Scalable solution processing of NiOx nanoparticles.

Peter James Armstrong
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SCALABLE SOLUTION PROCESSING OF NIOX

NANOPARTICLES

By
Peter James Armstrong
B.S., Utah State University, 2018
M.S., University of Louisville, 2021

A Dissertation
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in Partial Fulfillment of the Requirements
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A Dissertation Approved on

November 21, 2023

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DEDICATION

To my parents, James and Lori Armstrong and all my brothers and sisters. I would not have made it without your support.
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ABSTRACT

SCALABLE SOLUTION PROCESSING OF NIOₓ NANOPARTICLES

Peter Armstrong

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Perovskite solar cells (PSCs) are a promising alternative to silicon-based photovoltaics. However, PSCs face several challenges due to shortcomings in their stability, module efficiency, and scaled production. Although PSCs is still a young field of research, significant attention has been given to demonstrating power conversion efficiencies that are on par with traditional silicon. With that target reached, converting the laboratory demonstration into practical materials to increase access and abundance of solar energy are among the next large targets for the field. This comes with material challenges for perovskite and their companion charge transport layers (CTLs). Among the charge transport materials often used, NiOₓ nanoparticles have stood out as a leading material for an efficient, stable, and scalable CTL.

In this dissertation the scalable deposition of NiOₓ is addressed through compositional design and solvent engineering. Two NiOₓ nanoparticle formulations have been developed and deposited by scalable coating methods to fabricate functional PSC devices. Inks were analyzed by zeta potential, TGA, and theoretical solvent analysis. Film quality was
characterized by SEM and $J-V$ analysis. Using compositional design, NiO$_x$ nanoparticles were successfully suspended in a nonpolar solvent system. It was found that the addition of large ligands was unnecessary for particle stabilization in a chlorobenzene-based solution, and that the presence of these ligands significantly obstructed charge extraction.

Through further work with solvent engineering, a water based NiO$_x$ suspension that did not require additional ligands was developed. This NiO$_x$ formulation allowed for rapid large area coating on both blade coating and slot die coating systems. Utilizing intense pulsed light (IPL) annealing, processing time was further decreased with an increase in device performance. When used in a slot die coating system with IPL we were able produce a champion device PCE of 12.23%.

In this dissertation the stability of the novel SnO$_2$/Ag interface was also explored. Perovskite ion migration is a leading source of degradation with the formation of AgI a common by product. A series of imidazoles were evaluated to identify structural features that contribute to an effective blocking layer. It was found that imidazoles with conjugated planer systems and hydrogen bonding heteroatoms were able to prevent ion migration and retain device performance.
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CHAPTER 1.0 INTRODUCTION

1.1 Lay summary

Solar energy is the most abundant resource on the planet and has no greenhouse gas emissions. Developing materials that are highly efficient and affordable at capturing this energy is a major step towards creating a green energy future. Current solar materials like silicon require extreme temperatures, dangerous chemicals, and slow modular processing to produce. A new alternative material to silicon is perovskites solar cells. Perovskites solar cells can be made using methods like a traditional printing press. Perovskites are made by coating a conductive plastic or glass substrate with a solution, which when dried, will crystallize into the perovskite absorber layer. By controlling how the ink dries we can control the perovskite shape and properties. When the perovskite is coated between two secondary layers and finished with a metal contact it can be used to collect solar energy. This dissertation focuses on the development of the secondary layer materials called charge transport layers for large area coating. Specifically, NiO\textsubscript{x} nanoparticles are used as an anode material for the PSC. This dissertation will explore the effect of adding different supporting organic compounds to stabilize the nanoparticles in solution. Also explored will be the use of different alcohols to affect the stability of the nanoparticles ink while increasing coating speed. Perovskites are not perfect and have some stability issues still. One of those problems is ion migration through the perovskite to the metal contact. In this dissertation
the addition of a small molecule blocking layer between the perovskite and charge transport layer will be used to prevent this migration.

