations²
3. Investigation of effect of environmental conditions on material stability and device performance
- Study of degradation process by continuous monitoring of morphological and structural changes of $\text{CH}_3\text{NH}_3\text{PbI}_3$ upon exposure to high humidity conditions
 - Monitoring of performance of devices exposed to high humidity conditions
 - Examination of device stability under measurement conditions

² Measurements by Dr David GACHET, Attolight AG, Switzerland

1.4 Scope of this Report

Sections 1.5 to 1.7 present a brief introduction to structural concepts of perovskite materials with focus on organic-inorganic layered perovskites. A literature review summarizes latest developments in applications of hybrid lead halide perovskites in solar cell applications. Experimental details of the preparation of all types of samples relevant to this report as well as characterization procedures are presented in section 2. Results section 3 and 4 present thorough characterization of the morphology of $\text{CH}_3\text{NH}_3\text{PbI}_3$ on micro-and nanoscale using sophisticated techniques such as High Resolution Transmission Electron Microscopy (HR-TEM)³, Scanning Electron Microscopy (SEM) and optical methods. Relationship between morphology of the hybrid perovskite and the nature of the substrate and deposition method is discussed. Sections 5 and 6 on photophysical characterization attempt to correlate fluorescence and Cathodoluminescence (CL) to morphological features. Various deposition techniques are compared. The measurements and training for Fluorescence Lifetime Imaging were supported by Dr. Mai Thu Khuc from SPMS and the Cathodoluminescence measurements by Dr. David Gachet at Attolight AG, Switzerland.

A study on the stability of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in realistic conditions in tropical environment presented in section 7 investigates effects of degradation on morphology, crystal structure and device performance. Section 9 includes a brief overview on possible future works.

³ TEM supported by Ms Yanan FANG

1.5 Perovskites: Basic Structural Concepts

Out of the common structural families one that is frequently linked to extraordinary material properties is the perovskite group. Since its discovery in the material that lend its name to this large family, Calcium Titanate (CaTiO_3) in 1839, a number of natural and synthetic perovskites have been discovered and their properties have been extensively studied and one representative of the perovskite family has even been argued to be among the most common minerals in the earth's crust, namely magnesium silicate (MgSiO_3).³³ The perovskite structure is frequently found in oxides where the oxygen is located at the face centers forming an oxygen octahedron. A cubic perovskite type unit cell of $Pm\bar{3}m$ framework structure consists of five atoms and can be found in compounds with formulae of AMX_3 where M represents a metal cation that can adopt octahedral coordination and X an anionic species. Together M and X represent an infinite network of corner-sharing MX_6 octahedra. The charge in the cell is balanced by the presence of a metal cation at the centre between octahedra. However, although the ideal simple cubic perovskite structure where $(0, 0, 0)$ is occupied by the species represented by A , M located at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the position at the face centre $(\frac{1}{2}, \frac{1}{2}, 0)$ occupied by the anionic species has been found in e.g. CsSnBr_3 ³⁴ it is not the most common case and lot of perovskite-type materials possess more complex, distorted structures.³⁵

1.6 Organic-inorganic Hybrid Perovskites

1.6.1 Properties

Combination of organic and inorganic components as composite materials on non-molecular (i.e., macro scale) has shown the possibility to combine typical characteristics of both classes, often resulting in materials with striking properties.

Inorganic materials with typical properties such as high temperature resistance, mechanical hardness, ferroelectricity and a range of magnetic properties usually lack the possibility for low-temperature and low-cost fabrication. Organic compounds on the other hand can be synthesized and processed at low temperatures and allow for fabrication in simple processes such as spin-coating, drop casting, spinning or stamping. Aside from simple processing they offer properties such as polarizability and organic electroluminescence.³⁶ Typically, mobilities in organic materials are strongly limited owing to weak interactions originating from the prevalent van-der-Waals forces and thus far inferior to those obtained in inorganic materials. Combination of organic and inorganic components is not limited to the micro scale. Composites with perovskite structures where organic and inorganic components alter at molecular scales have been a field of intense research in the last decades and materials with properties not native to either component has been realized.^{37–39}

Figure 1.1 Representation of single-layer perovskite with monoammonium cation

Typically, these hybrids are of the types $(\text{NH}_3\text{-R-NH}_3)\text{MX}_4$ or $(\text{R-NH}_3)\text{MX}_4$ where X represents Br_2 , Cl_2 , or I_2 and adopt layered perovskite structures. Inorganic and organic components individually form layers. The inorganic component (e.g. metal halides) forms sheets of corner-sharing octahedra as in the AMX_3 structure discussed above. Such inorganic layers have been termed “perovskite-sheets” due to structural similarities to the classical AMX_3 structure when a one-dimensional cut is applied along the (100) direction.³⁶ It has been demonstrated that such inorganic sheets can be synthesized by simple means in a range of orientations and with higher dimensionalities and multiple orientations by modifications of the precursor solution compositions.⁴⁰ For organic cationic components two cases of arrangement are possible, depending on the nature of the cationic species. If represented by a monoammonium the component forms bilayers while monolayers are formed for diammonium species. The organic components are

determining the degree of interaction within the inorganic components and can be modified to tailor the structure and properties of the hybrid material.⁴⁰ Characteristics of perovskites of the type $\text{CH}_3\text{NH}_3\text{Sn}_{1-x}\text{PbI}_3$ have been found to be highly dependent on the synthetic route employed. Constantinos et al. have recently demonstrated that the products can behave as n-or p-type semiconductors dependent on only the synthetic route employed.³⁸

Plumbohalide hybrid perovskites are self-assembling structures. Dependent on the arrangement of the PbX_6 octahedra layered perovskites of this class can form 0D, 2D and 3D structures.⁴¹ Respective structures differ considerably in exciton binding energy with values decreasing from as high as 342eV for 0D to 1.633eV for 3D networks.⁴² The high exciton binding energies are a consequence of the difference in bandgaps and dielectric constants between the inorganic component and the organic sheets where the inorganic sheets possess considerably larger bandgaps than the inorganic component.⁴³ Lead halide based layered perovskites have received attention due to a range of intriguing characteristics including electroluminescence and scintillation properties.⁴⁴

Optical properties as well as band structures can be tuned by variation of the halide or partial substitution of the latter. An example is $\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{Cl}_x$ where the exciton peak can be shifted towards the blue with increasing content of Cl.⁴³ Among hybrid perovskite materials containing Pb(II), Ge(II) and Sn(II) prepared by self-assembly, properties analogous to quantum-well structures have been identified; their inorganic component is of metallic or semiconducting in nature and alternates with organic layers sheets

possessing large HOMO-LUMO energy gaps.⁴⁵ Dependent on the location of the conduction and- valence bands of organic and inorganic components respectively, the inorganic components (“perovskite sheets”) can act as wells for positive and negative charges. If the band gap of the inorganic sheets is large, combination with a small HOMO-LUMO energy gap cation can reverse well and energy barriers.⁴⁶ Modifications to the length of the organic cation as well as the number of inorganic sheets can be used to achieve separation of wells for electrons and holes into different layers as well as the width of respective layers. Tailoring of the latter can be achieved through modifications to composition of the precursor solutions and preparation of PbI_2 based organic-inorganic quantum wells has been realized by dual source evaporation.⁴⁷

1.7 Literature Review: Applications for Perovskites in Solar Energy Conversion

Recently, metalorganic halide perovskites for solar energy conversion in electrochemical devices have received a lot of attention and numerous reviews have been published on the matter.^{48–50} With tunable band gaps, high absorption coefficients, large carrier mobilities and simple synthesis and processing hybrid perovskites have been found to represent a promising alternative to dyes. The scheme below gives a brief overview of the most important “stepping stones” in the evolution of this technology.

Figure 1.2 Schematic overview of evolution of perovskite solar cells summarizing selected publications

Metalorgano halide perovskites in solar energy conversion: pioneering works

In 2009 Kojima et.al presented the possible application of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ as sensitizers in liquid electrolyte based solar cells. While in their initial studies in 2009 the overall device performance was still comparatively low and not exceeding 3.8% PCE, a number of research groups have since engaged in exploration and further development of possible uses of this class of materials for low-cost energy conversion.^{51–55}

Im et al. reported impressive 6.5% PCE with $\text{CH}_3\text{NH}_3\text{PbI}_3$ as absorber material In 2011 after optimizing pioneering work.⁵⁶ The device is based on the classical architecture for DSCs with liquid electrolyte incorporating a mesoporous TiO_2 layer and I^-/I_3^- redox couple in ethyl acetate electrolyte. Under optimized conditions superior performance of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ sensitized system to a comparable reference device sensitized with N719 was shown. In particular the photocurrents achieved by the dye sensitized system were inferior, reaching only $9\text{mA}/\text{cm}^2$ compared to $16\text{mA}/\text{cm}^2$ in the perovskite-sensitized device. Im et al. attributed this difference in photocurrents to the differences in absorption coefficients. While the absorption coefficient for N719 can be estimated to be $1.5 \times 10^3 \text{cm}^{-1}$ at 540nm it is $1.5 \times 10^4 \text{cm}^{-1}$ at 550nm for $\text{CH}_3\text{NH}_3\text{PbI}_3$, i.e. the dye's absorption coefficient is one order of magnitude lower than respective coefficient of the hybrid perovskite material.

The devices were categorized as “quantum dot solar cell”, emphasizing the alleged importance of $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoclusters of uniform size distribution that are formed on

the surface of TiO_2 particles. Such structures with dimensions in the quantum-dot range had been reported in the early work of Kojima *et.al* for the similar material $\text{CH}_3\text{NH}_3\text{PbBr}_3$ as well but neither group could present further characterization or demonstrate the role of named structures.

While device stability was limited due to the dissolution of the sensitizer in the liquid electrolyte, the 6.5% PCE reported in 2011 was the highest then-reported photon conversion efficiency (PCE) for quantum-dot based electrochemical solar energy conversion devices.⁵⁶

Although the findings from 2009 and 2011 reported a new class of sensitizer, the PCEs reported did not generally represent extraordinary numbers in the overall field of liquid Dye-Sensitized Solar Cells yet. Commonly poor stability of the metal organic halide perovskite materials in polar organic solvents commonly employed in typical electrolytes are greatly limiting the application of this class of material in liquid-type quantum dot sensitized solar cells.

Solid-state perovskite solar cells: unprecedented PCE for sensitized solar cells

In 2012, all-solid state devices incorporating $\text{CH}_3\text{NH}_3\text{PbI}_3$ were reported for the first time.^{54, 4} The values of 9.7% PCE under full sun achieved by Kim *et.al* represented unprecedented values in the field of solid-state sensitized solar cells. Device architectures resembled that of common ssDSCs; where fluorine-doped tin oxide coated with a dense

⁴ Devices based on Al_2O_3 were reported almost simultaneously. Their development is discussed in detail in the following section.

layer of TiO_2 and a transparent mesoporous layer of anatase TiO_2 nanoparticles represent the photoanode, spiro-OMeTAD the hole conducting material and evaporated gold the counter electrode. The photoanodes were prepared accordingly to liquid systems reported previously.^{56,57} High photocurrents of $17\text{mA}/\text{cm}^2$ and open-circuit voltages of 888mV were reported for cells with optimized parameters.

