Preparation and Characterization of Lead Halide Perovskites

Towards sustainable, cost-effective and upscalable solar cell manufacture

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Abstract

The perovskite solar cell (PSC) is a recent contender within the photovoltaic research field. In a matter of a few years, the power conversion efficiency (PCE) of the PSC has catapulted from 4% to above 22%, which represents one of the fastest developments in the field. The PSC band-gap tunability makes them interesting for use in tandem solar cells with other established solar cell technologies. This thesis focuses on exploring the photophysics of the perovskite material as well as the development of different perovskite preparation processes and materials for potential use in large-scale manufacture and tandem solar cell applications.

First, the photoconductivity of a perovskite film deposited on different metal oxide nanoparticle layers is investigated. The results show that the perovskite can generate free charge carriers without the presence of an electron acceptor.

Secondly, we constructed PSCs with a conducting carbon-nanotube film, as a replacement for both the hole-selective layer and the metallic back electrode, which yielded a PCE of 15.5%. Furthermore, we explored the preparation of semitransparent PSCs for tandem solar cells by using atomic-layer deposition (ALD) for depositing a thin electron-selective metal-oxide layer. We were successful using ALD directly on a perovskite layer without damage to the perovskite. Although the PSCs did not yield high PCE, the study marks a step in further development for direct ALD deposition onto the perovskite.

Finally, we developed two different methods concerning sustainable manufacture of PSCs. The first method was based on the synthesis of the mixed-ion (FAPbI$_3$)$_{0.87}$(MAPbBr$_3$)$_{0.17}$ perovskite in ambient air, which had hitherto only been possible in inert atmosphere. The best PSC was obtained by depositing the perovskite onto a 50°C warm substrate in ambient air yielding a PCE of 17.7%. In the second method, only non-hazardous solvents, water and isopropanol, were used in the synthesis of Cs$_{0.1}$FA$_{0.9}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$. It is the first publication of mixed inorganic and organic cation perovskite synthesis using a two-step preparation procedure with only non-hazardous solvents and the process yielded a PCE of 13.0%. The method allows for complete ionic control of the perovskite and further variation and improvements are therefore possible.

Keywords: perovskite solar cells, perovskite, photoconductivity, carbon nanotubes, transparent contact, ambient processing, water-based

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Ungr var ek forðum,
för ek einn saman,
þá varð ek villr vega;
audigr þóttumk,
er ek annan fann,
maðr er manns gaman.

(Hávamál, 47)
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I Probing Photocurrent Generation, Charge Transport, and Recombination Mechanisms in Mesostructured Hybrid Perovskite through Photoconductivity Measurements
Kári Sveinbjörnsson, Kerttu Aitola, Xiaoliang Zhang, Meysam Pazoki, Anders Hagfeldt, Gerrit Boschloo and Erik M. J. Johansson
Journal of Physical Chemistry Letters, 2015, 21, 4259-4264

II Carbon Nanotube-based Hybrid Hole-Transporting Material and Selective Contact for High Efficiency Perovskite Solar Cells
Kerttu Aitola*, Kári Sveinbjörnsson*, Juan-Pablo Correa-Baena, Antti Kaskela, Antonio Abate, Ying Tian, Erik M. J. Johansson, Michael Grätzel, Esko I. Kauppinen, Anders Hagfeldt and Gerrit Boschloo
Energy and Environmental Science, 2016, 9, 461-466

III Atomic Layer Deposition of Electron Selective SnO₂ and ZnO Films on Mixed Halide Perovskite: Compatibility and Performance
Adam Hultqvist, Kerttu Aitola, Kári Sveinbjörnsson, Zahra Saki, Fredrik Larsson, Tobias Törndahl, Erik Johansson, Gerrit Boschloo, and Marika Edoff
ACS Applied Materials & Interfaces, 2017, 9, 29707–29716

IV Ambient Air-Processed Mixed-Ion Perovskites for High-Efficiency Solar Cells
Kári Sveinbjörnsson*, Kerttu Aitola*, Jinbao Zhang, Malin B. Johansson, Xiaoliang Zhang, Juan-Pablo Correa-Baena, Anders Hagfeldt, Gerrit Boschloo and Erik M. J. Johansson
Preparation of Mixed-Ion and Inorganic Perovskite Films Using Water and Isopropanol as Solvents for Solar Cell Applications

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* Shared first authorship.

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Contribution report

My contributions to each of the papers are discussed here below;

I  Planned and carried out most of the experimental work. Analyzed the data and wrote the manuscript.

II  Carried out the experimental work and analyzed the data along with KA. The carbon-nanotubes were synthesized by AK. YT performed Raman spectroscopy and AA performed IMPS.

III  Planned the experimental work along with AH and KA. Carried out the experimental work related to the synthesis of the perovskite and solar cell measurements. AH performed the ALD deposition and carried out the material characterization and was the main responsible for the manuscript.

IV  Planned and was responsible for the experimental work. Carried out most of the experimental work along with KA. Analyzed the data and wrote the manuscript.

V  Was the main responsible for the study. Planned and carried out most of the experimental work along with NKKT. Analyzed the data and wrote the paper. SS, UBC and HR were responsible for the X-ray photoelectron spectroscopy.
Extended bibliography

The following are publications I have contributed to, during my time in the postgraduate studies, but are not included in this thesis.

1. Enhanced Crystallinity in Organic–Inorganic Lead Halide Perovskites on Mesoporous TiO\textsubscript{2} via Disorder–Order Phase Transition
   Byung-wook Park, Bertrand Philippe, Torbjörn Gustafsson, Kári Sveinbjörnsson, Anders Hagfeldt, Erik M. J. Johansson and Gerrit Boschloo
   *Chemistry of Materials*, 2014, 26, 4466–4471

2. High-Efficiency Dye-Sensitized Solar Cells with Molecular Copper Phenanthroline as Solid Hole Conductor
   Marina Freitag, Quentin Daniel, Meysam Pazoki, Kári Sveinbjörnsson, Jinbao Zhang, Licheng Sun, Anders Hagfeldt and Gerrit Boschloo
   *Energy and Environmental Science*, 2015, 8, 2634-2637

3. Fine Tuned Nanolayered Metal/Metal Oxide Electrode for Semi-transparent Colloidal Quantum Dot Solar Cells
   Xiaoliang Zhang, Carl Hägglund, Malin B. Johansson, Kári Sveinbjörnsson and Erik M. J. Johansson
   *Advanced Functional Materials*, 2016, 26, 1921–1929

   Yong Hua, Jinbao Zhang, Bo Xu, Peng Liu, Ming Cheng, Lars Kloo, Erik M. J. Johansson, Kári Sveinbjörnsson, Kerttu Aitola, Gerrit Boschloo and Licheng Sun
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5. Acceptor–Donor–Acceptor Type Ionic Molecule Materials for Efficient Perovskite Solar Cells and Organic Solar Cells
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   *Nano Energy*, 2016, 30, 387-397
6. **Dry-Deposited Transparent Carbon Nanotube Film as Front Electrode in Colloidal Quantum Dot Solar Cells**
Xiaoliang Zhang, Kerttu Aitola, Carl Hägglund, Antti Kaskela, Malin B. Johansson, Kári Sveinbjörnsson, Esko I. Kauppinen and Erik M. J. Johansson
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7. **High Temperature-Stable Perovskite Solar Cell Based on Low-Cost Carbon Nanotube Hole Contact**
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*Journal of Power Sources*, 2017, **344**, 11-14

9. **Enhanced Current Collection in Double-Cation Inverted Perovskite Solar Cells by Vapor Treatment and Using C60 as Electron Transporting Layer**
Zahra Saki, Kerttu Aitola, Kári Sveinbjörnsson, Wenxing Yang, Ute B. Cappel, Sebastian Svanström, Håkan Rensmo, Erik M. J. Johansson, Nima Taghavinia and Gerrit Boschloo
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Abbreviations and Symbols

\[ \beta \] Exciton concentration
\[ \theta \] Angle
\[ \lambda \] Wavelength
\[ \sigma \] Conductivity
\[ \varphi \] Photon flux
\[ \mu \] Charge mobility
\[ A \] Area

ALD Atomic-layer deposition
AM1.5G Air-mass 1.5 global
a-Si Amorphous silicon
ATR Attenuated total reflectance
\[ A_\lambda \] Absorptance
\[ c \] Speed of light
CB Conduction band
CE Counter electrode
CIGS Copper-indium-gallium-selenide
CNT Carbon nanotube
c-Si Crystalline silicon
CZTS Copper-zinc-tin-sulfide
DMF \( N,N \)-dimethylformamide
DMSO Dimethyl sulfoxide
DSSC Dye-sensitized solar cell
e Elementary electron charge
EDS Energy dispersive spectroscopy
\[ E_g \] Band-gap
ESL Electron-selective layer
FA Formamidinium
FF Fill factor
FTIR Fourier transform infrared spectroscopy
FTO Fluorine-doped tin oxide
\[ G \] Charge-carrier generation rate
GBL \( \gamma \)-butyrolactone
\[ h \] Planck constant
HJ Heterojunction
HOMO Highest occupied molecular orbital
HSL Hole-selective layer
HTM  Hole transport material

i  Current

IBC  Interdigitated back contact

IPA  Isopropanol

IPCE  Incident photon-to-collected electron efficiency

$I_s$  Spectral irradiance

$J$  Current density

$J_{sc}$  Short-circuit current density

$k$  Rate constant

$l$  Length

MA  Methylammonium

MOx  Metal oxide

MPP  Maximum power point

mp-TiO₂  Mesoporous TiO₂

$n$  Electron concentration

OC  Open-circuit

OPV  Organic photovoltaic

$P$  Power

$p$  Hole concentration

P3HT  poly(3-hexylthiophene-2,5-diyl)

PCBM  phenyl-C₆₁-butyric acid methyl ester

PCE  and η  Power conversion efficiency

PE  Primary electron

PSC  Perovskite solar cell

$r$  Effective ionic radius

$R$  Resistance

$R_λ$  Reflectance

SC  Short-circuit

SE  Secondary electron

SEM  Scanning electron microscopy

SiSC  Silicon solar cell

Spiro-OMeTAD  2,2,7,7-tetrakis(N,N-di-p-methoxyphenylamine)-9,90-
spirobifluorene

SPO  Stabilized power output

SQ limit  Shockley-Queisser detailed balance limit

$t$  Tolerance factor

$T_λ$  Transmittance

$U$  Charge-carrier recombination rate

$V$  Voltage

VB  Valence band

$V_{oc}$  Open-circuit voltage

WE  Working electrode

XRD  X-ray diffraction
Introduction

Aim of the Thesis
The main goal of the thesis is to investigate and characterize the lead-halide perovskites, and to explore further development of the processing techniques for making the material, so they might be used for large-scale manufacturing of solar cells. We studied the photophysics of bulk methylammonium lead triiodide perovskite films using photoconductivity measurements. We also developed a metal-free carbon-based electrode as a contact for the perovskite solar cells and investigated the aspect of depositing transparent electrodes directly onto the perovskite material. We designed a procedure for making high efficiency perovskite solar cells under normal ambient air conditions, a process which had thus far mostly been conducted under controlled and inert atmospheric conditions. Lastly, we devised a procedure for the synthesis of complex mixed-ion perovskite materials using only water and isopropanol as solvents.

The thesis is also tailored to provide a short primer of the topics covered in the research papers. The 1st chapter, here below, gives a brief introduction to the perovskite solar cell field in general and some of its branches. The 2nd chapter contains discussion and categorization of the various perovskite solar cell preparation processes and presents the characterization methods employed in the research papers. The 3rd chapter is an overview of the papers included in this thesis and the 4th chapter is a summary of the whole thesis.

Climate Change and Renewable Energy
Skepticism is a concept which symbolizes a healthy mindset, unless following the words climate-change. There is overwhelming and indisputable evidence for the fact that the Earth’s climate is warming and that it is because of increased man-made greenhouse gas emissions. The significant rise in anthropogenic greenhouse gas emissions, such as CO₂, can be explained by mankind’s increased energy demand, which so far primarily has been addressed with burning fossil fuels. At the time of writing, the Earth’s climate has warmed by 1.1°C since 1850 and is expected to hit at least 3°C by 2100. The effects caused by global warming are, among others, more frequent extreme weather incidences, increase of oceanic acidity, rising sea levels due to
melting polar icecaps, and inhabitable land areas due to extreme temperature changes. A 3°C increase will result in a sea level increase of 2 meters in 2100, which is more than enough to sink many densely populated cities in the world.

The fact that the climate conditions will not improve in the next several decades is disheartening. For most of us, it signifies that our generation will only experience the environmental decay caused by global warming. Climate change is, without a doubt, one of the toughest challenges that mankind has faced. Although the problem and its effects are multifaceted the solution is in principle simple – phase out fossil fuels and progress towards renewable energy sources.

![Figure 1. Left) Photograph of healthy corals in the Great Barrier reef, Australia. Right) Photograph of bleached corals in the Great Barrier reef. Today, over 85% of the corals have been affected due to oceanic temperature changes.](image)

A multitude of different methods exist to capture and sequester CO₂, but the most permanent solution to climate change is to evolve to an electric economy based on sustainable energy production. Renewable electricity production, which does not involve combustion, is possible through hydro, wind, geothermal, oceanic-wave, and solar power. In only one hour a staggering amount of energy, which corresponds to the global annual energy demand, hits the Earth in the form of sunlight. This leads to the argument that if 0.08% of the Earth’s surface, which corresponds approximately the size of Sweden, was covered by solar-panels with 20% power conversion efficiency (PCE) the global energy demand could be met. One advantage of solar panels is that they can be installed anywhere, and the wide-range of different solar technologies makes it possible to employ them in various conditions. However, there are regions of the world that do not receive much sunlight. Therefore, it is important to recognize that other renewable energy sources, in combination with solar cells, will also play a large part in our progress towards a renewable electric society.
Solar Cells

Working Mechanism

The p-n Junction

The basic principle of any solar cell is that light is absorbed to create a potential difference between two electrodes. This phenomenon, known as the photovoltaic effect, was first observed by Edmond Becquerel in 1839. A solar cell usually consists of a photoabsorber, which absorbs light to excite electrons ($e^-$), and two selective contacts to spatially separate the photogenerated charges, i.e. the excited $e^-$ and the electron deficiency (hole, $h^+$). Without any physical separation of the photogenerated charges to the two different electrodes no photovoltage will appear. This separation of charges can be introduced, for example, by creating an electric field in the material of the solar cell, which will cause the $e^-$ to move in one direction and $h^+$ in the other. The charge separation results in a current flow and, along with the potential difference between the electrodes, generates electric power when connected to an external circuit. Charge separation by an electric field is common in solar cells which are comprised of a p-n junction, such as crystalline silicon (c-Si) solar cells. Schematic illustrations of a classical
silicon solar cell and the charge separation process are presented in Figure 3. The p-n junction can be constructed by doping one part of the Si semiconductor with elements yielding movable positive (p) charges, $h^+$, and another part with elements yielding mobile negative (n) charges, $e^-$. When those two parts are combined it results in the formation of a p-n junction and the difference in charge concentration between the two parts generates an electric field over the so-called depletion region. Once the semiconductor has successfully absorbed a photon, an $e^-$ is excited from the valence band (VB) to the conduction band (CB), leaving behind an $h^+$ in the VB and resulting in the formation of an electron-hole pair ($e^-h^+$), also known as an exciton. The $e^-h^+$ pairs dissociate to form separated free-charge carriers, i.e. $e^-$ and $h^+$, which randomly diffuse until they either reach their respective contacts or the depletion region. When the excited $e^-$ reaches the depletion region it experiences an attraction towards the electric field and a beneficial potential difference in the CB by travelling from the p-doped Si to the n-doped Si. Conversely, the $h^+$ is repelled by the electric field and experiences an unfavorable potential difference in the VB. Similarly, in the occurrence of absorption in the n-type layer, the $h^+$ that reaches the depletion region is pulled by the field whereas the $e^-$ is repelled. This promotes $e^-$ to be collected at the n-contact and $h^+$ at the p-contact and as a result a current is generated in the device.