1.2 Scope of dissertation

This dissertation describes a series of three studies investigating the effect of ink formulation and composition on the performance of charge transport layers (CTLs) in perovskite solar cells (PSCs). These studies include: 1) Solvation of NiO\textsubscript{x} for hole transport layer deposition in PSCs; 2) Scalable solution processing of Cu: NiO\textsubscript{x} nanoparticles for PSCs; and 3) Evaluation of imidazole blocking layers for perovskite stability.

Synthesized ligands were characterized by Fourier transformed infrared (FT-IR) spectroscopy, UV-Visible spectroscopy, and thermal gravimetric analysis (TGA). Ink stability was evaluated using optical observations in conjunction with digital images, dynamic light scattering (DLS) for particle size, and Zeta potential. Theoretical solvent evaluation was done using Hansen solubility parameters (HSP). Synthesized NiO\textsubscript{x} and perovskites coatings were characterized by x-ray diffraction (XRD), and UV-Visible spectroscopy to verify phase retention during processing. Solar devices were electronically characterized using current density - voltage ($J-V$) analysis and electrochemical impedance spectroscopy (EIS). Coatings of NiO\textsubscript{x} and perovskite where also investigated using scanning electron microscopy (SEM) to evaluate the effects of ink formulation on microscopic film uniformity.

Chapter 1 of this dissertation includes an overview of this dissertation and introduction to PSCs and several of their research challenges. The state of current global
energy and solar is also discussed to provide context for current perovskite interest and research targets. Chapter 2 is comprised of the experimental procedures for the synthesis and characterization of the various NiOx nanoparticles and supporting ligands that were investigated. Also presented is the methodology used for the fabrication of perovskite devices and their characterization. Specifics for $J-V$ analysis will be presented. Chapter 3 contains solvation of NiOx for hole transport layer deposition in PSCs. A series of xanthate ligands are tested for the solvation of NiOx into a chlorobenzene solution. The effects of ligands on particle stability and film formation are discussed in relation to the resulting device performance. Chapter 4 discusses the scalable solution processing of Cu: NiOx nanoparticles for PSCs. Specifically, the effect of solvent formulation is investigated in relation to ink stability, processability, and finally device performance. Alcohol suppression of the vapor pressure and surface tension of water is utilized to increase processing speeds of large area coatings. Chapter 5 is the evaluation of imidazole blocking layers for perovskite stability. Specifically, this investigation explores preventing ion migration through a SnO$_2$ coating on top of the perovskite layer. The effect of various functional groups on an imidazole platform are investigated in relation to perovskite stability. Chapter 6 contains final thoughts and conclusions on the use of NiOx on large scale coatings and some thoughts on the future directions for perovskites and metal oxide coatings at scale.

1.3 Global Energy Outlook

The modern global energy landscape is an intricate web of economic and political pressures that have significant effects on the daily lives of all individuals across the globe. The sensitivity of the delicate balance between energy production, consumption, and distribution has been shown at large over the last couple years as geopolitical events and
global crises have disrupted supply chains and shifted entire markets. Current energy consumption projections show an 80%-150% increase in global energy usage by the year 2050. At the same time, estimates project renewables to increase from 30% of global energy to 65%-88%.4

On top of the need for energy security, to reach the environmental promises of the Paris accords carbon emission will need to drop by 30-45% by 2030 compared to 2019 levels and net zero by 2050.5 Current policy and implementation rates are only projected to reach 10% reductions in this same period.5 To meet current targets, renewable installations will need to increase 3x by 2030 and then 7x again by 2050.4 This is putting significant pressure on expanding current renewable production and the development of cheaper, more effective technologies to accelerate roll out. Together the economic, political, and environmental interests are aligning to push for a significant energy shift to a new green energy future.