Devices of similar architecture have been prepared in a range of colors by tuning the band gap of the absorber by modifications to the halide component and reached efficiencies of up to 12.3% PCE under full sun illumination.⁵⁸ Solar cells based on one dimensional TiO_2 nanostructures have achieved efficiencies of up to 9.4% with $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 4.9% for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ with TiO_2 nanorods.^{53,59}

Numerous alternatives to spiro-OMeTAD have been successfully tested in $\text{CH}_3\text{NH}_3\text{PbI}_3$ sensitized TiO_2 based devices with efficiencies reaching efficiencies up to 5.3% with PCPDTBT, 6.7% with P3HT and 9% with PTAA.⁵⁵ Abrusci et al. presented a novel device architecture incorporating the polymeric HTM P3HT and a self-assembled monolayer of C_{60} (C_{60}SAM) functionalizing mesoporous TiO_2 .⁶⁰ While efficient electron transfer to the C_{60}SAM was demonstrated the fullerene layer inhibits charge transfer to the underling wide band gap semiconductor and confines the charges to travel in the hybrid perovskite, reducing energy losses associated with charge transfer to the semiconductor. This reduction in losses lead to enhanced open circuit voltages and resulted in PCE of 6.7% for devices incorporating P3HT and 11.7% for spiro-OMeTAD.

Recently, Burschka et al. reported an impressive 15% PCE for devices based on mesoporous TiO_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ prepared by a sequential deposition method.⁶¹ The method presented allowed for complete containment of the perovskite material within the pores of the oxide scaffold, possibly enabling higher degrees of pore filling by the hole transport material.

Etgar et al. demonstrated that issues associated with pore filling of the HTM may well become a question of the past with devices incorporating metalorgano halide perovskites. They demonstrated the possibility to eliminate the HTM completely by making use of hole transport capabilities of the hybrid perovskite. In devices based on anatase (001) TiO_2 nanosheets and solution processed $\text{CH}_3\text{NH}_3\text{PbI}_3$ the latter is successfully demonstrated to function as both absorber and HTM. Said devices reached power conversion efficiencies of up to 5.5% under full sun illumination and 7.3% at lower light intensity.⁶²

Aside from hybrid organic-inorganic perovskites CsSnI_3 , an inorganic perovskite, has been found to be a suitable candidate for applications in sensitized mesoscopic solar cells. With a direct band gap of 1.3eV and high hole mobility of $585\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ one of the four polytypes of this inorganic perovskite has been successfully employed as HTM in all-solid state dye sensitized solar cells.⁶³ Upon doping with 5% F and SnF_2 , respectable 8.51% PCE were reported with N719 dye, a result superior to efficiencies obtained with spiro-OMeTAD in comparable devices.⁶⁴ A feature of particular importance in CsSnI_3 based devices is an observed red-shift of the absorption edge at 789nm which leads to superior performance in red and infrared regions. Tests in devices without N719 dye revealed that

CsSnI₃ can act as sensitizer and HTM simultaneously although at ~0.2% efficiencies for dye-free devices ranged more than one order of magnitude below those where a dye acted as sensitizer. CsSnI₃ can be solution processed and applied to the mesoporous photo anode by spin-coating. The material was reported to solidify and crystallize upon solvent evaporation without further heat treatment.

From insulating scaffolds to planar devices: Al₂O₃-based systems

Reports from 2012 demonstrated that wide-band gap mesoporous semiconductors essential for dye-sensitized systems are obsolete and possibly even unfavorable for solar energy conversion with metalorganic plumbahalide systems.⁶⁵ Lee et al. impressively demonstrated PCE of up to 10.9% under full sun illumination in devices based on CH₃NH₃PbI_{3-x}Cl_x as absorber with mesoporous Al₂O₃ as scaffolds for the perovskite component and spiro-OMeTAD as HTM. The electronically inert nature of Al₂O₃ does not allow injection from the perovskite to its conduction band, confining the electrons to travel within the CH₃NH₃PbI_{3-x}Cl_x. This is a fundamentally different principle to that of dye-sensitized systems where electron injection into a semiconductor and charge transport through the latter are indispensable.⁶⁶

Compared to TiO₂ based reference devices with the same device architecture the inert scaffold showed to be highly favorable with regards to the V_{oc} attained which was several hundred millivolts higher than those obtained with the semiconducting oxide reference device. Termed “meso-superstructured solar cells” based on insulating Al₂O₃ generate V_{oc} over 1.1V due to reduction in energy losses at the absorber-scaffold interface. Charge transport through CH₃NH₃PbI_{3-x}Cl_x could be shown to be significantly faster than through

TiO₂. Sensitization of TiO₂ by CH₃NH₃PbI_{3-x}Cl_x could be confirmed by photo induced absorption spectroscopy (PIA) but as expected free electrons could not be detected in the insulating scaffold; while oxidized species in applied HTM could be observed for both cases. Devices based on the same architecture were recently reported with ZrO₂ as replacement for Al₂O₃.⁵²

Use of a new low-temperature, binder-free approach for the fabrication of the mesoporous Al₂O₃ layer for systems with CH₃NH₃PI_{3-x}Cl_x has allowed for conversion efficiencies of up to 12.3%.⁶⁷ In course of their study of the relationship between device performance and thickness of the mesoporous component the authors found the J_{sc} and simultaneously the internal quantum efficiency (IQE) to increase with decreasing scaffold thickness, reaching almost 100% IQE at ~5% PCE upon complete removal of the mesoporous component. In these planar architectures the perovskite represented highly crystalline layers of thicknesses of up to several hundred nanometer thickness. The results confirmed that hole transfer to an HTM is not necessary for generation of sufficiently long-lived species with sufficiently large diffusion lengths that allow for successful transport through the comparatively thick perovskite layers. They further argue that devices of such planar configuration essentially represent p-i-n-junctions where the perovskite represents the intrinsic (i) component.

Optimization of the morphology of solution deposited CH₃NH₃PI_{3-x}Cl_x thin films significantly improved the perovskite coverage for planar device architectures, leading to peak PCE values of 11.4%.⁶⁸

Recent reports of planar devices based on uniform $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films deposited by dual-source vapor deposition have shown power conversion efficiencies of up to 15.4% ($12.3\% \pm 2.0\%$).⁶⁹

Recently, the electron-hole diffusion lengths in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ have been investigated by means of transient absorption and photoluminescence-quenching.⁷⁰ It was found that diffusion lengths for holes and electrons exceeded $1\mu\text{m}$, which exceeds the absorption depth five-to-ten-fold. Values for electron and hole diffusion on $\text{CH}_3\text{NH}_3\text{PbI}_3$ were found to only range around 100nm which is close to the absorption depth.^{70,71} However, authors argue that due to the similarity in derived values for diffusion coefficients as well as diffusion lengths for both species could also be an indication for the predominantly diffusing species to be a weakly bound exciton.⁷⁰

1.8 Choice of Materials

With regards to ongoing research in the area of perovskite-based solar cells as outlined in the literature review in the previous section, it was decided to examine morphological and photophysical properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ polycrystalline films on a range of substrates that typically find application in solar cell devices. Mainly, two types of mesoporous oxide films, one where electron injection into the conduction band is possible (TiO_2), and one where injection is inhibited (ZrO_2), served as substrates.

TiO_2 has been a standard material for dye-sensitized solar cells and a large number of publications have demonstrated its suitability for perovskite-based devices. ZrO_2 was used for a number of reasons. Firstly, it served as an alternative to Al_2O_3 which has been under thorough investigation since the first reports of Al_2O_3 based MSSCs. It is commercially available as nanopowder in a broad range of sizes and can be processed into mesoporous thin films using similar procedures as for TiO_2 . Aside from such preparative considerations, it was necessary to provide a mesoporous substrate on which the perovskite material can form similar morphological features as on TiO_2 for measurements where electron injection should be inhibited in order not to interfere with the measured signals. This was primarily important for Cathodoluminescence measurements and analysis of the fluorescence lifetimes using the FLIM setup.

2 Experimental Procedures

2.1 Sample Preparation

Samples relevant to this report are of the following types:

- mesoporous oxide films loaded with $\text{CH}_3\text{NH}_3\text{PbI}_3$
- chemically etched glass coated with $\text{CH}_3\text{NH}_3\text{PbI}_3$
- solar cell devices with spiro-OMeTAD as HTM and gold as counter electrode

2.1.1 Mesoporous oxide films

Mesoporous films of TiO_2 and ZrO_2 were prepared by manual screen-printing. For TiO_2 a commercial paste (Dyesol 18 NRT, $d < 20\text{nm}$) was diluted with absolute ethanol in 1:3.5 weight ratio and left to stir for no less than 12h to achieve a homogeneous suspension and kept in an ultrasonic bath for 20min before use.

ZrO_2 paste was prepared from non-stabilized commercial ZrO_2 particles (SkySpring Nano, $d < 30\text{nm}$). For paste preparation, particles were suspended in large quantities of absolute ethanol. After homogeneous suspensions were obtained, α -terpineol and ethyl cellulose were added as binders and the mixture left to homogenize for two hours. After pulsed ultrasonication suspensions were decanted and excess solvent rapidly evaporated in a

rotary evaporator. In order to obtain desired viscosities the as-prepared paste was diluted with ethyl cellulose gels (70 and 80cp, 10wt% each in ethanol, 70:80 = 1:1) and left to stir for 12h prior to use.

Films were prepared by single layer manual screen printing on thoroughly cleaned FTO-coated glass. Deposited films were sintered at 500°C for 30min. Samples were loaded with $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solution by spin coating. Solution-loaded films were left to dry for 30min at 100°C, dark coloration indicates $\text{CH}_3\text{NH}_3\text{PbI}_3$ formation.

2.1.2 $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor

The synthesis of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is simple and can be carried out in air. Due to the sensitivity of the final material as well as the hygroscopic nature of the solvent γ -butyrolactone (GBL) and the high relative humidity in the laboratory all synthesis of the precursor solutions as well as deposition and thermal treatments were carried out under nitrogen.