![Figure 3. Left) Schematic illustration of a silicon solar cell (SiSC). Boron atoms (yellow spheres) are used for p-doping the silicon and phosphorous atoms (pink spheres) are used for n-doping. An anti-reflecting (AR) coating (yellow layer) is generally deposited on the silicon to avoid reflective losses in the SiSC. At the p-n interface a depletion region is formed where the $h^+$ from the B atoms have recombined with the $e^-$ in the P atoms. Right) An energy diagram of the absorption event in the Si semiconductor. A valence-band (VB) electron (blue sphere) is excited by a photon ($\gamma$) to the conduction band (CB). The hole (green sphere) formed in the VB travels to one contact, while the excited electron (red sphere) in the CB travels to the other due to beneficial band-bending in the Si material.](image-url)
Thin film and emerging photovoltaics

Thin film solar cells, such as copper-indium-gallium-selenide (CIGS), copper-zinc-tin-sulfide (CZTS) and amorphous silicon (a-Si), use hole- and electron-selective layers (HSL and ESL) in combination with $p-n$ or $p-i-n$ junctions to selectively allow either $h^+$ or excited $e^-$ to pass through and spatially separate the photogenerated charge carriers, which results in a potential difference as in the c-Si solar cell. When grown, the CIGS and CZTS materials are intrinsically $p$-type and because of $n$-type doping limitations they need a dissimilar semiconductor to create a $p-n$ junction. In this case the $p-n$ junction is called a heterojunction because $n$- and $p$-type materials are not of the same material. The heterojunction, and a compositional gradient design of the semiconductor itself, shifts and bends the CB/VB band-structure in the material as to make it easy for the excited $e^-$ and hard for $h^+$ to pass through the ESL and vice-versa for the HSL.

Organic photovoltaics (OPVs) are a different class of solar cells, of which the most efficient are based on the bulk heterojunction structure. A bulk-heterojunction OPV consists of layers or domains of two different organic materials, which can generate excitons and, together, separate the $e^--h^+$ pairs. In the simplest case, the OPV consists of a layer of phenyl-C61-butyric acid methyl ester (PCBM) and poly(3-hexylthiophene-2,5-diyl) (P3HT). The P3HT absorbs most of the incoming visible light resulting in exciton formation. At the PCBM/P3HT interface the energy level matching of the two materials facilitates charge-separation, so that the excited $e^-$ is transferred into the PCBM layer whereas the $h^+$ remains in the P3HT layer. The charge carriers then diffuse to their respective contacts.

Dye-sensitized solar cells (DSSCs) present another way of charge carrier separation. These devices generally contain organic-molecules, dyes, which adhere to a wide-bandgap semiconductor. The dye absorbs the incoming light and due to favorable matching between the redox energy level of the dye’s excited state and the CB of the wide-bandgap semiconductor, the excited $e^-$ is injected from the dye to the CB of the wide-bandgap semiconductor. The $h^+$ in the dye is then regenerated by means of a liquid electrolyte or a solid-state hole-conductor. In 1991, O’Regan and Grätzel presented a DSSC, based on sensitizing a mesoporous network of TiO$_2$ nanoparticles with organic dyes as the light absorber, with a 7.1% PCE. The use of a porous TiO$_2$ structure to increase the surface area, and hence the amount of dye able to be loaded in the solar cell, is widely regarded as a breakthrough in the field of DSSCs since the discovery of semiconductor dye-sensitization. The elegant working mechanism of this system relies on the ultrafast injection of excited state $e^-$ from the organic dye into the CB of the TiO$_2$ semiconductor and the slower recombination processes. The devices typically use a liquid-based electrolyte to regenerate the $h^+$ in the dye and to complete the circuit.
The Relationship between Photoabsorber and the Solar Spectrum

The performance of a photoabsorber in a solar cell is largely influenced by its ability to absorb photons. One of the main factors that determine which photon energies a semiconductor photoabsorber can absorb is the band-gap ($E_g$) of the material. $E_g$ is defined as the energy difference between the VB and CB in a semiconductor photoabsorber. The ideal $E_g$ of a photoabsorber for use in a solar cell depends on the light emission spectrum of the radiating body from which photons are to be harvested. In 1961, Shockley and Queisser published a detailed balance PCE limit of single-junction semiconductor solar cells, known as the Shockley-Queisser (SQ) limit, which can be observed in Figure 4a. As the graph shows, the highest attainable PCE for a single-junction solar cell is around 30%, but in more recent work this has been established to 33.8%. By using a single semiconductor with, for example, an $E_g$ of 1.5 eV all photons of higher energy will generate charge-carriers with an energy corresponding to the $E_g$ and photons with lower energy than the $E_g$ will not be absorbed.

Figure 4. a) A figure from Shockley and Queisser’s work showing the theoretical maximum attainable PCE, $\eta$, for a single-junction solar cells as a function of the semiconductor band-gap, $V_g$. b) The solar spectral irradiance as a function of wavelength and photon energy. The AM0 extraterrestrial spectrum is depicted by a blue color while the reference AM1.5G spectrum is depicted orange.

The sun is our source of light and its spectral irradiance as a function of wavelength and energy is depicted in Figure 4b. The spectra of the sunlight at the Earth’s surface are generally described by using the air mass (AM) coefficient. The extraterrestrial sunlight spectrum, which can be observed in space, has not passed through the atmosphere and is called AM0. When the light has passed through the atmosphere perpendicular to the Earth’s surface it is called AM1. In solar cell research the AM1.5G spectrum, which is observed at the surface of earth when the sun is at an azimuth angle of 48.19°, is used as a reference spectrum. It is a standardized value meant to represent the direct and
diffuse part of the global solar spectrum (G). The AM0 and AM1.5G spectra differ somewhat, due to light scattering from molecules and particles in the atmosphere and from absorption from molecules like H₂O, CO₂, and CO. Scattering causes the irradiance to decrease over all wavelengths, but more so for high energy photons, and the absorption from molecules cause several dips in the AM1.5G spectrum as can be seen in Figure 4b.

The Photovoltaic Market

**Single-Junction Solar Cells**

Silicon solar cells (SiSCs) are sometimes portrayed as a stagnant technology, despite dominating the photovoltaic market and presenting the one of the cheapest sources of electricity in the world with prices < US$ 3c/kWh in Mexico, Saudi-Arabia and Abu-Dhabi. The structure of the SiSC and the device manufacturing methods have improved tremendously since the first versions. The passivated-emitter and rear cell (PERC) SiSC technologies, which yield higher PCEs than the conventional structure, are expected to claim market-domination within 10 years because of their compatibility with the conventional SiSC manufacturing processes. However, the present SiSC PCE record of over 26% has been reached with a combination of heterojunction (HJ) and interdigitated back-contact (IBC) SiSCs. Market projections also indicate that these HJ-IBC structures are slowly increasing their market share and will most likely dominate market sometime after or around 2030. In short, SiSCs present the cheapest means to produce electricity and, considering the value of the SQ limit, it is unlikely that other solar cell technologies will soon manage to compete with Si for industrial generation of electricity by single-junction photovoltaics. However, this does not mean that all new solar cell technologies are destined to fail in the shadow of the SiSC.

For instance, the c-SiSC may not be applicable or efficient for all situations. Building integration of solar cells may require low module weight, flexibility, semitransparency, and aesthetic design. Because c-Si is a brittle material it requires thick glass substrates to support it, which makes the solar cells relatively heavy and inflexible. Semitransparency can be achieved at the cost of absorber material thickness and hence photocurrent generation, and aesthetics are generally an opinionated subject. OPVs offer great flexibility, and low weight and can be used on surfaces which are not straight or surfaces which require dynamic flexibility. However, OPVs have mostly achieved niche uses due to their low PCEs. DSSCs offer a great variety of vibrant colors due to the use of dyes and they can, along with semitransparency, provide aesthetic designs. Furthermore, DSSC have shown to be superior to other solar cells when it comes to harvesting light of low-intensity such as for indoor applications. CIGS and CZTS solar cells are generally constructed in a thin film
architecture made possible by the large absorption coefficient of the photoabsorbers. The materials used in this architecture allow for flexible modules of low weight.

**Tandem Solar Cells**

A famous saying goes, “If you can’t beat them, join them.”, which accurately describes the mindset one must adopt on new solar cell technologies to adapt to the governing market share of SiSC. Tandem solar cells are, as the name describes, two or more different solar cells stacked on top of each other to harvest as much light as possible with as few energetic losses as possible, as illustrated in Figure 5.

![Figure 5. Schematic illustration of a simple two-junction tandem solar cell with four contacts. Light (γ) enters the cell from the top and passes first through the large $E_g$ top cell where the high-energy photons are harvested. The low-energy photons ideally pass through the top-cell without interaction and into the small $E_g$ bottom cell where they can be harvested. In a monolithic tandem solar cell, the insulative layer and the transparent contacts around it are replaced with a recombination layer. The top cell, through which the light passes first, should absorb the high-energy photons and the bottom cell should absorb the remaining low-energy photons. The benefit of combining the layers in such a way is that with a large $E_g$ top layer the high-energy photons will result in formation of high-energy](image-url)
electrons. When the two cells are connected in series this leads to the generation of higher voltage output of the tandem device on a smaller area, compared to disconnected individual single-junction cells, and hence a larger power output. The 30% PCE limit does not apply to tandem solar cells but they are still subjected to detailed balance and the losses thereof. The addition of a photoabsorber with an $E_g$ of around 1.7 eV on top of the c-SiSC, to create a tandem solar cell, could result in a device with a PCE above 40%.

The market will likely shift towards tandem modules in the future because the total cost of the solar energy is considerably lowered with each incremental percentage of the solar cells PCE. In the tandem solar cell market, it might not be certain that c-SiSCs will still be able to dominate the market because the $E_g$ of c-Si (1.1 eV) cannot be tuned much. Specifically, the low $E_g$ thin film technologies such as CIGS or CZTS are of specific interest for these purposes as their $E_g$ can be tuned somewhat to match the ideal $E_g$ of the top cell photoabsorber.25,26

**Perovskite Solar Cells**

The perovskite mineral was discovered in the early 19th century and named after the Russian mineralogist Lev Perovski. It was not until 1926 that Victor Goldschmidt analyzed this family of minerals and described their crystal structure.27 The perovskite crystal structure, shown in Figure 6a, is of the form ABX$_3$, where A is a cation, B is a metal cation and X is an anion. The crystal structure consists of corner-connected BX$_6$ octahedra where A fills the space between the octahedra. A common example of a crystal with this structure is calcium titanate (CaTiO$_3$), which is one of many naturally occurring perovskites on Earth. Many of the oxide perovskites exhibit useful magnetic and electric properties including double perovskite oxides such as manganites, which show ferromagnetic effects and giant magnetoresistance effects.28

**Hybrid Organic-Inorganic Perovskite Materials**

A hybrid organic-inorganic perovskite material, methylammonium lead triiodide (MAPbI$_3$), was first synthesized in 1978 by D. Weber along with several other organic-inorganic perovskites, see Figure 6b.29,30 The idea of combining organic moieties with the inorganic perovskites allows for the use of the full force and flexibility of organic synthesis to tailor the electric and mechanical properties of the perovskites to specific applications.31 In the work by Weber it was discovered that this specific subclass of perovskite materials could have photoactive properties and in 2009 Kojima et al. fabricated the first hybrid organic-inorganic perovskite solar cell using MAPbI$_3$ as the photoabsorber.32 This first organic-inorganic PSC was manufactured imitating the conventional DSSC structure. A TiO$_2$ working electrode was coated with
MAPbI$_3$ and MAPbBr$_3$ and a liquid electrolyte was used for hole transport. However, as mentioned by Im et al. in 2011, the stability of the solar cells was very bad because the perovskite material simply dissolved in the liquid electrolyte, causing the PSC to lose 80% of their original PCE after 10 minutes of continuous light exposure.  

Kim et al. and Lee et al. published the first solid-state PSCs, around the same time in 2012, where PCEs of 9.7% and 10.9% were obtained, respectively. In both cases, the solar cell took inspiration from the layers of a solid-state DSSCs, where the photoabsorbing material is loaded in a mesoporous layer of TiO$_2$ nanoparticles and covered by a layer of the organic hole-transport material (HTM) Spiro-OMeTAD. A transparent conductive oxide, fluorine-doped tin-oxide (FTO), was used as the front contact and metallic gold or silver as the back contact. As will be discussed later, Lee et al. obtained their record PCE by using a mesoporous Al$_2$O$_3$ nanoparticle scaffold instead of TiO$_2$, which sparked doubt to whether the PSC was an electron-injection based device or not. A plethora of different layer architectures have been published since for the PSCs but the world record PSCs, which have yielded a PCE of 22.7%, still use an architecture based on TiO$_2$ and Spiro-OMeTAD. However, recent results also show that the HTM layer must be modified for improving the solar cell stability.  

![Figure 6](https://example.com/figure6.png)

**Figure 6.** a) Cubic crystal-structure of a ABX$_3$ type perovskite. The A-cation is depicted by a yellow sphere, the B-cations by red spheres and the X-anions by blue spheres. The B-cations and X-anions form an octahedral network depicted by gray polyhedral. b) The same perovskite structure but for MAPbI$_3$. The MA-cation is in the center, Pb(II) is depicted by gray spheres and I$^-$ by purple spheres. Drawings were produced by VESTA.  

In Figure 7a, a simplified estimation of the energy band-diagram for the FTO/TiO$_2$/MAPbI$_3$/Spiro-OMeTAD/Au PSC is shown. The diagram shows
how the CBs of the perovskite and TiO$_2$ match to promote a flow of excited electrons from the MAPbI$_3$ into the TiO$_2$ and all the way to the FTO. Similarly, the highest occupied molecular orbital (HOMO) level of the HTM matches with the VB of the MAPbI$_3$ to allow for efficient regeneration of the holes in the perovskite semiconductor. Figure 7b presents a schematic representation of the layered structure of the PSC. It shows how light enters from the bottom side, travels into the photoabsorbing MAPbI$_3$ medium, in which the excited charge-carriers are generated, and can be reflected from the gold electrode to make a second pass through the photoabsorbing layer. In Figure 7c one can see a photograph of the PSC. Each gold square represents a single solar cell with dimensions of 0.3 cm$^2$ and the gold bar on the bottom of the substrate is the working electrode contact to the FTO layer. A side-view of the same substrate, see Figure 7d, shows that the solar cell layer is practically invisible to the naked eye because its thickness is roughly a million times thinner than the diameter of an average sand grain.

Figure 7. a) Energy band diagram of a typical MAPbI$_3$ perovskite solar cell and b) the structure of the different solar cell layers. c) Photograph of lab-scale MAPbI$_3$ perovskite solar cells with identical layers as in the diagram to the left with a 10 Euro cent coin for scale. d) Side view of the same sample and coin.

Compositional Optimization of the Perovskite

Despite the promising PCEs of the MAPbI$_3$ solar cells the material has several flaws which pushed the field towards exploring different perovskite compositions. Concerns regarding the presence of lead in the devices were among the first to be voiced. Furthermore, the MAPbI$_3$ perovskite material did not appear entirely chemically stable and studies showed that it might also not be thermally stable.$^{39,40}$ Degradation studies by Kim et al. in 2017, showed that the MA$^+$ cation evaporated and escaped the perovskite structure at 80°C, a typical working condition temperature for a solar cell, resulting in the formation of
crystalline PbI₂.⁴⁰ The instability of the MAPbI₃ PSC is presumably the greatest concern for a successful commercialization. However, this instability of MAPbI₃ was not the main reason for the research field to explore different perovskite compositions. In the dawn of the PSC research field, a few organic-inorganic perovskite crystal structures were known to be photoactive but had not been tested in solar cells yet.³¹ Therefore, there was a large curiosity driven interest in discovering and testing new materials possibly capable of similar, or greater, feats as the MAPbI₃.

In his work in 1926, Goldschmidt introduced a tolerance factor \( t \) for the perovskite crystal structure.²⁷ By comparing relative sizes of the ions, \( t \) can give an indication of whether a certain combination of the ABX₃ ions can form a perovskite. The equation for \( t \) is:

\[
t = \frac{r_A + r_X}{\sqrt{2} (r_B + r_X)},
\]

where \( r_A \) is the radius of the A-cation, \( r_B \) is the radius of the B-cation and \( r_X \) is the radius of the X-anion. Figure 8 illustrates the sizes of several relevant ions for the composition of the lead-based perovskite. The values of the ions effective radii are also presented in Table 1. Photoactive perovskites have a \( t \) between 0.8 and 1, where the crystal structures are tetragonal and cubic, and are often referred to as black- or \( \alpha \)-phases. Hexagonal and various layered perovskite crystal structures are obtained with \( t > 1 \) and \( t < 0.8 \) results in orthorhombic or rhombohedral perovskite structures, all of which are not photoactive. The photoinactive phases are generally referred to as yellow- or \( \delta \)-phases. With \( t < 0.71 \) the ions do not form a perovskite. Researchers have thus used the \( t \) as a compass to explore different possible compositions of the photoactive perovskite materials.