American renewable energy production is currently 20% of its total energy produced. Broken down into the different components, hydro makes up 6.3%, wind contributes 9.2%, solar is 2.8%, and others make up 1.7%.6 Of these solar and wind currently have the largest room to grow. From 2008 to 2018, solar installations increased from 1 GW to 51 GW. In contrast, in 2023 29.1 GW of new installations are expected to come online.7,8 The Solar Industry Association projects that solar installations in the US will triple over the next 5 years due to strong government policies, lowering production costs, and increasing demand across all sectors.9 To reach these lofty energy goals, next generation photovoltaics (PV) is attracting major interests with significant investments
being made into research and development of thin film photovoltaics, tandem devices, concentrated solar, and solar thermal storage.

1.4 Advantages of Solar

Solar is a logical source of clean energy. More than 173,000 TW of solar energy hit the earth continuously. This amount of energy far exceeds the global energy usage 10,000 times over. That energy plays a vital role in creating the stable planet we enjoy today. Solar energy is the driving force behind the Calvin cycle in plants and bacteria via energy collection through chlorophyll and phycoerythrin. The balance of the energy absorbed by earth from the sun and reemitted as blackbody radiation is critical to having a habitable planet. This balance has been threatened as increasing CO₂ and methane emission have increased the greenhouse effect, resulting in less energy emission into space. PVs once installed have zero carbon emission leading to them being highly favored by environmentalists.

Unlike other energy sources, solar can be implemented in almost any location with minimal assembly, limited mechanical hazards, and no noise pollution. Not needing to be centralized in a single location with large infrastructure, solar can be installed as a diffuse energy source via roof top installation, mixed land use applications, or integrated into windows. Reutilizing land mixed used solar can help slow the loss of natural environments. Utility scale implementation of solar farms will still play a vital role in securing our energy future.

Solar does have several challenges that need to be addressed. Solar is a low-density energy source when compared to traditional fossil fuels. As such, large surface areas are
required to match the energy production. As of 2012, utility scale solar farms require an average of 3.7 acres/GWh/yr for a fixed panel farm.\textsuperscript{11} Mixed land use of installations is one of the leading solutions for this problem. Residential solar has been incentivized through programs such as reverse metering. Improving the efficiency of the solar panels is another major component of improving energy production. While reliable, solar is an intermittent power source and having efficient reliable energy storage is vital for solar to be successfully implemented at scale.

1.5 The Power of Light

Sunlight is a classical form of blackbody radiation consisting of energy waves from the entire electromagnetic spectrum. From Planck’s Law the relationship of energy and photonic wavelength are shown to be inversely related. Equation 1.1 shows Planck’s law where $E$ is energy, $h$ is Planck’s constant, $c$ is the speed of light, and $\lambda$ is wavelength.

$$E = \frac{hc}{\lambda}$$  \hspace{1cm} (1.1)

At high wavelengths, light has low energy (radio waves) while at low wavelengths they have high energy (gamma rays). Graphically, this is demonstrated in Figure 1.1a,b with the AM0 spectrum plotted by wavelength and photon energy. An important observation from the solar spectrum is the inconsistency across different wavelengths. These inconsistencies are important when optimizing energy collection. The ability of a PV material to absorb light is dependent on several key components: spectral content of incident light, radiant power density, and incident angle of the light with the cell. As shown in the AM1.5G spectrum, the atmosphere has several high absorption stretches through the IR (water and CO\textsubscript{2} dominantly) (Figure 1.1c). Even though the IR region has a higher flux,
with flux being the quantity of photons for a given wavelength, this region of light is less optimal when compared to the lower flux, but uninterrupted higher energy region that is the visible to ultraviolet light (Figure 1.1d). For this reason, solar cells are designed to collect the visible and ultraviolet light portions of the solar spectrum.²

For light to be absorbed and turned into electrical energy, the energy of the photon must be equal to or greater than the band gap energy. This absorption and the resulting electric current/voltage is called the photovoltaic effect. Upon absorption of a photon, an electron is excited from the valence band to the conduction band creating an electron-hole pair. Extraction of the excited electron into an external circuit leads to the generation of electricity.