As a first step, methylammonium iodide $\text{CH}_3\text{NH}_3\text{I}$ was synthesized by mixing hydroiodic acid (57wt% in water, Sigma Aldrich) with methylamine (40% in Methanol, TCI) in a round-bottom flask and left to stir vigorously at 0°C for 2h. The resulting clear solution was evaporated in a rotary evaporator and the produced white precipitant collected, repeatedly washed with ethyl ether until the solvent stayed colorless. The resulting powder was dried in vacuum at 60°C for no less than 24h. Purity of the compound was confirmed by solution-based NMR prior to use in synthesis and no further purification was performed. Where not indicated otherwise, methylammonium iodide in powder form

was mixed with PbI_2 (99.9%, Alfa) in equimolar ratio in γ -butyrolactone (Sigma, Aldrich) to form the precursor solution for the preparation of $\text{CH}_3\text{NH}_3\text{PbI}_3$. This solution was deposited onto respective substrates by spin coating of 60ul at 4000rpm for 40s. Solution concentrations were adjusted by dilution from a stock solution of about 37wt%. Stock solutions were kept at 70°C at least 12h prior to dilution and filtered using PVDF syringe filters prior to deposition. Substrates loaded with the perovskite forming solution were dried at 100°C for 30min after spin coating.

2.1.3 Sequential deposition

Solutions of 1M PbI_2 were prepared by dissolving the metal salt in dimethylformamide (DMF) at 120°C under vigorous stirring for 15 min. Hot solutions were deposited by spin-coating at 4500-6000rpm for up to 120s and annealed at temperatures ranging from 70°C to 250°C for 0.5 to 4.5h. Upon cooling, PbI_2 coated samples were immersed into solutions of $\text{CH}_3\text{NH}_3\text{I}$ in 2-propanol (IPA) of concentrations of 8-20mg/ml until uniform coloration was achieved. Samples were immediately dipped into IPA to remove excess reactants and dried by spinning at 4000rpm for 20s. Crystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$ was formed upon annealing at 100°C for 30min. Solution preparation and deposition were carried out in a dry air box (rel. humidity 10-20% at 20°C).

2.1.4 Chemically roughened glass

In order to obtain chemically and electronically inert, slightly roughened surfaces, microscope glass slides (Sail Brand) were chemically etched using concentrated sodium hydroxide solution. The glass slides were cleaned in Decon soap solution, rinsed with DI

water and placed into 10M NaOH solutions for 24h. After completing this step the solutions together with the glass slides were heated to 85°C for no less than 6h. Samples were cooled to room temperature, and repeatedly rinsed in DI water. To ensure removal of residual negative charges from the surface the glass slides were dipped into dilute hydrochloric acid for 2min.

2.1.5 Device fabrication

CH₃NH₃PbI₃ loaded samples as prepared in 2.1.1 were loaded with hole transport material by spin-coating. Solutions with composition of 0.180M 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-OMeTAD, Merck), 0.060M bis(trifluoromethane)sulfonamide lithium salt (LiTFSI, 99.95%,Sigma Aldrich) and 0.190M 4-tert-butylpyridine (tBP, Sigma Aldrich) in anhydrous chlorobenzene were spin-coated onto CH₃NH₃PbI₃-loaded mesoporous films at 4000rpm for 40s. Solutions were prepared in a nitrogen glovebox. 50ul of solution were used for each sample. The deposition process was carried out at ca. 10-20% relative humidity in a dry air box. Gold counter electrodes were evaporated onto the as-prepared films in a thermal evaporator.

2.2 Characterization

Field Emission-Scanning Electron Microscopy (SEM)

For morphological characterization of the surfaces of all samples secondary- and backscattered electron images were collected on a JEOL 7600F field emission scanning electron microscope at 10kV. Samples were coated with platinum prior to imaging using a sputter fine coater (JEOL) at 20mA for 20s to avoid charging effects originating from non-conductive components of the samples. For secondary electron images samples holders were tilted by 27°.

High Resolution Transmission Electron Microscopy (HR-TEM)

Samples were prepared by either ultrasonically dispersing a small quantity of substrate particles loaded with $\text{CH}_3\text{NH}_3\text{PbI}_3$ in acetone or chloroform, then placing a drop of suspension on a holey carbon-coated copper grid or by placing the copper grids directly onto loosened particles. High-resolution transmission electron microscopy (HRTEM) was carried out with a JEOL-2010TEM (JEOL, Tokyo, Japan $C_s = 0.5 \text{ mm}$ and $C_c = 1.1 \text{ mm}$) at 200 kV equipped with a double-tilt holder.

X-Ray Diffraction

X-Ray diffraction patterns were recorded on a Bruker D8 Advance diffractometer (Bragg-Brentano geometry) with a $\text{Cu K}\alpha$ X-ray tube operated at 40 kV and 40 mA. In order to avoid degradation under measurement due to high humidity ambient conditions scans did not exceed 90min for sensitive samples.

Photovoltaic Characteristics

Photovoltaic characteristics of the devices were measured with an AAA rated AM 1.5G solar simulator (model VS-0852) equipped with 500 W Xenon lamp and a Keithley source meter (2612A), calibrated to 100 mW/cm^2 using a Si photodiode (Fraunhofer).

Cathodoluminescence

Cathodoluminescence maps and point spectra were collected at Attolight AG, Lausanne, Switzerland by Dr David Gachet. The measurements were carried out at room temperature. Acceleration voltage was 5kV, the gun lens set at 1mA and the pinhole diameter set at $50\mu\text{m}$.

Fluorescence Lifetime Imaging

For the present study fluorescence and- fluorescence lifetime images were collected in a Nikon C1 Laser Scanning Microscope in combination with PicoHarp 300system (*PicoQuant*). A 650nm semiconductor laser (pulsed width 50ps, repetition rate 10MHz) was used as excitation source. Instrument response function and emission kinetics at 750nm were measured by placing 650nm and 750nm band-pass filters with 40nm bandwidths into the detection channel. Deconvolution of the measured kinetics allows for resolutions of up to 100ps. A schematic drawing of the measurement setup is depicted in Figure 2.1.

Figure 2.1 Schematic of setup for confocal fluorescence microscopy

Chronoamperometry

Development and stability of the photocurrent was characterized using a Potentiostat/galvanostat Autolab PGSTAT302 installed with FRA2 and photokit (Metrohm Autolab). All measurements were carried out in a Faraday cage and a LED was used as a light source. The potentiostat and LED were controlled by using Nova software.

3 Morphology: Effects of Deposition Method and Substrate

Optimization of the morphology of photo anodes for DSCs has received much attention since the very emergence of the field and countless attempts have been made on its optimization as discussed in 1.1. Particular attention has been paid to the design of structures with high surface areas that can easily be infiltrated by hole transport materials. In dye sensitized solar cells the absorber forms in the ideal case a monolayer on the surface it is deposited on; the morphology of the semiconducting oxide the dye is absorbed on thus does not significantly differ from the morphology of the bare photo anode. Although dyes can form aggregates which in some cases have been reported to significantly impact on the morphology of the dye-loaded photo anode usually morphological investigations for DSCs focus on the wide-bandgap semiconductor and not on the sensitizer.⁷²⁻⁷⁴ $\text{CH}_3\text{NH}_3\text{PbI}_3$ does not behave like a dye in morphological aspects and various groups have briefly addressed this issue.^{67,75} Understanding of the factors affecting the morphology adopted by $\text{CH}_3\text{NH}_3\text{PbI}_3$ is crucial for device optimization. The following section will present insights on the relationship between morphology of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and the substrate it is deposited on as well as a comparison between two deposition methods.

3.1 Single step deposition

Secondary electron images (SEI) of $\text{CH}_3\text{NH}_3\text{PbI}_3$ deposited from concentrated precursor solutions (40wt %) as described in 2.1.2 show that the material forms structures of up to $8\mu\text{m}$ in diameter with defined hexagonal shape and uniform dimensions when deposited on mesoporous TiO_2 substrates in air at ca. 70% relative humidity (Figure 3.1).

Figure 3.1 SEI (left) and BEI (right) of $\text{CH}_3\text{NH}_3\text{PbI}_3$ deposited on mesoporous TiO_2 from 40wt% precursor solution

The electron images also confirm that the structures are not flat but indeed represent thick, platelet-like islands. Despite their regular shapes and strongly defined contours the structures are in fact faceted polycrystalline agglomerates (FCAs), indicated by their rough surface.

Backscattered secondary electron imaging (BEI) allows determining the distribution of compounds according to the atomic number of the atoms they are composed of. Heavy elements (high Z) possess larger backscattering coefficients than lighter elements (small Z). Accordingly, the contrast in backscattered electron images corresponds to the atomic

weight of the components the detected signals originate from. Light (white) areas on BEI correspond to large backscattering coefficients of heavy elements such as lead while darker areas indicate lighter elements.

Figure 3.2 Backscattered electron image of $\text{CH}_3\text{NH}_3\text{PbI}_3$ on mesoporous TiO_2 deposited in nitrogen

Unlike EDX BEI does not precisely identify elements; it rather gives qualitative information on the distribution of different components in heterogeneous samples maintaining relatively high resolution and is particularly useful as a complementary technique to secondary electron imaging.

In the backscattered electron image in Figure 3.2 the dark grey areas correspond to the TiO_2 substrate. The white portions clearly represent the component with the highest atomic weight present in the sample and thus can be assumed to be $\text{CH}_3\text{NH}_3\text{PbI}_3$. Areas colored in grey (example indicated by arrow) thus correspond to a compound that must

be lighter than $\text{CH}_3\text{NH}_3\text{PbI}_3$ and heavier than TiO_2 . EDX confirmed the presence of lead and iodine for respective areas. Figure 3.3 shows the result of elemental mapping for lead using the Pb Ma line for identification. Combining the result from EDX and BEI it can be deduced that the grey areas represent a compound that is poor in either lead or iodine compared to the faceted domains. A possible candidate is PbI_2 although further testing is necessary to fully validate this finding.

Figure 3.3 EDX element mapping of $\text{CH}_3\text{NH}_3\text{PbI}_3$ loaded mesoporous substrate, red indicates counts for Pb

Concerning the shape of the faceted domains encountered two dominant habits could be observed; while most of the clusters formed from highly concentrated precursor solutions on mesoporous and rough substrates such as TiO_2 and FTO adopt hexagonal habit, stellar platelets or rhombic platelets can be encountered on mesoporous surfaces. The occurrence of crystalline domains of stellar habit is common and often encountered upon deposition from highly concentrated solutions when the growth is diffusion controlled.

Variations in the habit of such structures are often associated with variations in solvent evaporation rate and therefore the rate at which supersaturation is reached. In the case of deposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ from concentrated precursors solvent evaporation rates may differ considerably depending on the degree to which the atmosphere is saturated with respective solvent i.e. whether deposition is carried out in a small hermetic volume such as a dry- or glove box or in the open space of the laboratory in ambient conditions. Various materials exhibit similar varieties in morphology when deposited from highly concentrated solutions, e.g. fluorosilicates and ice crystals.⁷⁶

3.1.1 Insight to platelet formation and growth

A high magnification SEI reveals finer features of a platelet grown on ZrO_2 (Figure 3.4). At tilted angle it becomes clear that the structure is not flat but rather possesses a donut-shaped groove around its center while the rims remain thicker, indicated by arrow.