**Stabilization by Bromine**

Noh et al. found that by replacing the iodine in the MAPbI₃ by a slight addition of Br⁻ served to stabilize and enhance the photovoltaic properties of the MAPbI₃ perovskite and at the same time it increased the \( E_g \) of the perovskite.⁴¹ In fact, they also found that the \( E_g \) could easily be tuned from 1.57 eV for the pure MAPbI₃ to 2.29 eV for the pure MAPbBr₃ by controlling the I/Br ratio of the perovskite precursor solution. Regretfully, the MAPb(I₁₋ₓBrₓ)₃ perovskite tends to segregate into separate iodine and bromine rich domains when the material is exposed to light.⁴² A domain segregation of this type is, of course, a problematic phenomenon for any type of a solar cell. However, this only seems to affect perovskites with a composition range of around 0.2 < \( x < 0.85 \).
Figure 8. Schematic illustration of the effective ionic radii for some of the ions which can be considered for lead/tin perovskites. The ions are ordered with respect to their effective sizes.

Table 1. Effective radii of several relevant ions used and proposed for synthesis of lead/tin based perovskite materials for solar cell purposes.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Symbol / Formula</th>
<th>Effective Ionic radius (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead (II)</td>
<td>Pb^{2+}</td>
<td>119</td>
</tr>
<tr>
<td>Tin (II)</td>
<td>Sn^{2+}</td>
<td>118</td>
</tr>
<tr>
<td>Ammonium</td>
<td>NH_{4}^{+}</td>
<td>146</td>
</tr>
<tr>
<td>Methylammonium</td>
<td>MA^{+}</td>
<td>217</td>
</tr>
<tr>
<td>Ethylammonium</td>
<td>EA^{+}</td>
<td>274</td>
</tr>
<tr>
<td>Formamidinium</td>
<td>FA^{+}</td>
<td>253</td>
</tr>
<tr>
<td>Guanidinium</td>
<td>GA^{+}</td>
<td>278</td>
</tr>
<tr>
<td>Lithium</td>
<td>Li^{+}</td>
<td>76</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na^{+}</td>
<td>102</td>
</tr>
<tr>
<td>Potassium</td>
<td>K^{+}</td>
<td>138</td>
</tr>
<tr>
<td>Rubidium</td>
<td>Rb^{+}</td>
<td>152</td>
</tr>
<tr>
<td>Cesium</td>
<td>Cs^{+}</td>
<td>167</td>
</tr>
<tr>
<td>Fluoride</td>
<td>F^{-}</td>
<td>133</td>
</tr>
<tr>
<td>Chloride</td>
<td>Cl^{-}</td>
<td>181</td>
</tr>
<tr>
<td>Bromide</td>
<td>Br^{-}</td>
<td>196</td>
</tr>
<tr>
<td>Iodide</td>
<td>I^{-}</td>
<td>220</td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>SCN^{-}</td>
<td>220</td>
</tr>
<tr>
<td>Borohydride</td>
<td>BH_{4}^{-}</td>
<td>207</td>
</tr>
</tbody>
</table>

Layered Perovskite Formation with Large Organic Cations

Already established in David Mitzi’s work in 1999, organic cations with longer carbon chains than MA, such as ethylammonium (EA) and propylammonium (PA), do not yield a three-dimensional (3D) cubic-perovskite with the lead-halides. This is mainly because their ionic radii are too large.
These cations rather tend to form two-dimensional (2D) layered perovskite structures. Although the 2D-perovskites are photoactive and, due to their chemical tunability, can be functionalized with various organic moieties, they have not resulted in as efficient solar cells compared to the 3D-perovskites, unless embedded inside one.\textsuperscript{49,50} This is possibly due to the layered structure of the 2D-perovskite which presents a hindrance in terms of charge conduction and extraction. However, the stability of these perovskites is generally greater than that of the MAPbX\textsubscript{3} due to the higher boiling point of the longer carbon-chain cations.

**The Formamidinium Cation**

Cubic lead-halide perovskite structures can also be formed using the formamidinium cation (FA\textsuperscript{+}) which is somewhat in between the ionic size of MA and EA.\textsuperscript{51} The FA cation yields a perovskite with greater thermal stability than the MA cation, due to a higher boiling point of the FA compared to MA. Therefore, the FAPbX\textsubscript{3} perovskites have become very attractive to the research field because they can to a large degree be considered as superior to the MAPbX\textsubscript{3} perovskites. Although the FAPbX\textsubscript{3} perovskites did not yield record PSCs at the time they were first reported, researchers in the field were quick to pick up the material. Since then, FA-rich perovskite materials have been used in all of the efficiency record breaking PSCs.\textsuperscript{36,52–55} Furthermore, these materials most likely present the best opportunity for developing stable organic-inorganic perovskite solar cells.\textsuperscript{56}

The FAPbI\textsubscript{3} perovskite has an $E_g$ of 1.48 eV, which is ideal for solar cell applications. However, the material requires 150 °C heating to form the photoactive cubic perovskite phase and when cooled down below that temperature it quickly reverts to a photoinactive $\delta$-phase.\textsuperscript{53} Initially, the $\alpha$-phase of FAPbI\textsubscript{3} was stabilized by slight addition of methylammonium, forming MA\textsubscript{y}FA\textsubscript{1−y}PbI\textsubscript{3}.\textsuperscript{52} Furthermore, it was discovered that the structure could also be stabilized by mixing the perovskite with bromide forming, similar to its methylammonium predecessor, FAPb(I\textsubscript{1−x}Br\textsubscript{x})\textsubscript{3}. This lead to the discovery of the highly efficient and stable compositions of, (FAPbI\textsubscript{3})\textsubscript{1−x}(MAPbBr\textsubscript{3})\textsubscript{x} perovskite, commonly referred to as the mixed-ion perovskite.\textsuperscript{53} It should be noted that the conventional notation for the (FAPbI\textsubscript{3})\textsubscript{1−x}(MAPbBr\textsubscript{3})\textsubscript{x} perovskite may not be the best for describing the structure of the material. A more descriptive notation would be (MA\textsubscript{y}FA\textsubscript{1−y})Pb(I\textsubscript{1−x}Br\textsubscript{x})\textsubscript{3} as described in Figure 9. However, because the original notation was used in Papers III, IV and V, it will be used in this thesis unless otherwise stated. The use of larger organic cations, such as guanidinium (GA), have also been proposed as an additive to the MAPbI\textsubscript{3} crystal structure but the pure GAPbI\textsubscript{3} perovskite does not form a 3D-perovskite due to the large size of the GA\textsuperscript{+} cation.\textsuperscript{57,58}
Inorganic Cations

The thermal instability of perovskite materials with organic ammonium cations triggered interest in development of inorganic perovskite materials for solar cell applications. Inorganic cations do not evaporate as easily as the organic cations and they should therefore maintain greater stability at the working conditions of solar cells, where temperatures can rise above 80 °C. Cesium lead halide perovskites have almost 100 years longer history than the organic lead halide perovskites. As such, it is not surprising that Cs⁺ was the first inorganic cation to be introduced into the lead halide perovskite for making new photoabsorbing solar cell materials. Lee et al. introduced cesium into the structure of FAPbI₃ and, in similar manner as to addition of bromine, this stabilized the perovskite structure at room temperature and increased the PCE of...
the solar cells. Shortly thereafter, Li et al. mapped out the entire Cs$_3$FA$_{1-y}$Pb$_3$ range to determine the material stability of the alloy. The cubic phase of CsPbI$_3$ is not stable at room temperature, just like FAPbI$_3$. However, because FA$^+$ is slightly too large for the cubic perovskite phase ($t > 1$) and Cs$^+$ is slightly too small ($t < 0.8$) for it, the CsFA alloys yield a stable cubic perovskite phase. The cubic phase of CsPbI$_3$ has an $E_g$ of 1.73 eV, ideal for tandem applications with c-Si, which makes its instability at room-temperature somewhat unfortunate.

Conversely, the $\alpha$-phase of CsPbBr$_3$ is completely stable at room temperature. Its $E_g$ of around 2.36 eV is far too large to yield a PCE of more than 15% in single-junction but the material may still be of interest for tandem solar cells. In an attempt to combine the stability of CsPbBr$_3$ and the $E_g$ of CsPbI$_3$, Sutton et al. manufactured a mixed-halide CsPbI$_2$Br perovskite solar cell which resulted in almost a 10% PCE. However, the authors stated that even this material was not completely stable. Possibly due to ion-segregation, like in the mixed halide MA-perovskite, and subsequent phase transition of the CsPbI$_3$ domains to a $\delta$-phase.

Due to the small cation size of Rb$^+$, RbPbX$_3$ retains a orthorhombic crystal structure ($t < 0.8$) at room temperature, similar to the CsPbX$_3$. At temperatures above 330°C the CsPbI$_3$ transitions to a cubic phase but RbPbI$_3$ does not exhibit a crystal phase transitions prior to its melting point between 360-440°C. However, the use of a smaller anion, such as Cl$^-$, can yield a crystal phase transition for the RbPbCl$_3$ perovskite at lower temperatures than for the RbPbI$_3$.

**Alternative Anions**

As mentioned above, a slight addition of bromine to the MAPbI$_3$ or FAPbI$_3$ perovskites serves to both stabilize the crystal structure and increases the $E_g$. Lead bromide perovskites generally result in materials with larger $E_g$ than the lead iodide perovskites. Synthesis of organic lead chloride perovskites, such as the MAPbCl$_3$, has also been reported and studies show that these materials display an even larger $E_g$ than their bromide counterparts. Some of the first high efficiency perovskite solar cells were reported as a mixed-halide MAPb(I$_{1-x}$Cl$_x$)$_3$ perovskite because PbCl$_2$ was used as the lead precursor in this procedure. The role of the chloride anion in the mixed-halide perovskites has been a subject of debate within the research field of PSCs. However, studies have shown that chlorine doping can result in an Cl$^-$ inclusion of roughly 4% in the bulk perovskite crystal structure and that this inclusion has a substantial beneficial effect on the solar cells performance.

Several different non-halide anions, also called pseudo-halides, have been tested for formation of perovskite materials, such as borohydride (BH$_4^-$) and thiocyanate (SCN$^-$). However, pure organic lead borohydrides or thiocyanate perovskites have not been successfully synthesized despite that the ionic...
sizes are appropriate for the perovskite structure. In fact, the first lead borohydride perovskite, a tetragonal CsPb(BH$_4$)$_3$, was only first synthesized in 2014.$^{72}$

**Multiple-cation Perovskite Absorber**

In 2016 researchers at EPFL, Switzerland, reported a triple-cation based perovskite material for solar cells.$^{54}$ The material was formed from a precursor solution prepared in the same manner as for the best performing (FAPbI$_3$)$_{1-x}$(MAPbBr$_3$)$_x$ perovskite along with a slight addition of CsI. Deposition of this solution yielded a perovskite material which can be abbreviated as Cs$_{0.05}$MA$_{0.16}$FA$_{0.79}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$. As reported by Saliba *et al.*, the inclusion of Cs$^+$ served to further stabilize the perovskite structure and increase the PCE and the manufacturing reproducibility of the solar cells.$^{54}$ Further optimization would push the same researchers to add Rbl to the perovskite precursor solution.$^{55}$ This resulted in the formation of a quadruple-cation perovskite with a material composition of Rb$_{0.05}$Cs$_{0.05}$MA$_{0.15}$FA$_{0.75}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$.

**Perovskite Band-gap Origin**

The $E_g$ of the lead halide perovskites is defined by the lead halide framework.$^{74,75}$ The VB edge of the MAPbI$_3$ perovskite consists mostly of I 5$p$ orbitals overlapping with the Pb 6$p$ and 6$s$ orbitals, and the CB edge consists of Pb 6$p$ - I 5$s$ $\sigma^*$ and Pb 6$p$ - I 5$p$ $\pi^*$ hybridized orbitals. Similarly, bromide perovskites are defined by the 4$p$ orbitals of the Br atom and chloride perovskites by the 3$p$ orbitals of the Cl atom.$^{76}$ As we discussed above, the $E_g$ of the perovskite can be tuned by stoichiometric adjustment of the halide precursors. The fundamental reason for the $E_g$ changing, when the halide ratio in the perovskites are changed, is due to the difference in the binding energies of the halide $p$-orbitals. The $E_g$ of the perovskite is mostly mechanically affected by the choice of the cation, rather than directly electronically, since the cation is not part of the valence electronic structure.$^{77,78}$ However, due to the size difference of the cation, the Pb-X bond lengths and bond angles will be affected and thereby the valence electronic structure. Larger cations, such as the FA$^+$, push the Pb-X bond further apart than, for example, the Cs$^+$ cation resulting in a lower binding energy between the Pb and X, and hence lower $E_g$ of the FAPbX$_3$ perovskite compared to the CsPbX$_3$ perovskites. In Table 2 the band-gaps of various lead-halide perovskites are presented.

Table 2. Band-gaps (eV) of the various APbX$_3$ lead-halide perovskite materials as determined by optical measurements.$^{41,51,63,64,79}$

<table>
<thead>
<tr>
<th>APbX$_3$</th>
<th>Cl$^-$</th>
<th>Br$^-$</th>
<th>I$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$^+$</td>
<td>~3.2</td>
<td>2.36</td>
<td>1.73</td>
</tr>
<tr>
<td>MA$^+$</td>
<td>~3.1</td>
<td>2.29</td>
<td>1.57</td>
</tr>
<tr>
<td>FA$^+$</td>
<td>~3.0</td>
<td>2.23</td>
<td>1.48</td>
</tr>
</tbody>
</table>
To summarize, even though a certain selection of cation, metal, and anions results in a $t$ between 0.8 and 1 it does not necessarily mean that a stable perovskite material can be formed. Furthermore, if a perovskite can be formed with a certain set of ions we cannot say much about its $E_g$ unless we accurately predict the structure of its B-X framework.

## The Presence of Lead

One of the major drawbacks of lead perovskite solar cells is the presence of lead in them. The European Union's Restriction of Hazardous Substances directive has banned the use of lead in all electronics and electrical equipment, due to its toxic nature. For this reason, alternatives to lead as the metal cation in the perovskite photoabsorber have become a major research avenue.

A simple approach to replace lead is to take a step up or down within Group IV of the periodic table of elements. Flerovium is the element in the row below lead, a recently discovered element, barely radioactively stable, and because of its radioactivity perhaps not a suitable replacement for lead. Tin (Sn), which is in the row above lead, would be a good candidate for replacing Pb in PSCs because of its less-toxic nature. The synthesis of organic tin halides is as old as that of the lead halides. The MASnI$_3$ perovskite, which has an $E_g$ of 1.3 eV, has been reported for use in solar cells and yielded a PCE of 6.4%. However, the $+2$ oxidation state of Sn, required to form a perovskite, is not stable and the metal rapidly oxidizes to the $+4$ state upon exposure to oxygen or humidity in the air. This is a problem for the solar cell manufacturing process as well as for the working conditions of the device. Any exposure to air can cause immediate oxidation of tin and so far it has only been possible to measure the PCE of the pure tin halide PSCs with robust hermetical encapsulation of the devices. However, the Pb-based perovskites have been successfully mixed with Sn, and alloyed 50/50 Sn/Pb halide perovskites have yielded a 13.6% PCE. The most recent efforts within the Sn PSC field have been directed towards stabilization of the Sn$^{2+}$ cation with additives such as SnF$_2$. FASnI$_3$ solar cells have been prepared by help of these additives and yielded a PCE of 4.8%. However, the focus of the perovskite research field has shifted somewhat towards the inorganic CsSnI$_3$ perovskites due to the surprisingly efficient quantum-dot solar cells prepared with this material resulting in a PCE of 13%. Recently, bismuth (Bi) based photoabsorbers have also caught the interest of the scientists in the field as an option for replacing lead. While they do not reach high PCEs yet, the bismuth photoabsorbers present a non-toxic alternative to lead perovskites.

However, the large-scale manufacture of lead-containing PSCs might not be as appalling as it sounds. The optimal perovskite layer thickness in the PSC is typically around 500 nm, due to the strong absorption coefficients of the lead halide perovskites. This leads to a popular comparison within the perovskite field; if the lead from a single lead-acid car-battery were to be completely
converted to use in PSCs one could cover an area of approximately \(7000 \text{ m}^2\) with solar cell.\(^9\) Therefore, the prospect of commercializing lead-based perovskite solar cells might not be completely implausible considering the beneficial environmental impact for the climate that such a technology might present. The discussion for commercialization of lead perovskite solar cells is still open. Although one should never ignore the toxic nature of lead, the issue of lead exposure could be overcome by proper encapsulation and recycling of the lead-based PSCs.
Experimental

Preparation Processes
The solution-process manufacturing methods for the perovskite in the state-of-the-art PSCs can generally be divided into categories depending on the number of steps required to form the perovskite material. In the so-called one-step methods all the perovskite precursors are dissolved in a single solution and deposited onto a substrate of ones choosing. Upon the evaporation of the solvent the perovskite material forms. Two-step methods generally consist of a step-wise perovskite precursor addition, also known as sequential deposition, to form the perovskite of choice. Further manufacturing steps can be carried out to modify the perovskite material, or the precursors formed sequentially, but these are usually not referred to as more-than-two-step methods.