Figure 1.1. Spectral irradiance of the AM0 spectrum vs a) photon wavelength and b) photon energy. Spectral irradiance of the AM1.5G spectrum vs c) photon wavelength and d) Am1.5G spectrum plotted as photon flux vs photon energy. Images from pv lighthouse.²
The nature of the semiconductor material is critically important for optimizing the photovoltaic effect. The size of the band gap, if it is a direct band gap or indirect band gap, and charge carrier concentration are some of the key characteristics to be aware of. Most semiconductors have a band gap between 0.3 eV and 3.5 eV and are divided into direct band gap or indirect band gap materials. Classical band theory defines the band gap as the energy difference between the conduction band and valence band of a material. The valence band is the highest occupied energy level of a material at absolute zero. The conduction band is the lowest unoccupied allowed energy level of a material at absolute zero. These allowed energy states are derived from the periodic solution of the Schrödinger wave equation for an infinite crystal in three dimensions accounting for both energy and momentum components. When the momentum of the conduction and valence band align the band gap is a direct band gap. Materials such as lead halide perovskites have direct band gaps. When the momentum component is not aligned the material has an indirect band gap. Semiconductors with an indirect band gap require a phonon absorption or emission to undergo the momentum shift necessary for an excited electron to find an allowed energy state. A classic example of an indirect semiconductor used for solar applications is silicon. The additional requirement of a phonon absorption decreases the effectiveness of indirect semiconductors to undergo the photovoltaic effect, but this can be compensated for by increasing material thickness to usually more than 100 µm.

1.6 Solar Cell Types

The impact of the bandgap on the maximum possible power conversion efficiency (PCE) is demonstrated by the Shockley-Queisser limit. The Shockley-Queisser limit defines the theoretical maximum for a single junction cell assuming only radiative recombination
losses. Figure 1.2 shows the champion device performance of various photovoltaic materials in relation to the Shockley-Queisser limit as of 2016. From it we can see that crystalline silicon (c-Si) with a band gap of 1.12 eV falls well below the optimal band gap of 1.4 eV, while materials like GaAs, a type of III-V semiconductor, sits right on the optimal band gap at 1.42 eV.

Figure 1.2. Calculated Shockley-Queisser limit power conversion efficiency as a function of bandgap, record device performance for various photovoltaic materials as of 2016.3

c-Si currently makes up 90% of the solar market and is the most well-established solar technology to date and is projected to remain the dominant solar material as solar production increases in the next decades. They have a long track record of reliability and efficiency spanning all the way back to the 1950s.14, 15 c-Si has dominated the solar market due to its growth alongside microchip development, abundant source materials, and impressive stability. These advances are despite it having a less than ideal band gap, an indirect band gap that decreases light absorptivity, extreme material purity requirements, highly toxic chemical processing, long processing times and extreme processing
temperatures. c-Si holds a current record of 26.1% PCE but has seen little improvement over the last 20 years.\textsuperscript{1,16} Silicon research is still thriving with tandem and multi junction cells gaining attention to overcome the Shockley-Queisser limit for a single junction. Additionally, recycling of retired solar panels is receiving significant attention to reduce material loss from the precious metal components.\textsuperscript{17} Due to its dominance of the solar space all other solar materials are benchmarked against silicon as shown in Figure 1.3.

Current alternatives to c-Si include III-V materials such as GaAs, CdTe, and CIGS.

\textbf{Figure 1.3.} NREL record efficiency chart for single junction solar materials.\textsuperscript{1} GaAs are the highest performing single junction photovoltaic on the market currently. With a direct band gap of 1.42 eV, GaAs holds the record for the highest single junction device at 29.1% PCE.\textsuperscript{1} Grown into thin film wafers, GaAs cells are thin, light weight, and semiflexible. Widespread application has been restricted due the slow and expensive production processing making it cost prohibitive. For these reasons, plus having high
thermal stability and radiation resistance, GaAs is used almost exclusively in space applications where performance outweighs cost.\textsuperscript{18}