Figure 3.4 Formation on mesoporous TiO_2 with 20wt % precursor (left) and right: faceted domain on Zirconia (18.5wt %)

It can be observed that the grain size is not uniform throughout the structure but rather increases up to a fourfold from ca. 100nm at the center to up to 400nm at the perimeter. The features of the formations on then sample with low-concentration precursor on TiO_2 above already resemble the features of the faceted domains grown from highly concentrated precursors. Clearly defined, straight borders can be observed as well as larger amounts of material at the perimeter and the centre of the formation. The radial features may give some insight to the formation mechanisms of the faceted platelets and suggest dendrite-like growth. Reasons for the large differences between the zirconia and titania based samples may well be due to differences in wetting of the precursor solution on the different oxides. Indications for such were found on much smaller scale, discussed in section 4.

3.1.2 Effect of mesoporous substrate at identical amounts of material

While loading of identical amounts of $\text{CH}_3\text{NH}_3\text{PbI}_3$ could be achieved on TiO_2 and ZrO_2 by adjusting the precursor solution concentrations, morphologies encountered on respective substrates differ considerably (Figure 3.5).

On TiO_2 the formation of faceted domains of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is observed when precursor solution concentrations reach close to the solubility limit (~40wt% in GBL at room temperature). At 18.5wt % concentration, dense formations could not be observed under otherwise identical deposition conditions as shown in Figure 3.4; however, the BEI reveals the presence of lead-rich areas. Rhombic and hexagonal platelets of several microns in diameter can be observed on a ZrO_2 sample of identical optical density. As already

observed in previous sections, the formation of FCAs seems more favorable on ZrO_2 than on TiO_2 . The reason may lie in wetting of the precursor solution on the substrate surface.

Figure 3.5 Backscattered electron images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ loaded TiO_2 (left) and ZrO_2 (right) with identical optical densities

3.1.3 Effect of relative concentration: mesoporous substrates

Aside from overall precursor solution concentration, thickness of the underlying mesoporous layer⁷⁸ and pore volume, the relative concentration of the precursor solution was found to significantly impact on the morphology of the crystallized product.

Backscattered electron images in Figure 3.6 and Figure 3.7 are taken on samples of $\text{CH}_3\text{NH}_3\text{PbI}_3$ loaded mesoporous ZrO_2 films. Both coatings in Figure 3.6 were prepared from precursor solutions of the same overall concentration of 30wt%. Sample a) prepared from an equimolar mixture as commonly used in the fabrication of solid-state solar cells clearly exhibits the formation of strongly faceted crystalline domains. Sample b) prepared with an excess of $\text{CH}_3\text{NH}_3\text{I}$ of 20% possesses a strikingly different morphology. Faceted structures can still be observed, but at much smaller dimensions. The surface appears to be covered by a large number of uniformly distributed structures of ca. 100nm in diameter. The addition of excess $\text{CH}_3\text{NH}_3\text{I}$ (MA) to the precursor solution seems to limit the formation of large faceted crystalline agglomerates to some extent.

Figure 3.6 $\text{CH}_3\text{NH}_3\text{PbI}_3$ from 30% precursor a) equimolar mixture and b) prepared with 20% excess MA

Figure 3.7 $\text{CH}_3\text{NH}_3\text{PbI}_3$ from 18,5% precursor c) equimolar mixture and d) prepared with 20% excess MA

When the overall precursor solution concentration is sufficiently low, the formation of faceted agglomerates can be suppressed completely. Figure 3.7 shows micrographs of two samples prepared on identical zirconia scaffolds with overall precursor solution concentrations of 18.5%. While sample c) prepared with equimolar precursor still shows distinct formation of faceted agglomerates they remain absent in sample d) prepared with 20% excess of methylammonium iodide. To confirm that addition of excess amounts of $\text{CH}_3\text{NH}_3\text{I}$ does not inhibit the formation of the perovskite phase, films with 20% excess MA were prepared on quartz substrates. Corresponding XRD patterns are shown in Figure 3.8. Formation of the perovskite phase could be confirmed for both cases.

Losses of $\text{CH}_3\text{NH}_3\text{I}$ are possible during deposition at a number of stages; during precursor preparation due to prolonged heating as well as during the drying processes during spin coating and annealing. Indications for losses of $\text{CH}_3\text{NH}_3\text{I}$ during sample fabrication were

observed frequently under XRD as depicted in Figure 3.12 where reflections could be assigned to PbI_2 . The vapor pressure of $\text{CH}_3\text{NH}_3\text{I}$ is high in comparison with the low vapor pressure of the solvent γ -butyrolactone (1.5mmHg at 20°C).

Figure 3.8 XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films on quartz

In order to further investigate the effects of relative precursor concentrations on the formation of faceted agglomerates and other morphological features on mesoporous substrates, samples were prepared with excess amounts of PbI_2 . The developing morphologies are different from both cases a) and b) in Figure 3.7 but generally features strongly resemble case a).

In order to further study the effect of excess PbI_2 on the developing morphologies on mesoporous scaffolds samples were prepared with precursor concentration ratio of $\text{CH}_3\text{NH}_3\text{I} : \text{PbI}_2 = 1:1.1$. Contrary to $\text{CH}_3\text{NH}_3\text{I}$, the inorganic salt PbI_2 is thermally stable and has a low vapor pressure at room temperature. The PbI_2 content in the precursor solution is therefore expected to stay constant during processing; losses arising from evaporation during spin coating are not expected.

A prominent morphological feature found on samples of the latter type is the presence of apparently three dimensional structures formed on the surface of the mesoporous substrate (Figure 3.9). The structures extend to up to 10 μm in width and appear to be of porous nature. The BEI in Figure 3.9b) indicates either incomplete coverage of the substrate or formation of more than one phase from the precursor solution as indicated by the difference in contrast. The yellow arrows inserted on the image point to one area with high backscattering coefficient (light contrast) and area with lower backscattering coefficient (darker contrast). This finding is similar to observations on samples prepared from precursor solutions with equimolar ratios of the components.

Figure 3.9 a) SEI of $\text{CH}_3\text{NH}_3\text{PbI}_3$ on ZrO_2 from 18.5% prepared with 10% excess PbI_2 b) BEI of the same sample

3.1.4 Deposition on flat substrates

The formation of thin films of materials deposited from solutions firstly depends strongly on the interaction between the deposited material as well as the components of the deposited solution such as solvents, plasticizers, binders and dispersants with the substrate. Secondly, deposition method and thermal processing strongly impact the formation. Surface roughness, charge, and hydrophobic or hydrophilic nature of the substrate play a crucial role in thin film formation. Undesirable phenomena like dewetting, hole formation, cracking and delamination are commonly observed in thin films of all kinds upon non-optimized deposition processes and intense study of the mechanisms leading to their appearance can be necessary in order to achieve formation of dense films. Among other possible factors, the poor film formation of metal organic halide perovskites has been ascribed to the generally high boiling point and resulting slow evaporation rates of the solvents used for the preparation of their precursor solutions.³³ Due to the poor solubility of lead halide salts the range of compatible organic solvents available is greatly limited with γ -butyrolactone (GBL, boiling point 207°C), N,N0-dimethylformamide (DMF boiling point 154°C) and dimethyl sulfoxide (DMSO, boiling point 189°C) representing the most effective candidates. Heating the substrate prior to deposition is a simple method to achieve faster evaporation of the solvents. In the case of thin substrates such as microscope slides or wafers which cool rapidly employing infrared radiation lamps as heat sources might be a method of choice. Blending the precursor solution with polymers such

as polystyrene has shown to be effective for enhanced film formation and polymer films blended with $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ have been successfully fabricated,⁷⁷ however, films incorporating foreign material such as polystyrene may not be suitable for the application in solar cells.

While the formation of faceted polycrystalline domains could be observed on mesoporous substrates of TiO_2 , ZrO_2 and Al_2O_3 as well as on rough surfaces such as FTO coated glass no such domains were observed on smooth glass surfaces upon deposition using the single-step method described in 2.1.2. The material deposited on glass forms large clusters without defined shapes and occasionally dendrite-like formations but only incomplete surface coverage is achieved (Figure 3.10a).

Figure 3.10 Secondary electron image of $\text{CH}_3\text{NH}_3\text{PbI}_3$ deposited on a) plain glass and b) etched glass

Films deposited by spin coating on roughened glass substrates show distinctly different morphologies (Figure 3.10b). While the formation of shapeless clusters is still clearly visible, stellar structures and faceted domains similar to those found on mesoporous substrates are observed.

From the electron image in Figure 3.10b it becomes clear that overall surface coverage on glass can be greatly improved as compared to untreated glass without chemical functionalization of the surface. Enhanced surface roughness of the substrate may lead to confinement of small quantities of the precursor solution during spin coating, possibly resulting in slower drying rates and allowing more time for self-organization, crystallization and growth. This finding is particularly important for the fabrication of continuous thin films and devices based on flat substrates. There may be a number of reasons for the formation of this strikingly different morphology on smooth glass surfaces and an understanding of the factors determining the morphology of the material under such conditions is crucial for the optimization of devices that do not make use of scaffolds where continuous films of $\text{CH}_3\text{NH}_3\text{PbI}_3$ are desired.

Further optimization of the roughening process in combination with optimized drying rates may allow for formation of dense crystalline films. Such advances are important with regards to optimization of devices without mesoporous oxide layer where continuous films of the perovskite are desired.

Apparent absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ deposited on etched and plain glass collected exhibit distinctly different characteristics. While the spectrum of the material on

plain glass is featureless and flat, spectrum on etched glass is shows broad bands and overall rising nature.

Figure 3.11 apparent absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ on plain and etched glass

X-ray diffraction patterns of the two samples differ in that for the film deposited on the roughened surface the emergence of several peaks that do not correspond to $\text{CH}_3\text{NH}_3\text{PbI}_3$ at 12.6° , 25.4° and 38.6° is observed. They could be assigned to lead iodide; however, the reasons for their emergence could not be explained satisfactorily. Possible reasons are confinement of solution in the pores of the rough surface and increased evaporation of the organic component during spin-coating and heating.

Figure 3.12 XRD pattern of spin coated films on plain and etched glass

3.2 Sequential Deposition

3.2.1 Sequential deposition on mesoporous substrates

The morphology of $\text{CH}_3\text{NH}_3\text{PbI}_3$ deposited by the sequential deposition method differs considerably from that discussed in 3.1 for the single step deposition process.

Lead iodide deposited on mesoporous TiO_2 was found to form elongated, porous structures on the surface of the mesoporous scaffold. Upon conversion to $\text{CH}_3\text{NH}_3\text{PbI}_3$, clusters of approximately 100nm are formed uniformly distributed across the surface. The crystallized material forms a superstructure with uniform pore sizes ranging from 50-100nm (Figure 3.13).