One-step Methods
One-step methods were the first manufacturing processes to be published on solid-state PSCs. The solvents which are capable of dissolving the precursor materials at an appreciable concentration, are typically high-boiling point solvents such as $\gamma$-butyrolactone (GBL), $N,N$-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), $N$-methyl-2-pyrrolidone, and dimethylacetamide. The benefit of one-step methods, apart from using the least amount of steps possible for the manufacturing, is the compositional control they allow. The general process of a one-step method is presented in Figure 10 and entails:

1. Dissolving all precursor materials in one solution to yield a perovskite ink
2. Coating the perovskite ink on a substrate
3. Removing the solvent and, thereby, crystallizing the perovskite

Although the perovskite can form directly by solvent removal alone, this method is usually complemented by a step where the perovskite films is annealed at a specific temperature to finalize the reaction and improve the crystal quality and film morphology.
Figure 10. Schematic illustration of perovskite synthesis using the one-step method. All precursors are dissolved in the same solution and the substrate coated with the solution. Once the solvent has been removed from the coated substrate the perovskite forms.

Two-step Methods

Synthesis of organic-inorganic perovskite materials by two-step methods was first described by Liang et al. in 1998 and successfully applied to PSCs by Burschka et al. in 2013. The number of parameters that can be controlled are increased in a two-step method, but so are the number of possible elements that can go wrong. While these methods are generally hailed for greater crystallization control they are far more sensitive to human error and environmental changes. On the other hand, a benefit of these methods is that they allow for a greater choice of deposition techniques. The typical process of a two-step method is presented in Figure 11 and entails:

1. Dissolving a precursor in a solution to yield a precursor ink
2. Coating the precursor ink on a substrate
3. Removing the solvent to obtain a precursor substrate
4. Applying the second precursor to the substrate to start the perovskite crystallization reaction
5. Annealing the substrate to finalize the perovskite crystallization

Figure 11. Schematic illustration of the perovskite synthesis using a two-step method. The substrate is typically first coated with the metal salt layer and dried. The second step involves reacting the metal salt film with a second salt needed for the perovskite formation. Finally, the perovskite film is annealed if required.
It should be noted that the process described above does not cover all the possible two-step methods. For example, the first precursor does not necessarily need to be introduced as an ink but can also be introduced by vaporization. The final step of annealing may also not be necessary, e.g. for methods employing vaporization of the second precursor, because the film is already annealed during the reaction.

Deposition Techniques

Spin-coating

Spin-coating is by far the most popular technique of depositing perovskite thin films from solution with homogenous thickness. It has earned its favor in the research community due to its reliability and simplicity of application. Therefore, it is not surprising that all high-efficiency PSCs employ spin-coating in one (or more) steps of the device preparation. In short, spin-coating involves the application of a solution onto a substrate followed by spinning the substrate at a high rate, typically several thousand rounds-per-minute. The centrifugal force, arising from the rotating motion of the substrate, causes the solution to be spread outwards from the center of the substrate. The surface tension of the solvent holds the solution together while the centrifugal force pulls it apart. An air-flow inside the spin-coating chamber then partially dries the solution and resulting in an even thickness covering of a plasticized film on the substrate. The film is then fully dried either by further spinning or heating to leave only the solute behind. Spin-coating techniques can be split into the categories of static and dynamic, which refer to how the solution is applied to the substrate. Static spin-coating involves the dispersion of the solution while the substrate is not moving. Dynamic spin-coating then refers to a spinning substrate onto which the solution is dispersed, sometimes also called spin-casting.

Despite its ability to produce thin films of highly uniform thickness, spin-coating is not a good choice for upscaling of thin film manufacturing. To give an example, spin-coating is generally used with substrates with around 2x2 cm² size and it is not practical to coat substrates larger than 10x10 cm². During the application process most of the solution is flung aside and, unless specifically recycled, wasted. The rotating motion also results in a higher velocity of the substrate the further away it is from the center of rotation. This means that on the solution will experience a larger force on the edges of the substrate than in its center, which can result in a non-uniform layer thickness for large substrates. Thus, the larger the substrate is the higher the probability is of forming film defects.
Anti-solvent Crystallization of the Perovskite Film

Taking its inspiration from single-crystal growth methods, anti-solvent technique involves the addition of a specific solvent, in which the perovskite is poorly soluble, to the precursor solution. The addition of the anti-solvent into the precursor solution causes the perovskite to start crystallizing. This means that all the required chemical components of the perovskite material must be present in the same solution. Therefore, this technique is only used for one-step methods.

The anti-solvent preparation technique for PSC applications was first published by Jeon et al. in 2014, and at the time it resulted in a certified world record efficiency for PSCs. A perovskite precursor solution with a mixture of GBL and DMSO solvents was applied onto a mesoporous TiO₂ substrate for the spin-coating. During the spin-coating step, anti-solvent was injected onto the spinning substrate which causes the GBL:DMSO solvent to be pushed out from the perovskite precursor film. The result was a highly uniform precursor film which, upon annealing, formed a highly crystalline and uniform perovskite film. Subsequent world record efficiency PSCs have all employed the anti-solvent technique in the preparation process. Many perovskite anti-solvents are available and several of them have been reported for use with this technique. The most popular anti-solvents are toluene, chlorobenzene, dichloromethane and diethyl-ether. Employing this technique
usually results in rather high reproducibility of the obtained solar cells' performance. However, because it is usually combined with spin-coating, it is not an upscalable PSC manufacturing technique.

**Chemical Bath Dipping Deposition Method**

For a sequential perovskite deposition procedure of the perovskite, the most commonly employed one is to dip a solid Pb(II) salt precursor film into a chemical bath solution which contains the respective cations and anions. However, this technique sets some constraints on the chemicals used for the preparation process:

- The lead salt must be very soluble in a solvent to form the precursor film.
- The lead salt should not be soluble in the chemical bath.
- The resulting perovskite must not be soluble in the chemical bath.

There are a multitude of chemical combinations available and many have already been explored. In the techniques most simple form, as presented by Burschka et al., a solid film of PbI₂ can be dipped into a solution of methylammonium iodide (MAI) in isopropanol (IPA) for the MAPbI₃ perovskite to crystallize. PbI₂ is insoluble while MAI dissolves easily in IPA. The MAPbI₃ perovskite will, however, dissolve in IPA but the time it takes is long with respect to the perovskite reaction time.

**Other Perovskite Deposition Techniques**

Many of the available large-area perovskite deposition techniques use spray-coating, blade-coating or evaporation, in at least one of the perovskite preparation steps. While they are not the focus point of this thesis, these techniques deserve to be mentioned due to their role in industrial production of PSC modules. The major challenge with large-area manufacture of thin film solar cells is that the probability of film defects increases with the solar cell size. Laboratory scale PSCs are generally prepared and measured with small photoactive areas of less than 0.2 cm², but 1 cm² area solar cells may give a better indication of the device performance at larger scale than the small cells. On that end, PSCs have reached a PCE 20% on a 1 cm² scale, despite the use of spin-coating, and this result shows that the perovskite material can also perform well on a larger scale.

Co-evaporation of MAI and PbCl₂ was the first large-scale technique to be applied to the synthesis of perovskite films for solar cell applications. This method does not require solvents for the precursor chemicals but relies on direct evaporation of the individual precursors. The materials must be kept in separate crucibles maintained at different temperatures due to the inherently different boiling points of the materials. As such, co-evaporation does not directly fit the categorization of one- or two-step methods described above. At the time of publication this technique yielded a world record perovskite PCE
of 15.4% for small-area solar cells. The perovskite can also be formed sequentially by exposing the metal salt film to vaporized ionic salt. The metal salt film can be deposited on the substrate with any deposition technique and the ionic salt is vaporized and the film is exposed to it, which initiates the perovskite crystallization.

Blade- and spray-coating techniques both require the precursors to be in solution, therefore they can be employed by both one- or two-step methods. Slot-die coating has been used to manufacture MAPbI$_3$ solar cells and it is a technique that presents a practical way for solution based large-scale manufacture of perovskite solar cells. On 1 cm$^2$ area, this technique has yielded a PCE of 15%, and 10% on a large-area with 25 cm$^2$ PSC modules (17.6 cm$^2$ active area).

Characterization Techniques

Solar Cell Characterization

Current-voltage Characterization

To determine the PCE of a solar cell it is essential to measure its current-voltage ($i-V$) characteristics. This is done by shining light on the solar cell and measuring the current it generates as a function of bias voltages applied across its contacts. Typically, the current is converted to a current density ($J$) by accounting for the active area of the solar cell, thus resulting in a $J-V$ curve as shown in Figure 13a. With regard to the solar cells PCE, the most interesting part of the $J-V$ curve is in the quadrant in which the solar cell provides work. Electric power ($P$) is simply the current multiplied by the voltage and the $P-V$ curve is presented in Figure 13b. The point at which the solar cell yields the most power, $P_{\text{max}}$, also called the maximum power point (MPP), is highly relevant with regards to the operational power output of the device. The PCE of a solar cell, denoted with the Greek letter $\eta$, is the percentage ratio of the solar cells $P_{\text{max}}$ and the incident illumination power, $P_{\text{in}}$, so that:

$$\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{J_{\text{SC}} \cdot V_{\text{OC}} \cdot FF}{P_{\text{in}}}. \quad (2)$$

Although $\eta$ may be the most important value to determine for a solar cell, the other parameters are of large interest when it comes to describing the solar cells $J-V$ characteristics. The short-circuit current density ($J_{\text{SC}}$) is the current generated when no bias is applied, i.e. at short-circuit condition (SC). The open-circuit voltage ($V_{\text{OC}}$) is the maximum voltage that the solar cell can generate and is the voltage at which no net current flows in the circuit, i.e. at open-circuit conditions (OC). The fill factor ($FF$) of a solar cell is the ratio of the solar cells $P_{\text{max}}$ and its ideal power output, which is the product of its $J_{\text{SC}}$ and
$V_{OC}$. The $J_{SC}$, $V_{OC}$ and $FF$, can be used to analyze the quality of the solar cell. For example, the $J_{SC}$ of the device is strongly dependent on the absorptance and the $E_g$ of the photoabsorber, the $FF$ can indicate whether the solar cell has charge-carrier collection, or transfer, problems and recombination effects can be observed by the general shape of the $J-V$ curve as well as by a lowered $V_{OC}$.

![Figure 13](image)

*Figure 13.* a) $J-V$ characteristics of a typical MAPbI$_3$ perovskite solar cell under 1 sun illumination intensity (AM1.5G spectrum). b) Power curve of the same solar cell determined from the $J-V$ characteristics.

When measuring the $J-V$ characteristics of PSCs one should be aware that the choice of the $J-V$ scan parameters can affect the results. A phenomenon known as hysteresis can present itself in the $J-V$ scans which will result in anomalous $J-V$ characteristics and affects the calculated PCE from the curve. The PCE hysteresis is a term which is generally used when the choice of the $J-V$ scan parameters changes the calculated performance of the device. For example, a $J-V$ scan of a single PSC from OC to SC can yield a different $FF$ and $V_{OC}$ than a $J-V$ scan of the same PSC from SC to OC, as shown in Figure 14a-b. Different $J-V$ curves of the same PSC can also be obtained by changing the $J-V$ scan speed, as shown in Figure 14c. Although researchers were aware of it, the issue of hysteresis was not thoroughly addressed until 2014. Several ideas concerning the origin of the hysteresis in PSCs have been proposed, such as ferroelectricity of the perovskite material, slow filling and emptying of trap states, ionic-movement, and unbalanced charge-extraction, but consensus seems to have been reached on the last two being the major effects. If those issues are successfully addressed the hysteresis appears to be minimal. This is the case with most inverted PSCs, where charge-extraction is well balanced, and in PSCs with proper ionic management.

Because of the hysteresis effect, a discussion has evolved on how the PCE of a PSC should be effectively measured. To not overestimate the PCE, the $J-V$ curve should be measured slowly, at most at the scan speed of 10 mV/s, and in both directions without intentional bias charging, which could temporarily charge the solar cell, prior to the scan. However, individual $J-V$ curves might not be the best indicator of a PSCs working performance because the PCE of
the device may change over time. To deal with that issue, it has been proposed to use either the stabilized power output (SPO) or MPP tracking. In SPO, the \( J-V \) curve of the PSC is measured to find the \( P_{\text{max}} \) of the device. The solar cell is then kept at the voltage of \( P_{\text{max}} \) and the current output of the device is followed as a function of time to evaluate the PCE of the device. The benefit of this method is the simplicity of the measurement but because the solar cell is effectively kept at a single voltage. The device may, however, change its properties with time and the MPP voltage may also change during the SPO measurement. To better evaluate the real working performance of the solar cell it may be necessary to employ MPP tracking. MPP tracking functions in a similar way except that at specific time intervals the \( P_{\text{max}} \) of the device is reevaluated and the PCE of the PSC is calculated from the \( P_{\text{max}}/P_{\text{in}} \) ratio as opposed to just its current response.

Figure 14. \( J-V \) characteristics of perovskite solar cells with: a) moderately low hysteresis, b) large hysteresis, and c) the effect of the bias scan speed on the \( J-V \) curve. The curve obtained by averaging the OC to SC and SC to OC scans is depicted by a dashed line in a) and b).

At the PSC laboratory in Uppsala University, the \( J-V \) scans are carried out using a Keithley 2400 Sourcemeter and the illumination source is a Newport solar simulator with a 300 W Xenon arc lamp, which can generate high intensity light with a spectral distribution resembling the AM1.5G spectrum. A value of 1000 W/m\(^2\) illumination intensity, also called 1 sun, is used as a standardized value for testing solar cells. All our PSCs have an area between 0.2-0.3 cm\(^2\) but a shadow mask is employed to define the active illumination area of the device. The areas of the solar cell and the shadow mask can vary, but a rule of thumb is that the shadow mask should always be smaller than the area of the solar cell to avoid measurement errors. In most measurements of PSCs at Uppsala University we have used a round shadow mask with 4 mm radius, corresponding to an area of 0.126 cm\(^2\), and \( J-V \) scan speeds of either 10 mV/s or 50 mV/s.
Incident Photon-to-Current Efficiency

Another general characterization method for solar cells is the so-called incident photon-to-current efficiency (IPCE), also known as external quantum efficiency. In an IPCE measurement, a solar cell is irradiated with monochromatic light and its current output at that specific wavelength monitored. Knowing the number of photons that strike the solar cell each second, i.e. the incident photon flux, one can estimate the solar cells IPCE at that wavelength using the measured short-circuit current with the following equation:

\[
IPCE(\lambda) = \frac{J_{sc}(\lambda)}{e \cdot \phi(\lambda)} = \frac{J_{sc}(\lambda)}{e \cdot P_{in}(\lambda)} \cdot \frac{hc}{\lambda} = 1240 \frac{J_{sc}(\lambda)}{\lambda \cdot P_{in}(\lambda)},
\]

where \(e\) is the elementary electron charge, \(\phi\) is the photon flux, \(h\) is the Planck constant, \(c\) is the speed of light and \(\lambda\) is the wavelength of the light. The IPCE spectrum for a given solar cell is therefore highly dependent on the optical properties of the photoabsorbing material and the other layers in the solar cell. An IPCE spectrum of a MAPbI₃ solar cell is presented in Figure 15. At around 800 nm the solar cell starts producing current and this is consistent with the expected 1.55 eV \(E_g\) of the MAPbI₃ perovskite. All photons of higher energy than the \(E_g\) can be absorbed by the perovskite material but due to the optical properties of the solar cell layers, along with thermodynamic losses, the IPCE spectrum is not completely square shaped. The most obvious example of how the other layers affect the IPCE is the cut-off at approximately 350 nm. This is caused by absorption of a TiO₂ layer, which starts at around 400 nm, in this device and by the glass substrate it was deposited on. This cut-off does not pose a large issue for the solar cells performance under illumination from the sun because there are few photons below 400 nm in the solar spectrum. The downward slope of the spectrum from 450 – 750 nm is slightly more concerning and is indicative charge-collection problems at the back contact or back-reflection problems. Longer wavelengths, compared to shorter, are typically absorbed deeper in the material due to a lower absorption coefficient of the material. Apart from improving the back-contact charge collection, increasing the reflective properties of the back contact can help with general the absorption of the longer wavelengths in the bulk material.

The expected \(J_{sc}\) of the device can be calculated by integration of the solar cells IPCE and the AM1.5G solar spectral irradiance \((I_s)\) using the following equation:

\[
J_{sc} = \int e \cdot IPCE(\lambda) \cdot I_s(\lambda) \cdot d\lambda.
\]
Under most circumstances the $J_{SC}$ value obtained from an IPCE measurement should match well with the same value obtained from a $J-V$ measurement employing a light source with an AM1.5G spectrum. However, some discrepancies between the $J_{SC}$ obtained from IPCE and $J-V$ can surface that could, for example, be due to a non-linear current response of the solar cell with light intensity. This is because the monochromatic irradiance of the IPCE instrument is generally only a fraction of what one would receive from 1 sun illumination. To correct for this, it is possible to use a white-light bias which effectively irradiates the solar cell with 1 sun illumination intensity. Then, a modulated monochromatic light source is used to gauge the solar cells response to each wavelength.