After c-Si, CdTe is the second leading solar material and is the current leading industrial thin film material.\textsuperscript{19} Similar to GaAs with a direct band gap of 1.48eV,\textsuperscript{19} CdTe are thin film devices with high absorption across the solar spectrum. Unlike c-Si, which are fabricated through slow thermal driven crystal growth, CdTe is typically produced via evaporative methods and sublimation crystal growth significantly reducing processing times and temperatures.\textsuperscript{20} Current record performance is still below that of c-Si at 22.4%\textsuperscript{1}. Major concerns around CdTe, comes from the material used to produce it; cadmium is a well-known heavy metal toxin making cradle to grave monitoring a significant responsibility for these modules. Also, tellurium is a rare earth metal with earth abundance like Pt making its long-term viability questionable.\textsuperscript{21}

Copper indium gallium selenide (CIGS) is the last major solar technology currently available on the market. While CIGS are another thin film material that is typically produced through vapor phase evaporation/sputtering, alternative solution phases coupled with high temperature sintering methods are being developed.\textsuperscript{22} Fine tuning of the stoichiometry allows the CIGS to have a band gap that can be tuned from 1.0 eV up to 1.6 eV.\textsuperscript{23} This is extremely advantageous for absorption window tuning in tandem devices. Device performance records have surpassed that of CdTe with the current record having a PCE of 24.6%, but this is still behind that of c-Si.\textsuperscript{1} Further optimizing of stoichiometry and doping levels is a very active field of research for these materials, as are flexible tandem devices.\textsuperscript{24}
Reviewing the development of these solar materials reveals some trends in material and process selection. First, selection is based on band gap and light absorptivity. These are obvious requirements as performance is the highest regarded factor when generally comparing materials. However, additional criteria are material and process costs. As mentioned with GaAs and CdTe, both have near perfect band alignment but have significant material costs. Process costs have prevented GaAs from becoming a dominate technology and material costs slow down current CdTe production. Currently CIGS and CdTe have energy payback periods of under 12 months while c-Si is still about 3-4 years. This reflects the larger carbon footprint of the production process for each technology. A final consideration is tunability for applications in tandem or multijunction architecture. By stacking materials of various band gaps on top of each other, total light lost due to radiative losses can be reduced allowing solar module performance to surpass the Shockley-Queisser limit. Through various means of doping or alloying all the materials listed here have demonstrated band gap tuning. However, this process is easier with better control in CIGS, GaAs, and CdTe versus c-Si. Future solar alternatives will need to address these short comings while also maintaining the long-term stability that has become expected for solar modules. Further development and production of all forms of solar will be necessary to meet the ambitious energy targets that have been set by world leaders over the next 30 years.

1.7 Emerging PV

The three major types of emerging PV are CZTSSe (Cu₂ZnSn(SₓSeₓ-y)₄, organic photovoltaics (OPV) or dye sensitized solar cells (DSSC), and metal halide perovskites. CZTSSe has emerged directly from the work of CdTe and CIGS by replacing the more
expensive indium, tellurium, and toxic cadmium with earth abundant elements of zinc and tin. While promising, controlling phase purity, interface band alignments thermal stability, and a variety of other issues persist.28 OPV and DSSC are organic-based technologies that utilize polymers or dyes to capture light.29, 30 Flexible, lightweight, environmentally friendly, and low cost scalable processing make these materials very appealing. However, both technologies struggle with long term stability and performance due to the low absorptivity of polymers and sensitivity to oxygen and moisture.30

Metal halide perovskites or perovskites solar cells (PSCs) were first discovered by Miyasaka et al. in 2009 while working with DSSCs. Their initial devices, while not impressive by PCE standards at 3.81%, marked a breakthrough in solar technology.31 The PSC has a high absorption coefficient, high defects tolerance, tunable band gap, small exciton binding energies, long charge diffusion lengths, high carrier mobilities, earth abundant source materials, and low temperature processability.21, 31-36 In the 14 years since PSCs were first reported, they have skyrocketed to the front of solar research with current record performances of 26.1% placing its performance even with c-Si.1 PSCs have been demonstrated by a variety of solution and vapor processing methods, as single junction devices and tandems, on flexible and rigid substrates and has expanded into LEDs, quantum dots, and light sensors.37-39