The absence of large polycrystalline domains may allow better infiltration of the hole transport material into the mesoporous substrate, however, quantification of the accessible pore volume e.g. by Brauner-Emmett-Teller (BET) surface analysis and comparison of Incident Photon Conversion Efficiency (IPCE) spectra of complete solar cells prepared by sequential and single-step deposition at comparable optical densities is needed to make qualified assumptions on this matter. Burschka et al. demonstrated complete containment of PbI_2 within the mesoporous oxide layer.⁶¹

Figure 3.13 Backscattered images of PbI_2 deposited on mesoporous TiO_2 (left) and after conversion to $\text{CH}_3\text{NH}_3\text{PbI}_3$ (right)

3.2.1 Deposition on flat substrates: sequential deposition

As well as on mesoporous substrates the morphologies exhibited by $\text{CH}_3\text{NH}_3\text{PbI}_3$ prepared by sequential deposition on plain glass surfaces differ considerably from films formed by the single-step deposition method. As shown on the secondary electron images in Figure 3.14, a continuous crystalline film is formed composed of grains of regular size of ca. 100nm. The small agglomerates on the particle surface visible in the high magnification image correspond to platinum deposited by sputter deposition in order to reduce charging effects.

Figure 3.14 CH₃NH₃PbI₃ on glass deposited by sequential method

The result shows that the sequential deposition method leads to the formation of dense, continuous and uniform polycrystalline films with relatively smooth surfaces. This makes the sequential deposition method a suitable process for the simple fabrication of dense and continuous layers on smooth surfaces.

4 Nanoscale Morphology and Consequences for Electron Pathways

$\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ form structures of 2-3nm in diameter on the surface of TiO_2 nanoparticles when deposited from the single-step method. Various groups have reported these structures and termed them quantum dots (QDs)^{56,79} although no detailed characterization of electronic properties of said structures has been presented to date. In the course of this work, studies with HR-TEM⁵ on TiO_2 particles loaded with varying concentrations of precursor solutions showed that quantum dot density is hardly dependent on the precursor solution concentration. While the QDs were found to grow slightly larger when deposited from the 40wt% solution in comparison to those formed from 20wt%, this parameter was not found to affect the shape of the QDs. In-situ formation of quantum dots on TiO_2 is commonly achieved by successive ionic layer adsorption and reaction (SILAR), a multi-step process requiring precise control over experimental conditions.^{80,81} It is interesting to note quantum dots of $\text{CH}_3\text{NH}_3\text{PbI}_3$ are formed on TiO_2 in a single-step deposition method under relatively poorly controlled experimental procedures, indicating extraordinarily high tendency to self-assembly.

⁵ TEM by Ms Yanan FANG

Figure 4.1 HRTEM image of quantum dots (indicated by arrow) decorated on TiO₂ from 20% (left) and 40% precursor (right)

On ZrO₂ particles loaded with CH₃NH₃PbI₃ formation of quantum dots was not observed⁶. Leaving aside sensitivity to surface chemistry of in-situ formation of QDs, this finding is not surprising considering the fact that for charge transport in solar cell devices based on insulating materials a continuous formation of CH₃NH₃PbI₃ is necessary to offer electron pathways as charge injection into the scaffold is not possible as illustrated in Figure 4.2. We can thus assume that the material coats the surface of the scaffold particles or forms otherwise continuous structures throughout the mesoporous scaffold.

⁶ See appendix for HR-TEM image of insulator loaded with the perovskite material in single-step process

Figure 4.2 Schematic of charge transfer in TiO₂ and Al₂O₃ based devices

Figure 4.3 shows a simplified schematic drawing of possible electron pathways in solar cells based on sensitized TiO₂ and scaffolds where injection is not possible due to the position of the conduction band, e.g. Al₂O₃.

Figure 4.3 schematic drawing of possible electron pathways in injecting (left) or non-injecting devices (right)

Recently by Burschka et al. have reported impressive 15% PCE for their device based on a mesoporous TiO_2 film.⁶¹ $\text{CH}_3\text{NH}_3\text{PbI}_3$ deposited by the sequential deposition method based on works by Liang et al.⁸², described in detail in 2.1.3 adopts distinctly different nanoscale morphologies from that observed for the same material prepared by the single-step deposition method. HR-TEM⁷ imaging on TiO_2 particles loaded with $\text{CH}_3\text{NH}_3\text{PbI}_3$ using sequential deposition reveals the formation of dense layers of 2-4nm

⁷ TEM image by Yanan FANG

thickness encapsulating the TiO_2 substrate particles (Figure 4.4). The formation of such continuous encapsulating layers may be one main reason for the superior cell performances achieved in devices prepared with sequential deposition of the perovskites material, aside from possibly improved pore filling with the molecular hole transport material. Although the conduction band position of TiO_2 allows for charge injection from $\text{CH}_3\text{NH}_3\text{PbI}_3$, Lee *et al.* have demonstrated that charge transport in metal organic halide perovskites is up to ten times faster than through the semiconducting TiO_2 .^{65,67}

Figure 4.4 HR-TEM image of TiO_2 nanoparticles loaded with $\text{CH}_3\text{NH}_3\text{PbI}_3$ with sequential deposition method

The presence of a continuous “nano layer” of $\text{CH}_3\text{NH}_3\text{PbI}_3$ may be one of the key factors leading to resulting superior device performance when sequential deposition was employed. As charges do not necessarily have to be injected into the TiO_2 scaffold losses

associated with this injection process might be reduced. Aside from this, the presence of such continuous layers limits direct contact between the scaffold and the HTM, reducing the number of possible recombination sites.

5 Fluorescence Confocal Microscopy

In order to investigate possible relationship between the morphology of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and fluorescence characteristics in device-like configurations Fluorescence Lifetime Imaging (FLIM) on a confocal microscope was employed. This technique allows spatially resolving fluorescence intensity and fluorescence lifetimes. schematically shows the setup used for these measurements.

In this setup, signals contributing to the fluorescence image are emerging from one point in the focal plane while signals out-of-focal plane do not reach the detector as depicted as dashed lines in Figure 2.1.

FLIM has found application for characterization of materials and sample types of a broad range of classes from inorganic semiconductors to living cells.

All measurements included in this section were performed in ambient conditions (ca. 40% rel. humidity at 22°C). In order to minimize possible sample damage due to degradation under humid environmental conditions (discussed in detail in section 7 on material stability in tropical environment) all samples were stored in a nitrogen glovebox prior to measurement and only removed immediately before starting the measurement. Samples measured under FLIM were not re-used for any further characterization.

5.1.1 Single step deposition on TiO_2 with stoichiometric precursor

Figure 5.1 shows the surface of a sample of mesoporous TiO_2 loaded with 37wt% precursor concentration. Image b) is recorded in emission mode with the red colour code corresponding to emission intensity. The emission mode image shows that morphological features found using BEI (image of twin sample depicted in a) for comparison) are reproduced in the emission mode. High intensity emission signals emerge from the faceted crystalline agglomerate (FCA) and its sharp features are easily recognized. Emission is also recorded from the area surrounding the FCA, however, the distribution seems to be inhomogeneous and some areas appear to be only weakly or non-emissive. An area with no or weak signal is indicated by arrow.

Figure 5.1 a) BEI b) confocal microscope in emission mode and c) in FLIM mode images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ 37% on TiO_2

It should be noted that the difference in emission intensity between the FCA and the background recorded may not be a true characteristic of the sample but possibly due to the two structures lying in different planes. It has been observed that FACs can be as thick

as 500nm which makes it practically impossible to maintain background and FCA in focus at the same time. Aside from this instrumental factor it can be assumed that in the same geometrical sample area and volume more emissive material is present in the FCA.

The corresponding fluorescence lifetime image in Figure 5.1c reveals more information. Lifetimes of the detected fluorescence are correlated to a colour code with red corresponding to long lifetimes and yellow, green and blue corresponding to shorter lifetimes. The features of the FCA are easily recognized on this image type as well. The distribution of fluorescence lifetimes across the surface of the FCA appears to be not uniform throughout the structure.

While the centre of the FCA is uniformly coloured the edges of the structure show that the lifetimes obtained from those regions correspond to different, in this case longer lifetimes. In the regions around the FCA features encountered on the BEI and discussed for a twin sample in section 3.1 (Figure 3.1) are reproduced, indicating the emissive nature of the not clearly identified phase.

5.1.2 Single step deposition of stoichiometric precursor on mesoporous ZrO_2

In order to rule out effects on emission arising from possible injection into TiO_2 , $\text{CH}_3\text{NH}_3\text{PbI}_3$ loaded ZrO_2 was examined. SEI and BEI of twins of the sample are discussed in Figure 3.4, Figure 3.5 and Figure 3.7 and discussed in respective sections. Figure 5.2 shows images recorded in emission mode, transmission mode and FLIM mode of mesoporous ZrO_2 loaded with $\text{CH}_3\text{NH}_3\text{PbI}_3$ from 18.5wt% precursor solution. Both

emission and FLIM mode images reproduce the typical morphological features of FCAs formed on the mesoporous surface. As on the Titania sample discussed in the previous section, high emission intensity emerges from the encountered FCA while the surrounding area appears more weakly emissive. In this case as well the difference in intensity may be due to not only material characteristics but rather a combined effect of the latter and result of different focus planes.

The image collected in transmission mode reveals different degrees of transmission throughout the sample surface. The FCAs' features are reproduced with the FCAs' sharp contours clearly visible. It is evident that the transmission in each FCA is not uniform but a higher degree of transmission is observed from the centre of the structures. This confirms that the FCAs are not of uniform thickness but rather thinner at the centre with thickening at the perimeter, as discussed in 3.1.1.

Figure 5.2 18.5wt%CH₃NH₃PbI₃ on zirconia a) confocal microscope in emission mode b) transmission mode c) FLIM mode

The morphological features are also reflected in the distribution of lifetimes depicted on the image collected in FLIM mode. Distribution of lifetimes within the individual FCAs appears to be more uniform than on the sample discussed in the previous section. Aside

from this it is interesting to note that the background on this sample appears to be much more uniform in terms of distribution of fluorescence lifetimes than the sample consisting of $\text{CH}_3\text{NH}_3\text{PbI}_3$ deposited on mesoporous titania from a higher concentrated precursor solution. In this case there is no clear formation of “patches” of a possibly second lead rich phase. The fits of decays corresponding to the circled areas P1 and P2 on the FLIM image render lifetimes of 29.9 ns for the platelet (area P1) and 7.3ns for area P2.