![IPCE spectrum of a MAPbI$_3$ device. The IPCE onset at 800 nm is due to the absorption onset of the perovskite, and the decrease starting at 450 nm is because of absorption of the TiO$_2$ and glass. The dip at 650 nm is presumably caused by interference effects.](image)

**Figure 15.** IPCE spectrum of a MAPbI$_3$ device. The IPCE onset at 800 nm is due to the absorption onset of the perovskite, and the decrease starting at 450 nm is because of absorption of the TiO$_2$ and glass. The dip at 650 nm is presumably caused by interference effects.

### Material Characterization

**Photoconductivity**

When semiconductors, such as the lead halide perovskites, absorb light an excitation of their VB electrons takes place. The excited $e^-$ can relax through various pathways, but if exposed to continuous illumination the semiconductor will develop a population of excited $e^-$ in the CB. The excited $e^-$, whether free or bound as $e^- - h^+$ pairs, act as charge carriers in the semiconductor material and result in the materials increased capability of conducting charges.$^{110}$
As the illumination intensity is increased so is the semiconductors conductivity (\(\sigma\)) due to more charge carriers in the material. This process is called photodoping and the \(\sigma\) of a photodoped material is called photoconductivity.

The \(\sigma\) of a material is most reliably measured by use of a four-point probe system. Four-point probe setups consist of four equally spaced needle probes in a row that contact the material and while current is flowing between the two outer probes a voltage drop is measured between the two middle probes. However, if the material is extremely resistive many four-point probe systems fail at accurate measurements because the voltmeter in the system must be considerably more resistive than the sample to avoid the current from flowing through it. Another way to measure \(\sigma\) is by contacting the material to two equivalent and parallel conducting plate electrodes measuring the resistance, see Figure 16a. If the contacts between the plates and the material are ohmic (i.e. no contact resistance), and if the length of the material, \(l\), and area of the plates, \(A\), are known, the conductivity can be calculated by:

\[
\sigma = \frac{l}{A \cdot R},
\]

where \(R\) is the measured resistance between the plates. However, the contacts between the electrodes and the sample are seldom ohmic. The measured parallel plate resistance can then instead be described as a combination of the material resistance, \(R_m\), and the contact resistance, \(R_c\). Assuming \(R_c\) remains constant for the same material interface, \(R_m\) can be evaluated by sequential parallel plate measurements using several different distances between the plates. In the equations below, \(R_m\) is defined as the material resistance in the shortest channel and longer channels can be scaled in terms of \(x \cdot R_m\), so that:

\[
R_{\text{short}} = 2R_c + R_m, \quad (6)
\]
\[
R_{\text{long}} = 2R_c + x \cdot R_m, \quad (7)
\]
\[
R_m = \frac{R_{\text{long}} - R_{\text{short}}}{x - 1}, \quad (8)
\]

where \(x\) is a factor describing the relative difference between the shortest parallel plate distance and a longer parallel plate distance. \(R_{\text{short}}\) is the resistance measured over the shortest distance, and \(R_{\text{long}}\) is the resistance measured over longer sample distance. By depositing several metal contacts, with known dimensions, onto a semiconductor film it is possible to assume the parallel plate resistor architecture, but only if the distance between the contacts is orders of magnitude larger than the thickness of the film. Although parasitic currents cannot be avoided, their effects can be minimized through such an architecture. As can be seen from Figure 16b, the measured total resistance for a thin
film of MAPbI$_3$ (~500 nm thick) using lateral contacting follows a linear response with the distance between the electrodes. This suggests that the lateral contact architecture is an acceptable approximation of parallel plate resistors.

**Figure 16.** a) Schematic image of the lateral contact architecture proposed for measuring conductivity of very resistive thin films of MAPbI$_3$. b) The total measured resistance as a function of the distance between neighboring gold electrodes.

**Absorption Spectroscopy**

Light can interact with matter through absorption, transmission, reflection, and scattering. The absorption properties of a semiconductor have a large impact on the materials functionality in a solar cell and the spectral regions where the solar cell will harvest light are of general interest. The strongest irradiance, and largest photon flux, of the solar spectrum are in and around the visible spectral range. Absorption measurements in the ultra violet, visible and near infrared spectral regions (UV-Vis-NIR, 200-2000 nm), therefore, yield information on how the solar cell interacts sunlight. A classical UV-Vis-NIR spectrometer consists of one or more light sources to cover the spectral regions to be measured, monochromators to select the wavelength to be measured, a sample chamber, and a photodiode detector.

For solid materials, such as parts of or a complete solar cell, it is most appropriate to carry out transmittance and reflectance measurements to account for the full optical properties of the films. In a transmittance ($T_\lambda$) measurement the amount of light passing through the sample is measured and in a reflectance ($R_\lambda$) measurement the amount of light reflected from the sample is measured. It is important to collect light from all angles for an accurate measurement, because the absorptance ($A_\lambda$) of a sample is in principle not measured directly but calculated from the $T_\lambda$ and $R_\lambda$ of the sample. Light reflected, or transmitted, at the same angle as the angle of the incident light to the sample is referred to as being specular. However, a portion of the incident light can be scattered in all directions by the sample or reflected at an angle unequal to the angle between the incident light and sample. This light is then referred to as being diffuse and, if it is not detected, will be wrongly categorized as being absorbed by the material. The key part of the spectrometer that makes it possible to collect all the light interacting with the sample is called an integrating sphere. An integrating sphere is, essentially, a sphere where the inside has...
been coated with a highly scattering material. The sphere also has openings for the probing light, the detector, and the sample (depending on the measurement to be done).

As briefly mentioned above, the $A_\lambda$ of a material can be calculated by measuring first all the light that is transmitted through the material and second all the light that is reflected by the material. Together with the $A_\lambda$ of the material, these factors should account for all the possible light interaction scenarios and therefore the $A_\lambda$ of the material/film can be calculated by:

$$A_\lambda = 1 - T_\lambda - R_\lambda,$$  \hspace{1cm} \text{(9)}

where:

$$T_\lambda = T_{\lambda,\text{specular}} + T_{\lambda,\text{diffuse}},$$  \hspace{1cm} \text{(10)}

and

$$R_\lambda = R_{\lambda,\text{specular}} + R_{\lambda,\text{diffuse}}.$$  \hspace{1cm} \text{(11)}

By measuring a semiconductor's $A_\lambda$ spectrum it is possible to determine the optical $E_g$ of the material, i.e. the lowest amount of energy required for the material to absorb a photon and excite an electron from the VB to the CB.

**Photoluminescence Spectroscopy**

As described above, when a photon is absorbed, by a semiconducting material, an $e^-$ is excited from the material's VB to the CB. Unless the charge is extracted through a circuit the excited photoabsorber has two possible mechanisms for relaxation to its ground state, non-radiative or radiative. Radiative relaxation entails that the material emits a photon of an energy corresponding to its $E_g$. A strong photoluminescence from a photoabsorber is appealing because it indicates that there are few non-radiative recombination pathways in the material, such as surface defects, and therefore hints towards good material quality. Using a similar equipment as in absorption spectroscopy, the photoluminescence of a material can be monitored. Typically, the sample is illuminated with monochromatic light of higher energy than the expected emission and by using a second monochromator perpendicular to the incident illumination the emission spectrum of the sample can be collected.

**Fourier Transform Infrared Spectroscopy**

Fourier transform spectroscopies differentiate themselves from conventional spectroscopies by how the spectrum is collected. In Fourier transform infrared spectroscopy (FTIR), the sample is generally illuminated by a collimated broadband light source and a specific mirror configuration, called the Michelson interferometer, measures a so-called interferogram. Spectral
information of the sample can then be extracted from the interferogram by using a Fourier transform. In FTIR it is common to use a sampling technique called attenuated total reflectance (ATR) for measuring solid thin films or liquids. In the technique, the infrared light source passes through an ATR crystal which is in direct contact with the sample. The light is reflected numerous times inside the ATR crystal and in the sample. ATR generally yields fast measurements with good signal-to-noise ratio. The main benefit of this sampling technique is that any material can be measured without special sample preparation, because it can simply be placed on top of the ATR crystal and measured. However, due to optical limitations of the ATR crystals one is limited to a certain spectral range at which the crystal is translucent. For a ZnSe crystal this range is in wavenumber range 20000 – 650 cm\(^{-1}\), which corresponds to wavelengths of 500 – 15000 nm.

In general, the energy of infrared light corresponds to the vibrational energies of chemical bonds. Therefore, FTIR is to a large extent used to confirm the presence of specific chemical bonds and functional groups in the sample. For perovskite materials this can be particularly useful for, among others, detecting residual solvents. The most popular solvents, DMF and DMSO, contain C=O and S=O bonds which absorb strongly around 1700 cm\(^{-1}\) and 1100 cm\(^{-1}\), respectively. Pure perovskite materials generally do not contain any C=O or S=O bonds, and their presence in the FTIR spectra is therefore a strong indication of residual DMF or DMSO in the material.

**X-ray Diffraction**

The crystallographic properties, such as the crystal structure and lattice size, of materials are most readily studied by X-ray diffraction (XRD). The technique involves irradiating the sample with X-rays and monitoring how the X-rays are diffracted by the sample. For perovskite materials this is particularly useful to determine which crystal phase it has (cubic, tetragonal, etc.) and to evaluate the crystallinity of the material. Another benefit of this technique is that it is, in principle, possible to observe e.g. the progression of the perovskite formation, as well as its degradation. The perovskite precursors, particularly the lead compounds, have a rather distinct XRD pattern due to their crystallinity and are therefore, in most cases, easy to distinguish from the perovskite diffraction pattern. The presence of crystalline precursor compounds is a typical indication of an incomplete reaction, or degradation, of the perovskite.

**Scanning Electron Microscopy and Energy Dispersive Spectroscopy**

Electron microscopy is one of the most useful characterization technique for thin films as it allows direct observation of the material on a nanoscale. In Figure 17a a cross-section of a PSC imaged by SEM is presented and in Figure 17b an SEM topograph of a perovskite surface is presented. While predominantly used for imaging, scanning electron microscopy (SEM) is capable
of other extensive material characterizations made possible by a wide selection of detection systems in the microscope. The SEM setup functions so that a high-power electron beam is focused onto the sample and the interaction events between the electron beam and sample are monitored.

![Figure 17.](image)

One of the interaction events, when a primary electron (PE) from the electron emission source hits the sample, is that electrons from the samples atoms can get kicked out. These ejected electrons are called secondary electrons (SE). The SE detector is the most common for imaging because the SEs are generated in large numbers close to the surface of the material resulting in a high-resolution topographic image. The detector, however, is not capable of distinguishing the SE energies and the topographic contrast is therefore only based on the number of SEs detected, which results in a monochromatic image. Conventionally, white depicts many SEs where as black depicts few SEs. Another interaction event is the backscattering of PEs. Depending on the atomic mass of the sample atoms the PEs can be slingshot at different angles to a backscattering detector. This results in atomic mass contrast in the electron image. A third interaction event is an atoms emission of an X-ray upon generation of an
SE from the inner-shell of the atom and subsequent relaxation of the outer-shell electron to fill the hole. Therefore, it is possible to measure the elemental composition of the sample by means of energy dispersive spectroscopy (EDS), see *Figure 17c-d*, because the X-ray energy is dependent on the atoms electron shell energies.
Results

Photoconductivity of MAPbI$_3$

The charge-carrier generation properties of a new solar cell material, such as the lead-halide perovskite, are important to consider for future optimization of the solar cell. When Lee et al. published a record PCE of 10.9% in 2012 with a PSC based on mesoporous Al$_2$O$_3$, there was doubt as to whether the PSC was an electron injection based device. Previous publications had assumed that the perovskite acted as a TiO$_2$ sensitizer like dyes in the DSSCs, i.e. that the excited electron of the perovskite would need to be injected into the TiO$_2$ conduction band. Today, there is strong and convincing evidence that electron-injection from the perovskite to the TiO$_2$ nanoparticles is present, and furthermore, the record PCEs obtained in the past couple of years have always contained a thin layer of a mesoporous TiO$_2$ (mp-TiO$_2$). However, Lee et al. were the first to show that the perovskite material could function without a mp-TiO$_2$ nanoparticle network. This discovery would push the field towards different PSC architectures such as the inverted and the thin film planar PSC. The full force of the OPV field entering the PSC field has resulted in inverted PSCs with close to 20% PCE.

In Paper I, we probed the presence and analyzed the effect of the electron-injection by measuring the $\sigma$ of a perovskite film deposited on either TiO$_2$, Al$_2$O$_3$, or ZrO$_2$. Assuming no perovskite material differences, a change in the measured $\sigma$ in the presence and absence of TiO$_2$ would hint towards the presence of electron-injection because the electron-injection process is only possible when the perovskite is deposited on TiO$_2$. This is because the excited $e^-$ has a different mobility ($\mu$) in the TiO$_2$ CB than when it is in the perovskite CB. Additionally, the electron-injection process leads to the formation of two spatially separate charge-carriers, the $e^-$ in the TiO$_2$ CB and the $h^+$ left in the perovskite VB. Figure 18a depicts the photodoping process of the MAPbI$_3$ perovskite and Figure 18b shows the possible pathways for the charge-carriers to take in the sample.

As can be observed in Figure 19a-b, the results were somewhat different from what we initially expected. The difference in $\sigma$ for the perovskite films formed on the different metal oxides (MO$_x$) was too small to make strong conclusions regarding mobility differences and electron-injection. However, all samples presented an almost ideal square-root dependence of the $\sigma$ with illu-
mination intensity ($I_s$). A square-root dependence of $\sigma$ with $I_s$ is a strong indication for the presence of separate and free $e^-$ and $h^+$, of almost equal concentrations and mobilities. These results therefore clearly proved that an electron-acceptor was not needed to separate the photoinduced charges in the perovskite. Furthermore, if there are any excitons present they are either not participating in the conduction or simply in very low concentrations.

For any photoabsorber under thermal equilibrium, the charge-carrier generation rate ($G$) must equal the total charge-carrier recombination rate ($U$). If we assume that the generated charge-carriers recombine only via band-to-band recombinations (i.e. neglecting trap-assisted relaxations, thermal relaxations etc.) only two possible scenarios for recombination exist, monomolecular and bimolecular. A monomolecular recombination mechanism depends on the concentration of a single charge-carrier type, such as the exciton concentration ($\beta$), and a specific rate constant ($k$) while a bimolecular recombination mechanism depends on the concentration of two separate charge-carrier types, the electron concentration ($n$) and the hole concentration ($p$). The mono- and bimolecular charger-carrier generation rates can be written as:

$$G_{\text{mono}} = U_{\text{mono}} = k_{\text{mono}} \cdot \beta,$$

$$G_{\text{bi}} = U_{\text{bi}} = k_{\text{bi}} \cdot n \cdot p.$$ 

The $\sigma$ of a semiconductor is dependent on the concentration and $\mu$ of the respective charge-carriers so that:

Figure 18. a) The process of photodoping a MAPbI$_3$ perovskite material in presence of a TiO$_2$ nanoparticle (Gray sphere). By shining light on the photoabsorber, a population of excited $e^-$ in the conduction band of the perovskite (Red spheres), and holes in the valence band (Green spheres), is generated. The excited $e^-$ can then be injected into the TiO$_2$ nanoparticles due to favorable CB matching of the two materials. b) Possible charge-carrier pathways in the film. The perovskite CB $e^-$ has a possibility to be injected into the TiO$_2$ and travel to the contacts through the nanoparticle network as well as traveling within the photoabsorber itself. VB $e^-$ in the MAPbI$_3$ (Blue Spheres) can also contribute to the measured conductivity.
\[ \sigma_{\text{mono}} = e \beta \mu_p, \quad (14) \]

\[ \sigma_{\text{bi}} = e(n \mu_n + p \mu_p), \quad (15) \]

where \( e \) is the elementary charge and \( \mu_q, \mu_n, \mu_p \) are the mobilities of the exciton, electron and hole, respectively. In the case of free charge-carriers, the \( e^- \) and \( h^+ \) concentrations must be equal so that \( n = p \). If we now combine the equations above to see how the \( \sigma \) and \( G \) are related, we get:

\[ \sigma_{\text{mono}} = \frac{e \mu_p G_{\text{mono}}}{k_{\text{mono}}}, \quad (16) \]

\[ \sigma_{\text{bi}} = e(\mu_n + \mu_p) \sqrt{\frac{G_{\text{bi}}}{k_{\text{bi}}}}. \quad (17) \]

Because \( G \) is directly proportional to the incident \( I \), it follows that for a monomolecular recombination mechanism \( \sigma \) depends linearly on \( I \), whereas for a bimolecular recombination mechanism \( \sigma \) has a square-root dependence on \( I \). From the results in Figure 19b we could therefore conclude that, irrespective of the MOx scaffold, a bimolecular recombination was observed. We could also conclude that band-to-band recombination was dominating in the perovskite (and not trap-assisted). Furthermore, this indicated that the photoinduced charge-carriers consisted to a large majority of free \( e^- \) and \( h^+ \). This also lead to the conclusion that an electron-acceptor, such as the TiO2, is not necessary for the perovskite to form free charge-carriers.