1.8 Perovskite Solar Cells

This section will discuss the chemical composition of perovskite in relation to compositional flexibility bandgap control and related stability and scaling concerns. Also discussed is a model of the P-I-N junction, and an introduction to solution processing.
1.8.1 Composition

The flexibility of PSCs stems from the crystal structure shown in Figure 1.4. Perovskites have an ABX₃ crystal structure, where A is a monovalent cation, B is a divalent cation and X is a halide. PSCs derive their name from this crystal structure which was first discovered in Russia as CaTiO₃ and named in honor of Russian mineralogist Lev Perovski. In PSCs the A site is typically an organic cation such as methylammonium (MA⁺) and formamidinium (FA⁺) or cesium or some combination of these three. The B site is typically Pb²⁺ though some work has also been done with Sn²⁺. The halide is usually I⁻, with doping of Br⁻ and/or Cl⁻.

![Figure 1.4. ABX₃ crystal structure of metal halide perovskites.](image)

The most widely studied composition of PSC is the methylammonium lead iodide (MAPbI₃). Later variations such as the FAPbI₃, CsPbI₃, or mixed systems A site systems such as MA₀.₆FAₐ.₃₈Cs₀.₀₂PbI₃ have improved film stability and performance by increasing the Goldschmidt tolerance factor and octahedral factor. The tradeoff of adding FA or Cs is decreasing the band gap, however the improved phase stability, stable power output and electronic alignment are often considered worth the decreased band gap.
Mixed halide perovskites have also demonstrated improved performance and stability relative to phase pure perovskites.\textsuperscript{42} Halide doping with Br\textsuperscript{-} increases the band gap resulting in higher open circuit potentials ($V_{oc}$) and improved phase stability.\textsuperscript{43, 44} Chloride doping has a direct effect on crystal growth and has been used to increase grain size in deposited films.\textsuperscript{44} However, detrimental halide phase segregation can occur under illuminated conditions.\textsuperscript{45, 46} Improving lattice stability, reducing defect states at grain boundaries and film interfaces help prevent ion migration from occurring.\textsuperscript{47}

1.8.2 PSC Physics

As mentioned in section 1.5 the photovoltaic effect is the excitation of an electron from the valence band to the conduction band upon the adsorption of light followed by extraction into an external circuit. To prevent radiative relaxation of the excited electron a p-n junction is used to form a diode and extract the excited electron. In c-Si this junction is achieved through doping a portion of silicon with phosphorous forming a n-type semiconductor and another portion with boron forming a p-type semiconductor. In these systems n stands for electrons and p stands the absence of an electron, commonly referred to as holes and will be referred to as such moving forward. In PSCs this junction is better defined as a p-i-n or n-i-p junction depending on if the light passes through the hole transport layer (HTL) or electron transport layer (ETL) first, respectively.

Due to the work function being higher in p-type materials than n-type materials the electrostatic potential will be smaller on the n side of the junction resulting in an electrostatic field being generated. This built in field then drives the electrons to the n side and the holes to the p side of the junction. As charge equilibrium is established, major
carriers are depleted at the interface creating a barrier for major carriers while providing a low resistance path for minority carriers thus establishing the photodiode junction.\textsuperscript{48}

The perovskite absorber layer is considered an intrinsic material, having neither n-type or p-type doping, however when sandwiched between a p-n junction the electric field extends through the intrinsic layer driving photogenerated carriers to the contact edges. The movement of the charge carriers in the absorber layer can be modeled by solving the steady state electron and hole continuity equations as follows:\textsuperscript{49}

\begin{equation}
D \frac{\delta^2 n(x)}{\delta x^2} + \mu E(x) \frac{\delta n(x)}{\delta x} + G(x) - R(x) = 0 \tag{1.2}
\end{equation}

\begin{equation}
D \frac{\delta^2 p(x)}{\delta x^2} - \mu E(x) \frac{\delta p(x)}{\delta x} + G(x) - R(x) = 0 \tag{1.3}
\end{equation}

where \(n\) and \(p\) stand for electron and hole concentrations, respectively, \(D\) is the diffusion coefficient, \(\mu\) is mobility, \(G(x)\) is the position dependent photo-generation, \(R(x)\) is the carrier recombination in the absorber, and \(E(x)\) is the position resolved electric field within the absorber layer. Due to the long diffusion in perovskite \(R(x) = 0\) can be assumed.