5.1.3 Single step deposition of 20wt% precursor with excess MA on ZrO_2

As discussed in section 3.1.3, the relative precursor concentration has a strong influence on the morphology adopted by the final crystalline product. Images in Figure 5.3 were collected on mesoporous ZrO_2 loaded with $\text{CH}_3\text{NH}_3\text{PbI}_3$ from 19wt% precursor solution with 20% excess $\text{CH}_3\text{NH}_3\text{I}$. As expected no FCAs are to be identified regardless of the imaging mode. The emission intensity image in a) confirms the emissive nature of the material deposited and emission is detected from all over the surface. While some areas appear to emit more intensely than others this may be due to some agglomeration. In image b) in transmission mode the surface appears less uniform, indicating the formation of small agglomerates. Areas with lower degree of transmission correspond to areas of higher fluorescence intensity as compared to image a). Features on the FLIM image in c) strongly correlate to features identified in emission mode with the distribution of fluorescence lifetimes appearing to be relatively uniform.

Figure 5.3 19wt% precursor with 20% excess MA on ZrO_2 a) emission mode, b) transmission mode, c) FLIM mode

A three exponential fit of the entire depicted area results in average lifetime of 11.6ns.

5.1.4 Sequential deposition on mesoporous ZrO_2

Observation under confocal microscope in emission mode reveals homogeneous distribution of emission from films prepared by sequential deposition (Figure 5.4). As expected, FCAs or similar large structures were not observed. Observations made with the confocal microscope in transmission mode (image in the middle) reveal differences in morphology that could not be detected by other means. Several areas of lower transmission intensity could be identified, indicating thickening of present structures. Comparing these areas with the emission image to its left the areas corresponding to decreased transmission intensity appear to be slightly less emissive but the effect is not as strong as seen on the transmission image, indicating that aside from the perovskite formations the reason for decreased transmission might be the possibly inhomogeneous substrate.

The sequential deposition method and the single step method with excess $\text{CH}_3\text{NH}_3\text{I}$ give similar morphological characteristics on mesoporous surfaces observed under FE-SEM, as discussed in 3.2.1. In the case of sequential deposition observed emission seems to be uniformly distributed. The transmission image reveals some areas with reduced transmission; however, these may not be caused by the perovskite phase but rather by inhomogeneities of the mesoporous the substrate.

Biexponential fits of corresponding TCSPS curves render lifetimes of 11.7ns (0.81) and 7.1ns (0.19) which is very similar to results obtained for deposition with excess MA discussed in the previous section.

Figure 5.4 $\text{CH}_3\text{NH}_3\text{PbI}_3$ from sequential deposition on mesoporous ZrO_2 in emission, transmission and FLIM mode (fr.l.t.r)

It has been observed that the layer of PbI_2 deposited in the first step of the sequential deposition is highly uniform and appears to be continuous. Larger crystalline structures were observed only after exposure to the $\text{CH}_3\text{NH}_3\text{I}$ solution.

Results presented in this section show that fluorescence confocal microscopy can be used as simple, non-destructive tool to investigate the distribution of emission intensity and fluorescence lifetimes. It could be shown that the lifetimes of the encountered fluorescence in $\text{CH}_3\text{NH}_3\text{PbI}_3$ films depend on the deposition method as well as the morphology adopted by the material with longer lifetimes for FCAs and shorter lifetimes for smaller agglomerates. Recently photoluminescence in $\text{CH}_3\text{NH}_3\text{PbI}_3$ has been linked to defects induced during processing and the possibility to obtain PL inactive material from solution processing has been reported.³⁸ All samples prepared for investigation by FLIM presented in this section were found to be weakly emissive. The question if the emissive nature of the FCAs in particular is detrimental for the solar cell performance or if they merely present a hindrance for pore infiltration of the mesoporous substrate requires further investigation.

5.1.5 Summary

The results for fluorescence lifetimes measured by FLIM presented in this chapter are summarized in Table 5.1. Lifetimes of the fluorescence encountered on samples with FCAs correlate to morphological features; while on the FCAs lifetimes of 29.9ns were encountered, fluorescence lifetimes as short as 7.3ns correlate to some of the smaller surrounding agglomerates.

For all three examined cases, (single step, single step with excess MA and sequential deposition) integration of the entire scanned area of 20 μ m $\times$ 20 μ m lead to average lifetimes in the same range (11.6-11.7ns) although in the case where FCAs are observed this average includes the long lifetimes originating from the FCAs and much shorter lifetimes from the surrounding agglomerates while in cases without FCAs the distribution of lifetimes is far more homogeneous as can be seen on the respective FLIM images.

Table 5.1 Overview of results from Fluorescence Lifetime Imaging

Sample type	Morphology	Lifetimes from TCSPC
Single step on ZrO ₂ (Figure 5.3)	FCAs and small agglomerates,	29.9ns on FCA
		7.3ns on small agglomerates
		11.7ns, averaged whole area
Single step with 20%excess MA on ZrO ₂ (Figure 5.4)	No FCAs, small agglomerates uniform distribution	11.6ns, averaged whole area
Sequential deposition on ZrO ₂ (Figure 5.5)	No FCAs, small agglomerates, uniform distribution	11.7ns, averaged whole area

6 Identification of Phases by Cathodoluminescence⁸

Upon interaction of a material with electron beams and scattering of the beam as a consequence of its interaction with the sample multiple signals are generated in the interaction volume. Aside from backscattered electrons, characteristic x-rays and secondary electrons, Cathodoluminescence (CL) is generated while a non-metallic sample is scanned with a highly energetic electron beam, such as during observation under SEM. CL is a secondary phenomenon resulting from inelastic scattering of the beam.

CL analysis has been a common material characterization technique in a range of areas of materials research. It is commonly employed to study the band structure of non-metallic solids and in particular energy levels related to radiative decay.⁸³

Figure 6.1 Schematic of signal generation by electron beam

⁸ All CL data presented in this report is courtesy of Attolight AG, Switzerland and was collected by Mr. David GACHET

Application in characterization of minerals is particularly common as the CL signal in insulators can be directly be associated with traps induced by defects.⁸⁴

CL imaging allows collecting CL spectra from points on the sample for precise determination of differences in band structure in different areas on the sample. The creation of CL maps conveniently allows correlating morphological features emerging CL signal, facilitating assumptions on the present structures. This is particularly useful in the study of seemingly uniform surfaces in combination with EDX.^{85,86} Other than EDX, CL allows for identification of phases according to their band structure rather than the atomic number of their constituents and makes it possible to distinguish between phases of similar elemental composition without the need to rely on frequently inaccurate quantitative EDX. A practical example for the identification and localization of various phases with different band and-defect structures at similar or identical chemical composition is the analysis of zirconia ceramics.⁸⁶ Local CL with its high spatial resolution frequently approaching that of the present microstructural features allows for identification of defects in semiconductors as well as for observation of cracks on seemingly uniform samples while at the same time allowing for phase identification. Advances in instrumentation have even made it possible to examine and identify the location of quantum dots embedded within single nanostructures.⁸⁷

Cathodoluminescence has found application in a broad range of materials research including characterization of plasmonic structures,⁸⁸ inorganic semiconductors,⁸⁵ scintillators and phosphors,⁸⁹ natural minerals⁹⁰ and even biological samples.

6.1 Results

The results presented in section 3.1 point towards the presence of more than one lead rich phase present on mesoporous substrates loaded with $\text{CH}_3\text{NH}_3\text{PbI}_3$ formed from equimolar precursor solutions. Possible lead rich phases are $\text{CH}_3\text{NH}_3\text{PbI}_3$ and PbI_2 . EDX confirmed the presence of lead across the entire surface of the sample (Figure 3.3) but could not reliably quantify the ratio of lead to iodine within FCAs and around these structures.

Cathodoluminescence (CL) allows for investigation of a semiconductor's electronic band structure, defects and numerous other related properties. In combination with a scanning electron microscope it is possible to create maps of a semiconductor surface spatially resolving the distribution of signal wavelength or to determine the CL spectrum in a certain point of the sample. Using this tool it was possible to investigate the composition of encountered morphological features by comparison of encountered bandgaps with published values. Secondary electron images were collected at 5kV and CL maps were collected with a 150gpm/500nm blazed grating, a central wavelength of 650nm and an integration time of 50ms/pixel using a UV-vis CCD. The spatial resolution of the CL signal collection is expected to resolve features <100nm as the small acceleration voltage leads to comparatively small interaction volumes.

6.1.1 Single step deposition

Figure 6.2 shows the SEI, combined CL map and maps for individual wavelengths. Signals of three different wavelengths of 526nm, 746nm and 767nm could be resolved and maps

according to the distribution of the corresponding species were created. The blue colour code in Figure 6.2 c indicates the presence of a species with electronic transitions of $\sim 2.4\text{eV}$, corresponding to the wavelength of the CL signal of 526nm. The signal originates from the area on the sample not occupied by FCAs. Signal of two more wavelengths was detected and mapped, depicted in d) and e) of the same figure. The green and red colour code corresponds to signals of 746nm and 767nm. Thanks to the high spatial resolution of the technique it can be observed that the signals of the two respective longer wavelengths originate from the FCAs rather than from the surrounding area.

Figure 6.2 a) SEI b) combined CL map of c)-e)

In order to gather even more localized information on the CL signal, CL spectra were collected in specific points. Spectra were collected on FCAs as well as on the surrounding surface.

Figure 6.3 CL spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ from equimolar precursor on mesoporous ZrO_2

Spectra collected on an FCA (left Figure 6.3) exhibit one broad peak only at 764.7nm, corresponding to 1.62eV. This peak corresponds to the plumbotrihalide perovskite and was found to bleach easily under the electron beam. The energy is well in accordance with the published bandgap of $\text{CH}_3\text{NH}_3\text{PbI}_3$.³⁵ The broadening of the peak is an indication for defects or trap states.

Spectra collected on a point in an area that is not occupied by FCAs exhibit two broad peaks at 521nm and 740nm, corresponding to 2.4eV and 1.7 eV respectively. While 1.7eV may well correlate with $\text{CH}_3\text{NH}_3\text{PbI}_3$, the broad peak at 521nm is unlikely to correspond to the perovskite material while it matches with the reported bandgap of PbI_2 .

6.1.2 Sequential Deposition

As shown in section 3.2.1, the sequential deposition method leads to the development of a different morphology. While in the case of single step deposition BEI indicated the presence of multiple phases the results of the same method applied to films fabricated by the sequential method did not strongly indicate such. However, the spatial resolution of the BEI is by far inferior to that of CL analysis, resulting from the high acceleration voltages necessary (20kV was used in this case). Figure 6.4 shows SEI and corresponding CL maps on a film of $\text{CH}_3\text{NH}_3\text{PbI}_3$ prepared by sequential deposition.

Figure 6.4 SEI, combined CL map and individual maps of $\text{CH}_3\text{NH}_3\text{PbI}_3$ by sequential deposition on ZrO_2

From the combined CL map in Figure 6.4 it becomes clear that indeed at least two phases are present on the mesoporous surface. Signals of two wavelengths, 626nm (“red” signal) and 516nm (“blue” signal) were mapped, corresponding to 1.98eV and 2.14eV respectively. While on samples prepared by single-step preparation process signals were easily observed to originate from the FCAs the spatial signal distribution is strikingly different on the sample prepared by sequential deposition technique. The red signal here apparently originates from areas around or at the edges of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals and not from the surface of such crystals. Furthermore, no prominent peak with wavelengths around 750nm was observed at this magnification. The distribution of the blue signal of around 515nm is not obviously correlated to morphological features. The signal seemingly originates from areas around the perovskite crystals as well as from some smaller crystals but it is less uniformly distributed as the red signal which could easily be correlated to the areas around the perovskite.