A better explanation for the \( \sigma \) variations was found in the material quality differences of the perovskite film. The process of crystallizing the perovskite material can be incomplete and/or the formed perovskite crystals can have degraded, leaving behind crystallized domains of the lead halide precursor. Conveniently, crystallized PbI2 has a strong XRD peak at 2\( \theta \) of 12.6° originating from the (001) plane of its hexagonal crystal structure. MAPbI3 does not present any diffraction peaks close to that angle apart from the strong peak at 14.5° originating from the (002) and (110) plane of its tetragonal crystal structure. As can be observed from the XRD patterns in Figure 19c-d, these two peaks can easily be distinguished. The presence of a 12.6° peak in the XRD pattern of a lead iodide perovskite typically indicates domains of crystallized PbI2. Therefore, the crystallization progress and degradation of the perovskite can be followed by comparison of the intensity of the two diffraction peaks. The films formed by spin-coating MAPbI3 on TiO2 at 1500 rpm resulted in the lowest PbI2/MAPbI3 peak ratio and the same material formed with 6500 rpm resulted in the largest ratio. This can lead to two conclusions;
a) more perovskite material on the 1500 rpm sample or, b) the 1500 rpm perovskite film has fewer perovskite crystal defects. Using images from the SEM, the thickness of each film was accounted for when the $\sigma$-values, presented in Figure 19a-b, were calculated. Although PbI$_2$ is also a photoconductive semiconductor it is a very poor one and its contribution to the $\sigma$ can safely be neglected.\textsuperscript{115} This leads us towards concluding that fewer crystal defects in the perovskite yield larger photoconductivities. While it is not a groundbreaking discovery, these results explain why these samples exhibit very different $\sigma$. Furthermore, the same argument explains the difference in $\sigma$ for the perovskite on different MO$_x$ scaffolds.

![Graphs](image)

**Figure 19.** a) Measured conductivity ($\sigma$) of MAPbI$_3$ on TiO$_2$ as a function of illumination intensity ($I_s$), with the perovskite prepared using different spin-coating speeds. b) Measured $\sigma$ of MAPbI$_3$ on ZrO$_2$, TiO$_2$ and Al$_2$O$_3$ as a function of $I_s$, where the perovskite was prepared with a spin-coating speed of 3500 rpm. c-d) XRD of the respective films.

The observation of a dominating band-to-band recombination in the perovskite can explain why the PSCs show a good performance even with simple preparation processes from solution. Our photoconductivity investigation was
performed at a time when the PSC efficiency development in the research field was very rapid and one reason for the increased PSC performance was a better control of the perovskite formation. The increased photoconductivity with better crystal quality, as observed in our measurements, agrees with the PSC performance development in the field and is probably related to lower recombination via other channels than the main band-to-band recombination. Therefore, to reach even higher efficiencies than the current record efficiencies, these other recombination reactions should probably be further reduced.116

Alternative Electrodes
Carbon Nanotube Electrodes
Classically, the contacts for PSCs consist of a transparent conductive oxide on the front-side and a metal on the back-side. Because the PSC layer architecture initially imitated the solid-state DSSC, the first PSCs used silver and gold layers as the back-contact.34,117 Inverted perovskite solar cells commonly use aluminum as a contact due to its maturity in the OPV field.111 The metal contacts are usually thermally evaporated onto the solar cell and, in the long run, they can oxidize. Recent studies have also shown that they can diffuse into the perovskite structure to cause material degradation.118

We received films of single-walled carbon-nanotubes (CNT), grown by gas phase chemical vapor deposition and collected onto a porous filter paper from the gas, from our collaborators at Aalto University, Finland.119 The benefit of these CNT films is that they can be deposited onto a substrate by press-transferring under normal atmospheric conditions and the material is also very stable.119 Press-transferring is a process which entails placing the CNT films onto the receiving substrate and pressing down from the filter paper side with, for example, the touch of a finger. Then, the filter paper is peeled off e.g. with tweezers, leaving behind the CNT electrode. Once the CNT film has been successfully placed onto a substrate it must undergo a process known as densification, to improve its conductive properties.119 The densification is performed by placing a small amount of an organic solvent onto the CNT film and allowing the solvent to evaporate.

In Paper II, we used these CNT films to develop a hybrid HSL-CE which replaced the conventional stacked HTM and gold layers of the PSC. A photograph of a perovskite solar cell with a CNT back-contact and a gold back-contact is presented in Figure 20. For the conventional devices the gold contact is deposited onto the Spiro-OMeTAD HTM layer. However, because the densification process requires the use of solvent it was difficult to deposit the CNT films directly onto the Spiro-OMeTAD layer without risk of affecting the quality of the HTM layer. Instead, we deposited the CNT films directly
onto the perovskite layer. Depositing a metal contact directly onto the perovskite film is not ideal since they do not exhibit hole or electron-selective properties. However, the CNT films are slightly hole-selective and, as seen from the $J-V$ results in Figure 22, yield a much better solar cell when in direct contact with the perovskite layer compared to the gold contact.

![Figure 20](image_url)

*Figure 20.* A photograph of two perovskite solar cells. Both have identical electron-selective and perovskite layers, the left one has a hybrid CNT:HTM electrode (black strip in the middle) along with some silver paste used for contacting. The right one has a spin-coated Spiro-OMeTAD layer all over the perovskite layer, resulting in rainbow-like reflections, and thermally evaporated gold contacts. On the top of the image is an out-of-date 1 Swedish Krona coin for size comparison.

Along, the CNT-film does not make a good enough contact with the perovskite layer to result in high PCE's. However, by using the Spiro-OMeTAD HTM solution as the CNT densification medium we were able to improve the contact. This resulted in a composite CNT:HTM material which acts as a hybrid HSL-CE. SEM cross-section images of the solar cells can be observed in Figure 21a-b and, as they show, the quality of the perovskite layer is the same for both the CNT:HTM and the HTM/Au samples.

![Figure 21](image_url)

*Figure 21.* a) SEM cross-section images of (FAPbI$_3$)$_{0.83}$(MAPbBr$_3$)$_{0.17}$ perovskite solar cells on mesoporous TiO$_2$ prepared with a composite CNT:HTM CE, b) and with a layered HTM and evaporated gold CE. During cross-section sample preparation, some of the CNTs are dragged out of it. Though it may appear the CNTs are inside all layers, they are simply lying on top of the cross-section.
As can be seen from both the $J$-$V$ scans in Figure 22a and the $J$-$V$ parameters in Table 3, the CNT:HTM composites performed almost as well as the HTM/Au but with slight losses in all parameters. The losses might be explained by a slightly larger series resistance of the CNT electrode (13 $\Omega \ \square^{-1}$) compared to the Au electrode (< 1 $\Omega \ \square^{-1}$) or by recombination losses caused by the non-uniform contact between the CNT and perovskite. The IPCE spectra in Figure 22b shows that the current output for the CNT:HTM composite at longer wavelength is lower in the longer wavelength region (500 – 800 nm). However, the $J$-$V$ scans show approximately the same $J_{SC}$ and in recent results the $J_{SC}$ is slightly higher for the CNT:HTM solar cell than for the layered HTM/Au solar cell. In the IPCE measurement the light intensity is somewhat lower. Furthermore, the red light, above 500 nm, is absorbed rather uniformly in the perovskite film, as opposed to blue light which is absorbed closer to the window (FTO/TiO$_2$) layer. The difference of the IPCE spectra might therefore be explained by the absence of a reflective layer as well by charge-collection issues at the perovskite/CNT:HTM interface at low light intensities.

![Figure 22. a) $J$-$V$ scans of the PSCs with different HSLs and back-contacts. The solar cells were scanned in both direction with a speed of 10 mV/s to account for hysteresis effects. b) IPCE spectra of the same devices.](image)

The results from this study presented a world record efficiency for any type of solar cell with a carbon-based electrode at the time of publication. The films used in this Paper II had a sheet resistance of around 13 $\Omega \ \square^{-1}$. Furthermore, later studies showed that the CNT:HTM based PSCs have greater stability than the HTM/Au devices due to the diffusion of Au into the perovskite layer. As such one can claim that the CNT:HTM PSCs have the possibility of outperforming the HTM/Au based devices when the issue with the perovskite/CNT interface is resolved.
Table 3. Averaged J-V parameters from the scans in Figure 22. \( V_{OC}, J_{SC}, FF \) and \( \eta_{AVE} \) are the value obtained by averaging the OC-SC and SC-OC scans. \( \eta_{B,R} \) is the value obtained from the solar cell from OC-SC.

<table>
<thead>
<tr>
<th></th>
<th>( V_{OC} ) (V)</th>
<th>( J_{SC} ) (mA/cm²)</th>
<th>( FF )</th>
<th>( \eta_{AVE} ) (%)</th>
<th>( \eta_{B,R} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT:HTM</td>
<td>1.10</td>
<td>20.3</td>
<td>0.61</td>
<td>13.6</td>
<td>15.5</td>
</tr>
<tr>
<td>HTM/Au</td>
<td>1.14</td>
<td>22.3</td>
<td>0.70</td>
<td>17.7</td>
<td>18.8</td>
</tr>
<tr>
<td>CNT</td>
<td>0.97</td>
<td>20.3</td>
<td>0.46</td>
<td>9.1</td>
<td>11.0</td>
</tr>
<tr>
<td>Au</td>
<td>0.82</td>
<td>11.4</td>
<td>0.53</td>
<td>5.0</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Transparent Electrodes

One requirement for the use of PSCs as a top-cell in a tandem solar cell is that its window layers (i.e. the ESL, HSL and contacts) should be as transparent as possible in the spectral regions where the bottom-cell absorbs light. This disqualifies most metal contacts. Semitransparent metal contacts can be manufactured by decreasing the thickness of the metal layer which, in turn, results in a decrease of the layer's conductivity. A low conductivity contact can increase the series resistance in the solar cell and hence result in a FF and PCE loss. Furthermore, the deposition of a metal contact is typically a thermal evaporation process in vacuum and making ultrathin homogenous metal layer on a slightly rough surface can be difficult due to shading problems. The use of organic selective layers, such as Spiro-OMeTAD as an HTM, should also be avoided due to the absorption of organic compounds in the near-IR spectral region. Also, as we pointed out earlier, organic selective layers may present a stability issue in the PSC. In Paper III, we manufactured a PSC which would fill the abovementioned criteria. The idea was to sandwich the perovskite layer between two MOx layers, with one being hole-selective and the other electron-selective. Many MOx layers have been shown to be compatible and efficient in PSCs, the most common being TiO2, ZnO, SnO2, NiOx and MoOx.\textsuperscript{56,105,121,122} The first three are electron-selective while the last two are hole-selective. Depositing the perovskite onto one of the MOx layers is quite identical to the normal deposition procedures and usually not problematic. Depositing a thin MOx layer directly onto the perovskite surface is the main challenge and the compatibility of the deposition method with the perovskite is key to not degrade the perovskite.

Out of the several thin film deposition methods available, sputtering, evaporation and atomic-layer deposition (ALD), we chose ALD because it is generally considered to be the least abrasive method. Furthermore, it has the potential to yield conformal and uniform layers on a substrate, even if the surface is quite rough on the nano/microscale. Several studies related to the ALD deposition of a MOx on the perovskite have already been reported and showed that the MAPbI\textsubscript{3} perovskite completely degraded in the deposition process.
when H$_2$O, O$_3$ or O$_2$ plasma was used as the O source for the MO$_x$. Therefore, we studied ALD deposition on the mixed-ion (FAPbI$_3$)$_{0.83}$(MAPbBr$_3$)$_{0.17}$ perovskite. The mixed-ion perovskite offers better thermal and chemical stability, especially with respect to humidity, due to the inclusion of Br$^-$ and of FA$^+$ ions in the perovskite. As shown in Figure 23a, the mixed-ion perovskite layer was not visually affected by exposure to H$_2$O in the ALD chamber. Our XRD results and SEM images, which showed a sharp material interface, revealed no damage to the bulk crystal, meaning that if an interfacial layer, caused by exposure to H$_2$O, was present it should have at most a thickness of a few nanometers. Therefore, we chose water as an O source in the ALD process.

Because of our ALD precursor chemical inventory and because of the low number of MO$_x$ HSLs compatible with the perovskite, we chose to use NiO$_x$ as a bottom layer for our perovskite device. Thin layers of NiO$_x$ have already been shown to perform well as the HSL in a perovskite solar cell. The NiO$_x$ layer in our case was prepared by spin-coating a sol-gel onto FTO glass substrate and the perovskite was then deposited onto the NiO$_x$. In CIGS solar cells, a combination of ZnO and ZnO:Al, deposited by ALD and sputtering, is typically used as the ESL and front contact. Conveniently, both layers, and the combination thereof, have been shown to result in highly efficient and moisture resistant PSCs. As a result, it was an obvious choice to test a similar deposition of ZnO on the perovskite. Furthermore, because ESL layers of SnO$_x$ prepared by ALD had been shown to be more compatible with the mixed-ion perovskite than TiO$_2$ in a thin film planar PSC configuration, we chose SnO$_x$ as our second ESL for comparison.

In ALD, the metal is typically introduced as an organometal precursor molecule which then reacts with the O source, in our case water, to form the MO$_x$ layer. This happens sequentially by self-limiting half-reactions, meaning that the O-source and the organometal precursor are never in the ALD chamber at the same time. Initially, the O source is allowed to react with the substrate to be deposited until a fully OH-terminated surface has been formed. The excess O source is then pumped out and the organometal precursor introduced to the OH-terminated surface, which it will react with to form a metal-O bond. Once that reaction is complete, the excess organometal precursor is pumped out and the cycle begins anew with the O source. These cycles are repeated until the desired film thickness is achieved.

The interaction of the organo-metal precursors with the substrate can vary greatly depending on both the organic part and the metal of the precursor. In our case, we used diethyl-zinc (DEZ) as the Zn source, which is commonly used for deposition of ZnO on CIGS solar cells, and tetrakisdimethylamino-tin (TDMASn) as the Sn source. However, the question was whether the
chemical interaction between the perovskite surface and the organometal pre-
cursors allows for a similar growth, or whether other secondary reactions
would impede with the MOx film growth.

The ALD of ZnO turned out to destroy the perovskite layer whereas the
deposition of SnOx had visually no effect and there was no change observed
in the XRD either. The photograph in Figure 23a shows the films after the
ALD deposition of different materials. From these results one cannot conclude
whether it is the presence of Zn or the diethyl organic part which causes the
perovskite to degrade, but we could conclude that the Zn precursor is a lot
more detrimental to the perovskite than the Sn precursor. The SEM image in
Figure 23b shows a distinctive thin layer of SnOx on top of the perovskite
layer after the ALD deposition using the TDMASn precursor and H2O as an
O source.

Figure 23. a) Photograph of several mixed-ion perovskite films after exposure to H2O,
DEZ and TDMASn in the ALD reactor, or to the full procedure to form ZnO and
SnOx. b) SEM cross-section image of a perovskite film with a thin SnOx layer depos-
ited onto it by ALD. Here, the perovskite film was on a mp-TiO2 substrate because
this sample was used solely to study the chemical interaction of the perovskite and the
ALD process.

Because of our success with depositing the SnOx layer on the perovskite, we
made solar cells based on FTO/NiOx/Perovskite/SnOx configuration and con-
tacted the device in three different ways: a) by direct evaporation of gold con-
tacts for opaque devices, b) by sputtering a ZnO:Al layer followed by evapo-
ration of gold or, c) by sputtering ZnO:Al followed by evaporation of alumi-
num metal grids for the semitransparent devices. The reference device con-
sisted of a spin-coated PCBM layer followed by evaporation of a silver
contact. Our best device based on FTO/NiOx/Perovskite/SnOx/Au gave a PCE
of around 4% with 50 ALD cycles of the SnOx deposition, which translates
roughly to a 5-10 nm thick SnOx layer. As Figure 24a and Table 4 show, in-
creasing the SnOx layer thickness results in a decrease of the JSC. Furthermore,
all the J-V curves present an S-shape, which hints towards a formation of a
resistive layer or an energy barrier in the solar cell. Interestingly, all the
opaque SnOx/Au solar cells presented a charging effect, see Figure 24b. By
consecutive measurements from OC to SC, the best solar cell efficiency could be improved from 3.4% up to 7.8% mainly because of an increase of the $V_{OC}$ from 460 mV to 720 mV. Once the device had been charged to its maximum PCE a single scan in the opposite direction (SC to OC) would result in a substantial decrease of the $V_{oc}$. This process seemed almost completely reversible so by charging the solar cell again the $V_{OC}$ could once again be increased and by forward scanning the $V_{OC}$ was decreased. The $J-V$ parameters for this test are presented in Table 5.