Charge separation is illustrated in Figure 1.5 as \(E(x)\) is linear in the absence of doping or trap states. The charge generation profile of the absorber can be approximated by:

\begin{equation}
G_{\text{max}} = \int_0^\infty G_{\text{eff}} e^{-x/\lambda_{\text{ave}}} dx = G_{\text{eff}} \lambda_{\text{ave}} \tag{1.4}
\end{equation}

where \(G_{\text{eff}}\) and \(\lambda_{\text{ave}}\) are material specific constants averaged over the solar spectrum. Equations (3) and (4) can be solved analytically to derive the complete current-voltage
characteristics for both p-i-n and n-i-p architectures as shown below in Table 1.1 and equations (1.5-1.7):

\[ J_{\text{dark}} = (\alpha_f * J_{f0} + \alpha_b * J_{b0})(e^{\frac{qV}{kT}} - 1) \] (1.5)

\[ J_{\text{photo}} = qG_{max}(A - B e^{-\frac{t_0}{\lambda_{\text{ave}}}}) \] (1.6)

\[ J_{\text{light}} = J_{\text{dark}} + J_{\text{photo}} \] (1.7)

**Table 1.1.** Parameters of Equations (1.5-1.7) expressed in terms of the physical cell parameters.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{\alpha_f} )</td>
<td>( \frac{e^{\frac{q(V-V_{bi})}{kT}} - 1}{q(V-V_{bi})/kT} + \frac{D}{t_0 * s_f} )</td>
</tr>
<tr>
<td>( \frac{1}{\alpha_b} )</td>
<td>( \frac{e^{\frac{q(V-V_{bi})}{kT}} - 1}{q(V-V_{bi})/kT} + \frac{D}{t_0 * s_b} )</td>
</tr>
<tr>
<td>( A )</td>
<td>( \alpha_f * \frac{(1 - e^{\frac{q(V-V_{bi})}{kT} \frac{t_0}{\lambda_{\text{ave}}}})}{q(V-V_{bi})/kT} \frac{t_0}{\lambda_{\text{ave}}} - \frac{D}{t_0 * s_f} )</td>
</tr>
<tr>
<td>( B )</td>
<td>( \alpha_b * \frac{(1 - e^{\frac{q(V-V_{bi})}{kT} \frac{t_0}{\lambda_{\text{ave}}}})}{q(V-V_{bi})/kT} \frac{t_0}{\lambda_{\text{ave}}} - \frac{D}{t_0 * s_b} )</td>
</tr>
</tbody>
</table>

The parameters in Table 1.1 are functions of the physical parameters of the cell namely: \( t_0 \) is the absorber thickness, \( J_{f0}, s_f \) and \( J_{b0}, s_b \) are the dark diode current recombination and the effective surface recombination velocity at the front and back charge transport layers (CTLs), respectively, \( D \) is the diffusion coefficient, and \( G_{\text{max}} \) is the
maximum absorption. This model describes the basic physics of the p-i-n solar cell under operation and can be useful for device characterization and interpretation.

Implied throughout the entire model is a heavy dependence on the material properties of the absorber. These properties change with the composition of the perovskite, making perovskites highly tunable materials by simple alterations of the A, B, and X sites. Secondary, the composition of the CTLs is also directly linked to charge extraction and total device performance. A large variety of CTLs have been developed though the work of OPVs and DSSCs, which have been employed in PSCs with great effect. We will discuss more about CTLs in section 1.9.