Figure 6.5 shows a combined CL map on the same film taken at higher magnification as well as CL spectra collected at several points on the area shown on the SEI. Insets in the graphs show combined CL maps for that area with the cross indicating the points where respective spectra were collected.

As on the film prepared by single step deposition it was possible to identify the presence of at least two phases also at high magnifications corresponding to signals of 513-515nm (~2.4 eV) and 755nm (1.64eV), the latter probably corresponding to the hybrid perovskite. From observations at such high magnifications it becomes apparent that phase inhomogeneity is not limited to FCAs and regions without FCAs but is present at much

smaller scale, thus the material synthesized is far less homogenous than expected from XRD, EDX and BEI analysis.

Figure 6.5 CL map and CL point spectra on $\text{CH}_3\text{NH}_3\text{PbI}_3$ by sequential deposition

The presence of several phases in coatings prepared by the sequential deposition process is not surprising. In this method a crystalline layer of PbI_2 is applied to the surface of the substrate and later immersed into a solution of $\text{CH}_3\text{NH}_3\text{I}$ in an organic solvent. A colour change from bright yellow to brown is observed immediately upon immersion of the PbI_2 coated substrate into the iodide solution, however, visual inspection does not allow for

determination of the stage of the conversion. Early reports have suggested that the immersion time should exceed several hours in order to guarantee a complete conversion to $\text{CH}_3\text{NH}_3\text{I}$ without residual PbI_2 in the crystallized product.⁸² For this report, processing conditions optimized for solar cell devices were employed wherever possible, including for the preparation of all coatings fabricated by the sequential deposition method. Typical immersion times here do not exceed 20min. Furthermore it should be noted that in a porous system such as the one discussed in this chapter, complete conversion may require longer exposure of the PbI_2 loaded films to the iodide solution than flat, non-porous films due to processes related to infiltration of the PbI_2 filled mesopores and/or blocking of the latter by forming $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals on the top of the film. Aside from such considerations regarding the fabrication process the band structure of PbI_2 allows for transitions in the measured range of $\sim 2.14\text{eV}$, especially considering the broad nature of the peak.

Aside from the spatial distribution and origin of the red and blue signal being significantly different from the situation on the single-step sample the absence of strong signals corresponding to a band around 750nm in maps collected at this magnification is noteworthy. While on samples prepared via single-step deposition process a broad band around 750nm could easily be ascribed to the perovskite phase accumulated in FCAs, the area apparently occupied by the perovskite appears not to exhibit strong cathodoluminescence in this region and therefore appears black mostly black on the map at the same magnification. There are several possible reasons for the absence of such a signal that are worth to address. It should be noted that the absence of a detectable

signal does not confirm the absence of a phase corresponding to the signal generation. As has been noted in the previous section on single step samples, the signals around 750nm were easily bleached under the electron beam. Consequently it is necessary to consider the possibility that the signal was bleached completely and not detectable for that reason. Chemical composition of the perovskite phase on samples fabricated by both preparation methods is expected to be similar with a secondary phase of residual PbI_2 expected to remain after sequential deposition. The differences in CL properties of the two sample types indicate differences in band structure. From the present results no quantitative conclusions on the band structure were drawn but the findings may well represent an important step towards understanding the superior performance of solar cell devices fabricated by sequential deposition method over devices prepared from a single-step method at otherwise comparable fabrication details.

7 Stability in Tropical Environment

7.1.1 Background

Long-term material stability of all components of a device is essential to the development of commercial solar cells. As discussed in 1.1, a common drawback of sensitized solar cells over silicon cells is their inferior stability under exposure to harsh environment over long timespans.

Kim et al. demonstrated impressive long term device stability under full sun illumination for $\text{CH}_3\text{NH}_3\text{PbI}_3$ based cells stored in air without further encapsulation.⁵⁴ They observed an overall increase in PCE of 14% over the timespan of the experiment of 500h. While the V_{oc} was stable over the course of the experiment they observed an initial decrease in J_{sc} with the value stabilizing after 200h. A gradual increase of FF contributed to the overall PCE stability despite initial loss in J_{sc} . Despite the impressive device stability in the presented study it is important to assess the stability of the hybrid perovskite in humid environment. Hybrid metalorgano halide perovskites are known to decompose quickly upon exposure to moisture. The sensitivity of this class of materials has been ascribed to the hygroscopic amine group and decomposition has been addressed in a number of publications.^{33,91} $\text{CH}_3\text{NH}_3\text{PbI}_3$ has been reported to form yellow or colourless hydrates as well as the compound $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ first reported by Vincent et al. upon exposure to H_2O at temperatures below 40°C .⁹² Although investigations on the decomposition

behavior of $\text{CH}_3\text{NH}_3\text{PbI}_3$ have been carried out over the course of several decades exact determination of mechanism and products thereof remain under debate to date. Discussions on the stability of this material have mainly been focussed on structure and chemical decomposition but not thoroughly examined the impact of the material's decomposition or degradation on its morphology in thin films.

7.1.2 Effect on morphology and structure

In order to investigate the material stability of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in realistic conditions in tropical environment samples of $\text{CH}_3\text{NH}_3\text{PbI}_3$ coated on various substrates were stored in ambient conditions of >80% relative humidity at 24°C and X-ray diffraction patterns and electron images were collected several days until no further colour change was observed. Films of $\text{CH}_3\text{NH}_3\text{PbI}_3$ deposited on microscope slides by spin coating were found to rapidly show signs of decomposition. Upon exposure to the highly humid environment areas of yellow colouration appear on the originally black films and expand rapidly. Commonly decomposition occurs from the rims of the films towards the centre or spreads from morphological defects such as scratches and holes to the rest of the film. Figure 7.1 shows XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3$ collected directly after preparation and after seven days exposure to high humidity environment. Impurity peaks emerging due to decomposition are indicated with (*). Peaks at 12.62, 25.42 and 38.61 could be assigned to (001), (002) and (003) peaks of PbI_2 . Although the degradation mechanism could not yet be fully explained based on the results of the X-ray diffraction study it can be assumed that the inorganic components The peak intensity ratio of the decomposed sample indicates

strong preferential orientation along the a -axis. Unit cell parameters of the material were found to stay constant throughout the course of experiment with $a=8.86$ and $c=12.62$.

Figure 7.1 XRD pattern of $\text{CH}_3\text{NH}_3\text{PbI}_3$ exposed to >80% relative humidity at 24°C

Formation of structures with strong preferential orientation indicated by the XRD patterns collected was confirmed by scanning electron microscopy. Figure 7.2 shows secondary electron images complementary to the XRD patterns in Figure 7.1

Figure 7.2 secondary electron images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film after fabrication (left) and after seven days exposure to high humidity environment (right)

After only seven days of exposure to the experimental ambient conditions without encapsulation formation of large needle type structures growing across the entire sample surface was observed while the film colour changed from black to pale yellow. It should be noted that the HTM coated on top of the perovskite material in a solar cell device can act as barrier layer for moisture for some extent and therefore material degradation in a fully assembled device may happen at a different time scale from degradation observed for unprotected films as discussed in this section.

7.1.3 Effect on device performance

In order to assess the decomposition of the hybrid perovskite material on solar cell performance devices fabricated according to standard procedures described in detail in 2.1.5 were exposed to a range of conditions that represent realistic situations in device operation. All cells were stored in open circuit conditions.

Decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ strongly reflected in rapid decay of PCE of devices stored in a desiccator at 20% relative humidity without encapsulation in darkness. Upon increase of the short circuit current (J_{sc}) after the first 24h of storage and a slight improvement in fill factor (FF) followed rapid decay of the J_{sc} while the open circuit voltage (V_{oc}) seemed considerably less affected. While the device efficiency reached a peak value of 11.6% after 24h, primarily caused by the strong increase in J_{sc} , the device performance deteriorated rapidly after longer exposure to more than 20% relative humidity. A decrease of close to 50% PCE was observed after only four days exposure (Figure 7.3).

Figure 7.3 JV curves of device stored at >20% relative humidity monitored for four days

Table 7.1 cell parameters after storage at 20% humidity monitored over four days

Day	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
1	871	17.1	61.7	9.3
2	904	20.0	14.9	11.6
4	901	14.9	54.3	6.1

After four days the appearance of yellow spots indicated decomposed regions on the active area of the device. As the intact cell area could not be maintained at 0.2cm² no further measurement was undertaken.

For comparison, a device was stored in dry air in darkness and only removed for the duration of the measurements. Its IV characteristics were monitored over several days with results presented in Table 7.2.

Table 7.2 IV characteristics of solar cell stored in dry air in darkness

Day	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
1	899	18.3	63.2	10.5
11	967	18.0	63.3	11.0
25	984	14.8	65.1	9.8

The results of the monitored PCE confirm that the sensitivity of $\text{CH}_3\text{NH}_3\text{PbI}_3$ to moisture discussed in the beginning of this section reflects strongly in device performance monitored over time. Deterioration of device performance is confirmed to be an effect of material degradation due to exposure to moisture as devices stored in nitrogen were not found to undergo dramatic changes in device performance and no yellow spots possibly indicating material degradation were found on the sample surface.

Table 7.3 Device performance monitored under natural sunlight

Day	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
1	963	14.8	66.2	9.6
3	965	8.1	55.9	4.4
7	956	5.4	40.1	2.0

Table 7.3 shows performance evolution of devices stored in silica gel drying agent exposed to natural sunlight. After seven days small yellow spots can be observed on the

surface, indicating degradation of the perovskite material. After 15 days the material had completely degraded.

The results presented in this section confirm that $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cell devices do not undergo major changes in device performance when they are stored in darkness in dry atmosphere but undergo rapid degradation when exposed to common ambient conditions. If the degradation in performance results upon exposure to humid environments alone, prolonged exposure to sunlight or as a combined effect of both factors remains a question to discuss.

In order to achieve long term device performance stability in realistic ambient conditions, the development of reliable encapsulation techniques is crucial. Design of metalorganic halide perovskites with higher resistance to decomposition in humid environment is an issue that will have to be addressed in the future, particularly with regard to commercialization of solar cells based on this class of materials.

7.1.4 Stability under measurement conditions

In order to characterize internal processes of devices with differing morphologies such as discussed in 4 a range of techniques can be employed. Intensity Modulated Photovoltage Spectroscopy (IMVS) and Intensity Modulated Photocurrent Spectroscopy (IMPS) for example allow for determination of electron lifetime and electron transport time. In order to assess further the effects of nanoscale morphologies determination of the electron transport time is of particular importance.