![Figure 24](image) a) $J-V$ results for typical FTO/NiO$_x$/Perovskite/SnO$_x$/Au devices with different thicknesses of SnO$_x$ layers as well as a PCBM/Ag reference device. 200 cycles correspond roughly to a thickness of 25 nm. The $S$-shape of the curves hints towards the formation of a resistive layer or an energy barrier in the solar cell. b) $J-V$ curves of a single 50 cycle SnO$_x$ device scanned several times from OC to SC, followed by a single scan from SC to OC.

Table 4. $J-V$ parameters from the curves presented in Figure 24a.

<table>
<thead>
<tr>
<th>ALD cycles</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.50</td>
<td>16.7</td>
<td>0.38</td>
<td>3.1</td>
</tr>
<tr>
<td>20</td>
<td>0.44</td>
<td>18.8</td>
<td>0.42</td>
<td>3.4</td>
</tr>
<tr>
<td>30</td>
<td>0.51</td>
<td>20.0</td>
<td>0.40</td>
<td>4.0</td>
</tr>
<tr>
<td>50</td>
<td>0.52</td>
<td>20.4</td>
<td>0.45</td>
<td>4.8</td>
</tr>
<tr>
<td>100</td>
<td>0.49</td>
<td>7.5</td>
<td>0.10</td>
<td>0.37</td>
</tr>
<tr>
<td>200</td>
<td>0.28</td>
<td>1.0</td>
<td>0.13</td>
<td>0.04</td>
</tr>
<tr>
<td>PCBM/Ag</td>
<td>0.90</td>
<td>17.1</td>
<td>0.68</td>
<td>10.5</td>
</tr>
</tbody>
</table>

XPS depth profile also showed that the interface between the perovskite and SnO$_x$ layer was somewhat halide rich and it indicated that the halides might be present to some extent in the SnO$_x$ layer close to the perovskite surface. Therefore, the diffusion of halides from the perovskite layer across this interface might help explaining the charging behavior of the solar cells. It is also possible that some metallic exchange between the Pb and the Sn occurs, i.e. that the Sn diffuses into the perovskite or vice versa. During the ALD it is also
possible that the perovskite surface was not perfectly OH-terminated and the organometal precursor could therefore have reacted with a halide termination instead.

Table 5. *J*-*V* parameters from the curves presented in Figure 24b. All the scans are consecutive with 1-6 from OC to SC, and 7 from SC to OC.

<table>
<thead>
<tr>
<th>Scan</th>
<th><em>V</em>&lt;sub&gt;OC&lt;/sub&gt; (V)</th>
<th><em>J</em>&lt;sub&gt;SC&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th><em>FF</em></th>
<th><em>η</em> (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.46</td>
<td>19.1</td>
<td>0.38</td>
<td>3.4</td>
</tr>
<tr>
<td>2</td>
<td>0.55</td>
<td>20.5</td>
<td>0.47</td>
<td>5.4</td>
</tr>
<tr>
<td>3</td>
<td>0.58</td>
<td>20.4</td>
<td>0.50</td>
<td>6.0</td>
</tr>
<tr>
<td>4</td>
<td>0.64</td>
<td>20.9</td>
<td>0.53</td>
<td>7.1</td>
</tr>
<tr>
<td>5</td>
<td>0.68</td>
<td>21.0</td>
<td>0.53</td>
<td>7.6</td>
</tr>
<tr>
<td>6</td>
<td>0.72</td>
<td>20.8</td>
<td>0.52</td>
<td>7.8</td>
</tr>
<tr>
<td>7 - SC</td>
<td>0.55</td>
<td>20.6</td>
<td>0.45</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Interestingly, the semitransparent devices based on sputtered ZnO:Al contacts presented a photovoltaic performance, albeit with a PCE below 1% as shown in Table 6, and the XRD results indicated that the ALD SnO<sub>x</sub> layer provides at least some protection to the perovskite surface from the abrasive sputtering process. To summarize, despite the discouraging PCEs of the solar cells, we were successful in depositing a thin layer of SnO<sub>x</sub> directly onto the perovskite surface without damaging the bulk perovskite. It is possible that other organo-Sn precursors might result in a more beneficial perovskite/SnO<sub>x</sub> interface and that further optimization of the perovskite/SnO<sub>x</sub> interface might yield higher PCEs, and lower hysteresis, in the future.

Table 6. Summary of *J*-*V* parameters of the PSCs made with 50 ALD cycle SnO<sub>x</sub> along with the PCBM/Ag reference devices. *Only a single cell of this type gave a photovoltaic performance.*

<table>
<thead>
<tr>
<th>ESL/CE</th>
<th><em>V</em>&lt;sub&gt;OC&lt;/sub&gt; (V)</th>
<th><em>J</em>&lt;sub&gt;SC&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th><em>FF</em></th>
<th><em>η</em> (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO&lt;sub&gt;x&lt;/sub&gt;/Au</td>
<td>0.49 ± 0.04</td>
<td>19.0 ± 1.6</td>
<td>0.43 ± 0.03</td>
<td>4.0 ± 0.6</td>
</tr>
<tr>
<td>SnO&lt;sub&gt;x&lt;/sub&gt;/ZnO:Al/Au*</td>
<td>0.50</td>
<td>0.9</td>
<td>0.26</td>
<td>0.1</td>
</tr>
<tr>
<td>SnO&lt;sub&gt;x&lt;/sub&gt;/ZnO:Al/Metal grid <em>HSL side illumination</em></td>
<td>0.68 ± 0.06</td>
<td>4.8 ± 1.6</td>
<td>0.16 ± 0.03</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td>SnO&lt;sub&gt;x&lt;/sub&gt;/ZnO:Al/Metal grid <em>ESL side illumination</em></td>
<td>0.84 ± 0.09</td>
<td>3.0 ± 1.0</td>
<td>0.16 ± 0.03</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>PCBM/Ag</td>
<td>0.90 ± 0.01</td>
<td>16.6 ± 1.5</td>
<td>0.58 ± 0.08</td>
<td>8.6 ± 1.4</td>
</tr>
</tbody>
</table>
Sustainable Manufacturing

Ambient Processing of (FAPbI$_3$)$_{0.83}$(MAPbBr$_3$)$_{0.17}$ Perovskite

The most efficient PSCs to date are prepared under controlled and inert atmospheric conditions in a glovebox. Additionally, the solar cell studies reporting the use of an anti-solvent one-step method for mixed-ion perovskites have all been carried out in a glovebox. The anti-solvent procedure for MAPbI$_3$ works relatively well in ambient air, however, the same cannot be said for mixed-ion perovskites such as the (FAPbI$_3$)$_{0.83}$(MAPbBr$_3$)$_{0.17}$.

In Paper IV, we developed the anti-solvent procedure for preparing the (FAPbI$_3$)$_{0.83}$(MAPbBr$_3$)$_{0.17}$ mixed-ion perovskite in ambient air conditions. We noticed that the conventional procedure did not result in the desired precursor phase at room temperature in ambient air and annealing the film did not result in a high-quality perovskite film. By depositing the perovskite precursor solution onto warm (40-70°C) TiO$_2$ substrates we were able to obtain uniform and homogenous red precursor films, which after annealing yielded a high-quality perovskite material. We also discovered that the formation of the red precursor phase was crucial to the crystallization of the perovskite in ambient air. The manufacturing process of (FAPbI$_3$)$_{0.83}$(MAPbBr$_3$)$_{0.17}$ perovskite in ambient air is illustrated in Figure 25a. The only difference in our procedure compared with the conventional glovebox procedures is the substrate pre-heating step. A recent report shows that the red precursor phase is consistent with the formation of a 3D hexagonal polytype of the mixed-ion perovskite, which can form when the solvent is dried out and prior to the annealing of the perovskite.\textsuperscript{125}

Being able to crystallize the perovskite in ambient air brings about a considerable reduction in manufacturing cost, should an anti-solvent method such as this be industrialized, because the need for a controlled inert atmosphere is reduced. However, it should be noted that during the work we noticed that the procedure and the formation of this red phase was somewhat air humidity dependent. All the tests were done at a relative humidity of approximately 50% at 21 °C. At higher humidity it seemed more difficult to obtain the red phase with substrates colder than approximately 60-70°, and these substrates did not lead to successful perovskite crystallization.

It is quite apparent from the photos in Figure 25b, and especially from the $J$-$V$ results in Figure 26a-b and Table 7, that the most efficient solar cells were obtained by pre-heating the TiO$_2$ substrate at 50°C prior to the perovskite deposition. The champion solar cell obtained from this study resulted in an average PCE of 17.6%, with 18.8% when scanned slowly backwards from OC to SC and 16.4% when scanned forwards from SC to OC. These results may pave the way towards industrial perovskite manufacturing without an inert atmosphere, where only the humidity of the atmosphere must be maintained.
Figure 25. a) Schematic illustration of the mixed-ion perovskite deposition procedure performed in ambient atmosphere. b) Photographs of the perovskite films obtained with different substrate temperatures. Top row shows the pre-perovskite film obtained directly after spin-coating and the bottom row shows the corresponding perovskite film obtained after annealing at 100 °C.

Figure 26. a) Boxplot diagram showing the statistics of the PCEs obtained by heating the substrate at different temperatures prior to the perovskite deposition. b) $J$-$V$ curve of the champion solar cell obtained by heating the substrate at 50 °C prior to the perovskite deposition, along with an inset table of the $J$-$V$ parameters.
Table 7. Average J-V parameters of the champion solar cells obtained by depositing the perovskite solution onto a substrate of the respective temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>J_sc (mA cm^{-2})</th>
<th>V_oc (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>18.2</td>
<td>1.14</td>
<td>0.59</td>
<td>12.4</td>
</tr>
<tr>
<td>30</td>
<td>17.8</td>
<td>1.08</td>
<td>0.61</td>
<td>11.6</td>
</tr>
<tr>
<td>40</td>
<td>21.5</td>
<td>1.07</td>
<td>0.68</td>
<td>15.6</td>
</tr>
<tr>
<td>50</td>
<td>22.5</td>
<td>1.13</td>
<td>0.69</td>
<td>17.6</td>
</tr>
<tr>
<td>60</td>
<td>20.9</td>
<td>1.14</td>
<td>0.60</td>
<td>14.2</td>
</tr>
<tr>
<td>70</td>
<td>17.9</td>
<td>1.10</td>
<td>0.55</td>
<td>10.9</td>
</tr>
<tr>
<td>80</td>
<td>16.3</td>
<td>1.05</td>
<td>0.59</td>
<td>10.8</td>
</tr>
<tr>
<td>90</td>
<td>18.0</td>
<td>1.08</td>
<td>0.52</td>
<td>10.1</td>
</tr>
<tr>
<td>100</td>
<td>18.5</td>
<td>1.05</td>
<td>0.47</td>
<td>9.2</td>
</tr>
</tbody>
</table>

Water-based Preparation of Cs_yF_{1-y}Pb(I_{1-x}Br_x)_3

While the method described in the previous chapter presents the option to manufacture the mixed-ion perovskite solar cells in ambient air with the anti-solvent method it may not be industrially viable. The anti-solvent method inherently relies on spin-coating as the deposition method, and due to the use of hygroscopic organic solvents it is rather sensitive to ambient humidity. To address these issues, we developed a deposition method that did not utilize DMF or DMSO in Paper V. DMF presents a rather large health risk to humans due to its overall toxicity and DMSO due to its ability to permeate human skin, which thus allows other materials to be carried into the blood-stream. We also wanted to develop an ambient humidity independent procedure. These considerations lead us to review the prospect of using a two-step method for preparing the perovskite film. One-step methods generally make use of high-boiling point and hazardous organic solvents. In only one instance have MAPbI_3 films been successfully manufactured using low-boiling point and low-viscosity solvents, and that was done by concentrated methylammonium gas in acetonitrile, both of which are somewhat toxic. Procedures employing non-hazardous solvents for the chemical bath solution in two-step procedures are already well established, which makes the problem simpler because one only needs to consider the non-hazardous solvent application for the Pb(II) salt precursor film. Regretfully, lead halides are rather difficult to dissolve in most non-hazardous solvents, especially PbI_2. However, a plethora of different Pb(II) salts exist and luckily the use of a lead halide is not crucial for the formation of a perovskite material. In fact, efficient solar cells have been obtained using lead acetate, thiocyanate, nitrate and other salts. Most of these salts exhibit very high solubilities in water but the nitrate is of particular interest because it exhibits extremely poor solubility in all other non-hazardous solvents, which makes Pb(NO_3)_2 an excellent candidate for the chemical bath dipping technique described in the experimental section. As a
bonus, few solvents are less dependent on atmospheric humidity than water. Tsutomu Miyasaka's group in Japan, the same group that made the first lead halide PSC, published a paper in 2015 on a two-step deposition using a precursor film formed from a solution of Pb(NO$_3$)$_2$ in water.\textsuperscript{129} This film was then dipped into a solution of MAI in isopropanol (IPA) to form a MAPbI$_3$ perovskite. As discussed above, MAPbI$_3$ is perhaps not the perovskite material which will eventually be used in commercial solar cells due to its poor stability. MAPb$_{(1-x)Br_x}$I$_3$ PSCs, manufactured using a two-step method, have also been published before but, as mentioned in the introduction, these perovskites are susceptible to halide segregation.

We set out to develop a procedure for making a PSC in humid air but to do that we also wanted to use a perovskite material composition which could withstand some amount of humidity. The mixed Cs$_y$FA$_{1-x}$Pb$_{(1-x)Br_x}$I$_3$ perovskites were an attractive option due to their reported thermal stability and resilience to humidity.\textsuperscript{130} We introduced Cs$^+$ to the precursor solution as a nitrate and the resulting precursor film thus contained both Pb(NO$_3$)$_2$ and CsNO$_3$, neither of which are soluble in IPA. The two-step deposition procedure for the Cs$_y$FA$_{1-x}$Pb$_{(1-x)Br_x}$I$_3$ perovskite is depicted in Figure 27. The metal nitrate precursor film was dipped into a solution containing both FAI and FABr in IPA. In this bath the perovskite started to crystallize and after about 10 minutes it had formed completely. The perovskite film was then annealed at 100 °C to finalize the crystallization process.

![Figure 27. Schematic illustration for the perovskite deposition procedure based on dipping a precursor film, prepared from Pb(NO$_3$)$_2$ and CsNO$_3$ in water, into an organic halide salt bath.](image)

Because this was the first time a mixed organic-inorganic cation perovskite had been synthesized via a two-step method, we analyzed in detail whether introducing the cesium cation in this manner really resulted in its inclusion in the perovskite crystal structure. The material characterization in Figure 28a-b shows that this was indeed the case. By changing the amount of CsNO$_3$ added to the precursor solution, we were able to shift the $E_g$ of the obtained perovskite. We also observed a shift of the perovskite XRD peaks towards larger 2θ which is consistent with contraction of the crystal lattice upon introducing a smaller cation than FA$^+$, such as Cs$^+$. 

65
Figure 28. a) XRD of the lowest angle perovskite peaks for the Cs$_y$FA$_{1-y}$PbX$_3$ films synthesized using the water-based procedure. The shift of the peaks towards larger $2\theta$ is consistent with contraction of the perovskite unit cell due to introduction of Cs$^+$. b) UV-Vis spectra of the same films along with neat CsPbBr$_3$. Introduction of Cs$^+$ results in a larger $E_g$.

After a thorough optimization of the metal nitrate precursor solution concentration, the dipping bath concentration and the dipping bath duration, a solar cell with 13% PCE based on the composition of Cs$_{0.1}$FA$_{0.9}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ was obtained. The $J$-$V$ results for this record efficiency device, along with its MPP tracking, are presented in Figure 29a-b. The slow scans (10 mV/s) show that there is minimal hysteresis in the device but also that the device has a somewhat low shunt resistance. We expect that the low shunt resistance is the main limiting factor for the performance of this device. Perovskite solar cells made with a similar composition have yielded a PCE of 19% when using hazardous solvents.\textsuperscript{61,131} The low shunt resistance is most likely caused by an uneven perovskite film, see Figure 29c, which increases the probability of recombinations in the device.

In summary, we were able to synthesize a variety of Cs$_y$FA$_{1-y}$Pb(I$_{1-x}$Br$_x$)$_3$ perovskites by sequential deposition using only water and isopropanol as solvents. The best solar cells obtained with this method resulted in a 13% PCE which stabilized at 8.2% in an MPP measurement. While the performance of the obtained solar cells was somewhat limited by an uneven perovskite surface, it is expected that improvements of the film quality will result in efficiencies corresponding to the solar cells prepared using high-boiling point solvents.
Figure 29. a) J-V scans of the champion PSC obtained with the water-based synthesis procedure. The gradual development of the MPP is also depicted in the graph by a red dot. b) Results from the MPP tracking measurement of the same device. The PCE of the device appears to stabilize at ~8%. c) SEM image of the PSC cross-section.
Perovskite solar cells (PSCs) present a new technology for converting solar energy to electricity. Their rapid power conversion efficiency (PCE) development, from roughly 4% to over 22% in less than 10 years, has recently been the center of attention in the field of alternative solar cell research. The possibility of solution processing allows for a potential reduction in solar cell manufacturing costs once the technology has been properly established and upscaled. The ease of the band-gap \(E_g\) tunability for PSCs (~1.4 – 2.3 eV) makes them an excellent candidate for tandem solar cells, where the PCEs can surpass the 33.8% single-junction limit. Although the PSCs display promising PCEs, they have several drawbacks including the presence of lead, their long-term stability issues and hysteretic current-voltage characteristics. Recent reports have, however, shown that the latter two may be overcome and the use of lead in the solar cells remains an open discussion topic.

As **Paper I** discusses, the perovskite solar cell field has come rather far in understanding the photophysics of this new material. While first expected to be solely an electron-injection based solar cell absorber, our photoconductivity measurement results showed that the perovskite material is capable of charge separation without the presence of an electron acceptor. Furthermore, the results showed that the photoconductivity was not greatly affected by the defects in the material. This was consistent with other reports in the field, which hinted towards free electrons and holes being the majority charge-carrier in the material.

After this fundamental study, I focused my attention towards high PCE solar cells and new perovskite preparation procedures, rather than further delving further into the photophysics of the perovskite. In **Paper II** we explored the option of using a press-transferrable carbon-based electrode which resulted in a world record efficiency solar cell with a carbon electrode at the time of publishing. An efficiency of 15.5% was reached using a composite carbon-nanotube (CNT) film covered with a hole-transport material.

In **Paper III** we manufactured semitransparent PSCs for tandem solar cell applications. In collaboration with the CIGS group at Uppsala University, we successfully deposited thin films of SnO\(_x\) directly onto a mixed-ion perovskite surface using atomic-layer deposition without damaging the bulk perovskite. Regretfully, this did not result in highly PCE solar cells possibly because of chemical interaction between the SnO\(_x\) and the perovskite at the interface,
which presumably resulted in a formation of a resistive layer. However, this finding is a step towards the preparation of a large $E_g$ perovskite top-cells in a tandem structure.

The anti-solvent perovskite deposition method presents a technique which results in extremely uniform perovskite films of high quality and is, to date, the technique that results in the most efficient PSCs. However, as discussed in Paper IV, this procedure generally requires atmospheric control in the case of mixed-ion perovskites. We presented a procedure for the anti-solvent deposition of mixed-ion perovskite performed under ambient air conditions with 50% relative humidity. By depositing the perovskite solution on a warm substrate, we were able to obtain a very clear and homogenous red intermediate perovskite phase which resulted, in a later step, in perovskite films of high quality and gave a record PCE of 17.6%.

Water is detrimental for the formation and stability of the perovskite crystal. The synthesis of the lead halide perovskites, in the studies described above, generally requires the use of toxic high-boiling point solvents and some of which are also extremely hygroscopic. However, in Paper V we further developed a recent procedure where water and isopropanol were used as solvents for the synthesis of MAPbI$_3$. We synthesized the more stable Cs$_x$FA$_{1-x}$PbX$_3$ perovskites using the same non-toxic solvents. This was also the first reported procedure in which a mixed inorganic-organic cation perovskite was synthesized using a sequential deposition technique. With this procedure, a PSC with a PCE of 13.6% was obtained. It is expected that this procedure can be further improved to yield better performing devices. The limitation of the manufacturing method was a somewhat uneven perovskite film surface coverage, which resulted in a low shunt resistance and a loss in the open-circuit voltage. A more even perovskite film surface is expected to result in solar cells performing at a similar level as their toxic solvent-processed counterparts.
Acknowledgements

A two-page acknowledgement section will hardly be able to adequately describe the appreciation I have for my colleagues. Some of you I had a hard time placing correctly within a specific social group here below because you’ve been shifting around from group-to-group (you know who you are).

I’d like to begin this train of gratitude by acknowledging my main supervisor, Prof. Erik M. J. Johansson, who has always shown my work great patience and interest throughout the years and given me a lot of freedom in my research. Secondly, but not less so, I’d like to thank Dr. Kerttu Aitola (a.k.a The Ancient One, a.k.a Hávi, a.k.a Knower of 95% of all things) for your mentoring. In fact, you probably deserve a full page here. Thanks, for teaching me proper scientific writing and for always having my back. To Prof. Gerrit Boschloo, always approachable and enthusiastic about helping me. To Prof. Anders Hagfeldt, for showing me kindness and understanding, and for hosting me in EPFL. To Dr. Nick Vlachopolous for your contagious joy, not only of science, and for sharing your unfathomable scientific knowledge. I would also like to thank the people involved in proof-reading my thesis, apart from my supervisors, Malin Johansson, Jesper Jacobsson and Adam Hultqvist. The thesis is 2π-times better with your input.

To the wizard of the lab, Leif Häggman. I’m pretty sure half of my work couldn’t have been done without you. On that end, I’d also like to thank Michael Wang, for introducing me to electronics and helping me wrap my head around conductivities. To Dr. Nan Kyi Thein and Zahra Saki, thank you for a fruitful collaboration, enjoyable times in the lab and for being excellent little helpers!

To my fellow Ph.D. students and group members Roger, Huimin, Viktor, Hannes, Anuja and Markus. And to the seniors, Marina Freitag, Malin Johansson, Xiaoliang Zhang, Jesper Jacobsson. Thanks for the pleasant times in the lab and friendship throughout the years and good luck to yourselves! Thanks for all the fun and absurd lunch discussions and for putting up with me. To the old group members: Hanna, Wenxing, Meysam, Sandra, Susanna, Lei Yang, Park, Dongqin, Sagar, Jinbao, Anna Eriksson, Yan, Eva Unger, Narjes. You may have moved on, but I’ll always consider you part of my group. Previous visiting and master students, Rodrigo, Michael, Bianka, Melanie, Camillo, Valeria, Sofie, Su, Axel, Hua Wu, Carmen, Jonatan, Magnus, Martin and more.
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I owe a great deal of my knowledge about the perovskite material to the people at EPFL, particularly Dr. Juan-Pablo Correa-Baena. You showed me a great deal of patience and I thank you for it. Also, thanks to Michael, Fabrizio, Wolfgang, Antonio, Konrad for your collaboration and help. Special thanks also go to Jaenette, Kazuteru and the original members of Hagfeldts EPFL team and Simone Hagfeldt for hosting us in Lausanne during our visits there. To the collaborators and hosts at Aalto University, Prof. Esko Kauppinen, Prof. Janne Halme, Antti and the rest, thanks for your hospitality and for entrusting us with your carbon-nanotube films. To Adam Hultqvist, thank you for a great collaboration through the years and friendship. You are the go-to guy regarding questions about anything related to material science. On that note, I’d also like to acknowledge Tobias and Prof. Marika Edoff for your collaboration and discussions.

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To the people at the department administration, Ulrika, Åsa, Eva, Terese, The Annas, Susanne, Nina, Patrik, Jessica and Peter among others. Thanks for all your help with the Swedish bureaucracy and for getting me out of several train ticket fines. You are the best! To the course responsible for whom I was a teaching assistant, Felix, Christer, Nessima and Daniel. Thanks for suffering through my broken Swedish. Even though I still mix it Icelandic, I’d like to think I’ve gotten better at it.

Also, thank you Marina and Liisa for hosting us Sigga during our time of homelessness. To Kjell Jorner, thanks for all the Rullan lunches, burger exploration and friendship in general.

Finally, I’d like to thank my family at home in Iceland who, although fairly oblivious about my scientific endeavors, have supported me through thick and thin during my time in Uppsala. To my girlfriend Sigridur, you have been my rock throughout the years and provided me with priceless mental support and my main reason for waking up in the morning.
The global warming phenomenon, which has been decisively connected to man-made emission of greenhouse gases, leads to catastrophic environmental changes. As an example, the melting polar icecaps are expected to result in a 2-meter rise of the sea level by 2100, which threatens to drown many densely populated cities around the world. The greenhouse gas which is the most problematic, is carbon dioxide, CO₂. It has a place in the natural life cycle because most animals on Earth breathe in oxygen, O₂, and breathe out CO₂. Plants do the opposite. They use CO₂ along with water and energy, in the form of sunlight, to make carbohydrates as nutrients and release O₂ as a byproduct. Since the industrial revolution in the 19th century the natural balance of CO₂ has been upset because of the massive amounts of fossil fuels (i.e. coal, oil, gas, wood, etc.) burned to power our modern society. By burning carbon-based matter, such as carbohydrates, O₂ is consumed and there is a release of water, CO₂, and energy. This process is used to power cars, airplanes, ships, and to create electricity for all our worldly needs. In fact, it has been our main source of energy and has resulted in a disturbance of the natural CO₂ balance. When sunlight strikes the Earth a part of the light, called thermal radiation, is usually reflected back into space. However, the CO₂ molecule can trap this thermal radiation from the Earth and release it back as heat into the atmosphere, resulting in a greenhouse effect. The science of the problem should now start to become obvious:

\[
\text{Increased amounts of } CO_2 \text{ pumped into the atmosphere.} + \\
\text{The ability of } CO_2 \text{ to trap thermal radiation from Earth.} = \\
\text{Global Warming}
\]

Power can be generated without emitting any CO₂ by means of renewable energy. Typically, this is done by using wind turbines, hydropower plants, geothermal power plants or solar cells, to generate electricity. In this thesis, we focus on the last bit. These four technologies are fully capable of completely replacing all the coal, oil and wood we burn for power. In fact, by covering a land area corresponding to the size of Sweden (or 1/20th of the Sahara Desert) with solar panels the current world energy demand could be met by solar
power alone. Complete conversion from fossil fuels to an electric society powered by renewable energy is mankind’s best bet of surviving climate change.

Today, we have pumped so much CO$_2$ into the air already that the Earth’s climate will continue to warm for the rest of this century, until 2100. Converting completely to renewable energy sources is a time consuming political process, but the decisions, acts and changes we make today, will affect by how much the climate will have warmed in 2100 and whether it will still be warming or not.

This work focuses on a new type of a solar cell, called the perovskite solar cell (PSC). Although the material has a very old history, it was only first used in solar cells in 2009 and since then the performance of this new technology has reached almost the same level as crystalline silicon solar cells (SiSC). Manufacturing of PSCs could present a cheaper alternative to SiSCs. However, SiSC are so cheap to produce that it is tough for any new solar technology to enter the market. One additional advantage of PSCs is that they can be put on top of a silicon, or a similar solar cell, to give an even better performance than the SiSC alone. Devices with two, or more, solar cells working together on top of one another are called tandem solar cells. With such tandem solar cells, the land area required to yield the same amount of power as a normal solar cell would be considerably reduced.

![Silicon-solar cell farm at the Glava Energy Center, Sweden. Photo from private collection.](image)

*Figure 30.* Silicon-solar cell farm at the Glava Energy Center, Sweden. Photo from private collection.

In **Paper I**, we were interested in getting to know how this new perovskite material could generate electricity so well, i.e. why it only took 9 years for perovskite solar cells to do what took silicon solar cells 60 years.
All solar cells have at least two electrodes, a plus and a minus, just like on a battery. Normally, one of those electrodes is made with a metal and in the case of perovskite solar cells, the best performances are reached by using a thin layer of pure gold or silver. In **Paper II**, we used an electrode based on carbon. Films of carbon nanotube electrodes were already prepared on a piece of paper, so all we had to do was cut them into the shape we wanted and with the push of a finger, place them on our perovskite. With the carbon nanotube electrode, a solar cell performance close to that of a normal one with gold was obtained.

For tandem solar cells, the PSC must be on top of the SiSC, which means that the PSC must be half-transparent, i.e. not absorb the light the SiSC is supposed to absorb. Metal electrodes are not transparent unless they are made very thin, and thin metal films are too resistive to use for electrodes. In **Paper III**, we investigated the use of transparent electrodes on PSCs for tandem solar cell purposes. We were successful in depositing the transparent electrodes onto the perovskite, but the solar cells did not yield the expected performance. The most likely cause for the low performance is the formation of an insulating layer between the perovskite and the transparent electrode layers.

Today, the best performing PSCs are usually made in an oxygen- and humidity free atmosphere. In **Paper IV**, we modified a procedure for making highly efficient PSCs, which usually requires an oxygen- and humidity free atmosphere, to make the same material under normal air conditions. Another general requirement for making the perovskite materials in the solar cells is to use toxic and dangerous organic solvents. In **Paper V**, we focused on making a similar perovskite to the one in the best solar cells by only using water and isopropanol as the solvents, both of which are non-toxic.

These are only a few of the thousand studies in the world being done on PSCs today. Although they do not directly solve the problem of climate change, these studies will hopefully add value to making renewable energy sources more appealing and result in that one day even better solar cells can be manufactured.
Populärvetenskaplig svensk sammanfattning

Det globala uppvärmningsfenomenet, som har varit avgörande kopplat till människans utsläpp av växthusgaser, leder till katastrofala miljöförändringar. Som ett exempel antas de smältande polära isarna resultera i en 2 meter höjning av havsnivån året 2100, vilket hotar att dränka många tätbefolkade städer runt om i världen. En av de växthusgaser som är mest problematisk är koldioxid, CO₂. Den har en plats i den naturliga livscykeln eftersom de flesta djur på jorden andas in syrgas, O₂ och andas ut CO₂. Växter gör motsatsen. De använder CO₂ tillsammans med vatten och energi, i form av solljus, för att göra kolhydrater som näringsämnen och släpper ut O₂ som en biprodukt. Sedan den industriella revolutionen på 1800-talet har den naturliga balansen av CO₂ varit störd på grund av att massiva mängder av fossila bränslen (dvs. kol, olja, gas, trä etc.) bränns för att driva vårt moderna samhälle. Genom att bränna kolbaserade substanser, som kolhydrater, förbrukas O₂ och energi, vatten och CO₂ släpps ut. Denna process används för att driva bilar, flygplan, fartyg och skapa el för alla våra världliga behov. Det har varit främsta energikällan i världen och har resulterat i en störning av naturliga CO₂-balansen. När solljus träffar jorden återspeglas vanligtvis en del av ljusset, så kallat termisk strålning, tillbaka i rymden. CO₂- molekylen kan fånga denna termiska strålning från jorden och släppa tillbaka som värmee i atmosfären, vilket resulterar i en växthuseffekt. Vetenskapen runt problemet bör nu börja bli uppenbar:

\[
\text{Utsläpp av stora mängder CO}_2 \text{ i atmosfären} \\
+ \text{Förmågan hos CO}_2 \text{ att fånga termisk strålning från jorden} \\
= \text{Global uppvärmning}
\]

samhälle som drivs av förnybar energi är mänsklighetens bästa satsning för överlevnad och i positiv bemärkelse påverka klimatförändringarna. Idag har vi redan pumpat ut så mycket CO₂ ut till atmosfären att klimatet kommer att fortsätta att värmas upp under resten av detta århundrade, eller fram till 2100. Att byta helt till förnybara energikällor är en tidskrävande politisk process, men de beslut och förändringar vi gör idag kommer att påverka hur mycket klimatet kommer att ha värmts upp till år 2100 och om det kommer att fortsätta att bli varmare eller inte.


Figure 31. Kisel-solcellsgård vid Glava Energicenter, Sverige. Foto från privat samling.

I Artikel I var vi intresserade av att få veta varför det nya perovskit materialet kunde generera el så bra, dvs varför det bara tog 9 år för perovskit-solceller att nå samma verkningsgrad som det tog 60 år för kiselceller att nå. Vi upp-
täckte, bland annat, i denna studie att trots orenheter i perovskit-lagret, så fungerar perovskiten fortfarande i stort sett som en ren halvledare. Detta förklarar delvis varför det är ganska lätt att nå hög effektivitet med perovskite-solceller.


Studierna i denna avhandling är bara några av de tusen studierna i världen som görs på PSC:er idag. Trots att de inte direkt löser problemet med klimatförändringar, kommer dessa studier förhoppningsvis att öka möjligheten för att göra ännu bättre solceller, och i framtiden göra förnybara energikällor mer tillgängliga.
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