Both IMPS and IMVS are frequency dependent methods. In order to obtain valid data it is crucial for respective samples to be very stable under measurement and illumination over the entire duration of the measurement which commonly requires at least 20min.

In order to assess the device stability under measurement-like conditions, devices prepared according to the procedures in 2.1.5 were masked with black tape in order to define a cell area of 0.2cm^2 and illuminated using a white LED. Light intensity equivalent to 1 sun was adjusted by adjusting the light source-sample distance.

Figure 7.4 Development of current at 0V over time measured in 10s intervals

Generated photocurrent was monitored in 10s intervals of illumination over a duration of 600s at 0V. The results depicted in Figure 7.4 strongly indicate sample instability.

A decrease in photocurrent can be observed both over the entire duration of the measurement as well as observing the evolution of respective current during light pulses. During each light pulse the measured photocurrent decreases steadily. Over only 10min the measured photocurrent decreases from 5.2mA to 4.15mA, a mere 80% of the initial value. This significant decrease in photocurrent is expected to impact greatly on results obtained from any frequency dependent measurement, in particular on those with relatively long measurement durations.

Upon application of a 600mV bias the measured photocurrent follows a similar trend if the overall current drop over the entire measurement duration is considered. Evolution of the current within the light pulses, however, follows in inverse trend with the current steadily increasing.

Figure 7.5 development of current over time measured at 0V and 600mV bias with white LED

The results presented above confirm that cells of this type were not stable in terms of photocurrent, regardless of the application of an external bias. Although the rate of the current drop was found to decrease over time and the current appears to stabilize after certain duration of illumination this stabilization is not permanent as seen upon comparison of the results depicted in Figure 7.5 and Figure 7.4 which were all obtained from the same sample with an interruption of the measurement of ca. 90min during which the sample was stored in dry ambient in open-circuit.

The results from all three types of measurement indicate a strong degradation of the photocurrent over only short durations of irradiation. This finding confirms that it is not advisable to draw conclusions from photoelectrochemical characterization techniques that require stability of the photocurrent for prolonged amounts of time. Results from determination of electron transport time as well as electron lifetime by IMPS and IMVS will therefore not be included in this study.

8 Conclusions

The morphology of solution processed $\text{CH}_3\text{NH}_3\text{PbI}_3$ was found to be dependent on a number of factors. Identical amounts of the material loaded onto mesoporous structures of different oxides result in loaded distinctly different morphologies depending on the substrate. Faceted Crystalline Agglomerates (FCAs) are formed upon deposition of highly concentrated precursor solutions of equimolar ratio of the two components. Addition of methylammonium iodide suppresses the formation of FCAs. A simple way to greatly improve formation of thin films of the material on flat glass surfaces is a pre-treatment in NaOH. Sequential deposition of PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ results in homogeneous coverage on both mesoporous and flat substrates. Nanoscale morphologies of the material differ greatly depending on the material of the substrate particle as well as deposition method, either creating continuous ultra-thin coatings or nanoclusters. This leads to different possible electron pathways and optimization of the latter is important in device optimization.

A simple means to assess the distribution of the emissive material and identify FCAs is fluorescence confocal microscopy. Lifetimes of the fluorescence obtained from FCAs and surrounding covered areas differ while the sequential deposition method or use of excess MA in the precursor solutions leads to uniform distribution of emission intensity and lifetimes. There are indications for the formation of more than one phase upon single-step deposition which may be consequence of loss of the organic component during

fabrication. The perovskite phase formed upon sequential deposition seems to possess different CL properties from the phase obtained from single-step deposition.

$\text{CH}_3\text{NH}_3\text{PbI}_3$ is highly moisture sensitive and degrades rapidly upon exposure to ambient conditions in high-humidity environments. Devices with spiro-OMeTAD as HTM were found to be stable while stored in inert conditions while devices exposed to moderate levels of humidity were found to degrade rapidly.

9 Future Work

9.1 $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films

9.1.1 Development of simple deposition techniques for continuous thin films

With regards to recent publications on planar solar cell devices prepared by vapour deposition⁶⁹ it will be interesting and necessary to develop simple deposition techniques for formation of continuous, highly crystalline thin films of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and related compounds. Dual-source vapour deposition has been shown to produce such continuous films but the technique itself poses several practical difficulties especially for application in the laboratory scale. Firstly it requires relatively complicated setup consisting of a thermal evaporator with two sources that need to be individually controlled. Secondly the toxic nature of the material will make it necessary to either use a separate system for its evaporation or thorough cleaning of the chamber after each evaporation cycle to avoid cross-contamination. Also thermal evaporation is carried out under high vacuum which is time-consuming if a large number of samples or a large area requires use of large evaporation chambers. It would therefore be interesting to develop simpler deposition processes with simpler setups that eliminate the need for high vacuum conditions.

Possible candidates might be dip-coating or inkjet printing. Dip-coating in particular requires simple setups and provides flexibility in terms of substrate dimensions as well as material.

In order to successfully develop such deposition techniques it will be necessary to study in-depth the effect of the nature of the substrate on the formation of the perovskite material. During these studies it would be interesting to study possible favourable effects of physical and chemical surface modifications.

9.1.2 Effect of surface modifications to nanoscale morphology

Section 4 demonstrated that the morphology of $\text{CH}_3\text{NH}_3\text{PbI}_3$ on individual substrate particles differs considerably depending on deposition method and nature of the substrate particle. With regards to possible electron pathways through the perovskite it is desirable to obtain complete surface coverage of the substrate particles with a dense and continuous layer of $\text{CH}_3\text{NH}_3\text{PbI}_3$. While such coverage can be observed on ZrO_2 upon deposition by single-step method it is not obtained from the same method applied on titania. For continuous coverage on titania a sequential deposition method has to be employed. Reasons for differences in formation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ on varying substrate particles can be linked to their surface energy and charge, and other properties such as hydrophobicity or hydrophilicity. Modification of the surface of the substrate particles by acid or base treatment or exposure to surfactants is some of the possibilities to modify surface charge and possibly improve the surface coverage and will be interesting to investigate.

9.1.3 Development of porous thin films of $\text{CH}_3\text{NH}_3\text{PbI}_3$

As $\text{CH}_3\text{NH}_3\text{PbI}_3$ shows great promise in combination with electronically inert scaffolds in solar cell devices it would be interesting to create porous structures of the perovskite that can be infiltrated with the HTM directly. One possibility is the use of physical templates that may be removed after infiltration and crystallization of the material as have been used frequently to create mesoporous TiO_2 . As this material is solution processable and does not require high temperatures for crystallization it might be interesting to blend polymers that may form *schlieren* textures into the precursor solution directly and deposit the material by common methods.

9.2 Electrochemical device characterization

To further evaluate the effect of different morphologies of $\text{CH}_3\text{NH}_3\text{PbI}_3$ prepared by sequential and single step method further electrochemical device characterization will be carried out. In order to be able to compare the effect of variations in morphology on device performance and internal processes it is necessary to prepare devices with the same amount of $\text{CH}_3\text{NH}_3\text{PbI}_3$ loaded. This can be confirmed by optical means considering that scattering and reflection will be similar in both cases. Aside from this, samples can be prepared using inert scaffolds such as zirconia or alumina to assess the effect of scaffold bandgaps on measured properties. As results of this work have shown it will be highly important for any characterization work to be carried out in dry conditions with minimal exposure to moisture.

9.3 Material and device stability

9.3.1 Investigate material stability under natural sunlight and moderate humidity

Some results of this work have pointed to possible detrimental effects of moderate levels of relative humidity in combination with illumination with natural sunlight on the device and material stability. It would be both important and interesting to investigate such possible correlation of moisture and illumination on the stability under well controlled experimental conditions. With particular regards to the application of this material in solar cell devices it is crucial to ensure continuous material stability under sunlight in realistic application conditions.

9.3.2 Development of device encapsulation techniques

As the material was found to be highly moisture sensitive it is timely to develop reliable and durable encapsulation techniques for the devices. Such is necessary in both commercialization as well device characterization to ensure continuous material stability and uniform performance.

List of Publications

Journal Papers

1. Tom Baikie, Yanan Fang, Jeannette M. Kadro, Martin Schreyer, Fengxia Wei, Subodh G. Mhaisalkar, Michael Graetzel and Tim J. White.
The Synthesis and crystal chemistry of the hybrid perovskite (CH₃NH₃)PbI₃ for solid-state sensitised solar cell applications *Journal of Materials Chemistry A* ,1, 5628,2013
2. Photophysics of methylammonium lead iodide,the multi-tasking perovskite in efficient solid state solar cells
Mai Thu Khuc, Xi Zhu, Jeannette Medina Kadro, Gagik Gurzadyan, Subodh G. Mhaisalkar, Anders Hagfeldt, Rudolph A. Marcus, Haibin Su, Maria E. Michel-Beyerle *in preparation for PNAS*
3. Perovskite Photovoltaics: Morphology and Fluorescence
Jeannette Kadro, Mai Thu Khuc, Reinhard Haselsberger, Lin Ma, Dongqin Bi, Yanan Fang, Timothy J. White, Subodh G. Mhaisalkar, Anders Hagfeldt, Maria E. Michel-Beyerle *in preparation for submission to Angewandte Chemie International Edition*

Conference Contributions

1. Pablo Perez Boix, Jeannette Medina Kadro, Kunwu Fu, Nguyen Huu Loc, Subodh Gautam Mhaisalkar, Michael Graetzel.
Identifying Working Principles in High Efficiency Organometallic Halide Perovskites Solar Cell *MRS Spring Meeting 2013, B13.03*
2. Mai Thu Khuc, Dongqin Bi, Jeannette Medina Kadro, Reinhard Haselsberger, Gagik G. Gurzadyan, Anders Hagfeldt, Maria E. Michel-Beyerle Femtosecond Spectroscopy of Hybrid Organic-Inorganic Solar Cells Based on Mesoscopic CH₃NH₃PbI₃ Perovskite Structures *ICMAT13-A-3541 2013*

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Appendix

Section 3: Morphology: Effects of Deposition Method and Substrate

The secondary electron images below show the plain mesoporous substrates of TiO_2 and ZrO_2 used throughout the work included in this thesis. All mentioning of mesoporous substrates of TiO_2 or ZrO_2 refers to twins of the samples shown below if not indicated otherwise.

Figure A1: Mesoporous substrates of TiO_2 (left) and ZrO_2 (right)

Section 4: Nanoscale Morphology and Consequences for Electron Pathways

Formation of quantum dots (QDs) upon deposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solution could not be observed on ZrO_2 , as seen on the HR-TEM⁹ image below in figure A2.

Figure A2: ZrO_2 nanoparticles loaded with $\text{CH}_3\text{NH}_3\text{PbI}_3$ from equimolar precursor solution

⁹ HR-TEM image by Ms Yanan FANG