1.8.3 PSC Fabrication

Typical device preparation proceeds through a solution process in which a precursor solution is deposited on a conductive substrate precoated with a CTL, then thermally annealed to reach the desired crystalline phase. Investigated deposition methods have included spin coating, blade coating,\textsuperscript{50,51} ink jet printing,\textsuperscript{52} slot die coating,\textsuperscript{53} and gravure
Typical lab scale research has centered on spin coating with its variations of sequential coating, anti-solvent treatments, or solvent annealing. These techniques control perovskite grain growth through accelerated nucleation and solvent removal (anti solvent treatment), or by extending grain growth (solvent annealing). Sequential methods involve coating an initial layer of PbI$_2$ to form a porous lattice followed by a coating of MAI or FAI that then fills the pores. While spin coating is effective on the small scale, a key value in perovskites is their ability to be produced by more scalable methods.

Blade coating is a method of film deposition that uses a coating tool to spread a pre-deposited volume of ink across a substrate surface (Figure 1.6). This method utilizes shear forces and meniscus flow to leave behind a precisely metered wet film. This method can be used to coat uniform layers over large areas using simple tooling. Additionally, it can be used as a small-scale analog to larger slot die coating as the same principal solution physics are at play. A recent study by Siegrist et al. on the effect of blade coating parameters including blade speed, blade gap, ink concentration and volume, and stage heating. They conclude that blade coating of large area devices is best performed using a continuous solution supply with blade coating and further development of slot die coating.

While blade coating has a pre-metered volume of ink that is deposited during coating, slot die coatings utilize a continues feed of solution. This feed is run through a slit between an upstream and downstream die head (Figure 1.6). The quality of the film can be adjusted by altering the coating speed, flow rate, coating gap, viscosity of the solvent, angle of the slot die head, and air pressure on the upstream side of the coating. When utilized on a large-scale system, such as a roll-to-roll system, this method can coat extremely large areas at high speeds. Despite it being a very mature coating method, its optimization for
perovskite thin films have been challenging. Currently there are several active studies working to understand perovskite crystallization on the slot die platform.\textsuperscript{50,64,65}

**1.8.4 Drawbacks of PCS**

Perovskites are not without their fair share of challenges. Stability of the perovskite is the leading issue for PSCs as shown in Table 1.2 and described below. Perovskites hydroscopic nature make them prone to absorb water from the environment. Water penetration into the crystal lattice can deprotonate the MA\textsuperscript{+} converting it into methylamine which at room temperature will off gas from the film leaving PbI\textsubscript{2}.\textsuperscript{66} Free I\textsuperscript{-} can react with O\textsubscript{2} from the air and be oxidized to form I\textsubscript{2} with the regeneration of water creating a positive feedback loop of degradation.\textsuperscript{67}

UV light can also induce degradation leading to the release of HI and methylamine gas and leaving solid PbI\textsubscript{2}.\textsuperscript{68} This reaction can be accelerated at the interface of the perovskite with a TiO\textsubscript{2} or SnO\textsubscript{2} ETL interface. Since TiO\textsubscript{2} and SnO\textsubscript{2} are wide band gap materials that can absorb in the UV, photoexcited electrons from the ETL layer can catalyze the decomposition of the perovskite surface. We will specifically look at preventing this degradation pathway in Chapter 5. The third major degradation pathway is thermal degradation. Annealing is necessary to form the stable photoactive cubic phase, but extended heating at temperatures as low as 100 °C can decrease conductivity and
eventually lead to complete decomposition. For perovskites to be competitive with c-Si these intrinsic and external degradation factors need to be address.

**Table 1.2. Degradation mechanism of PSCs**

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water and O₂</td>
<td>$\text{CH}_3\text{NH}_3\text{PbI}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{NH}_3\text{I} (aq) + \text{PbI}_2(s)$</td>
<td>(i)</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_3\text{NH}_3\text{I} (aq) \leftrightarrow \text{CH}_3\text{NH}_2 (aq) + \text{HI} (aq)$</td>
<td>(ii)</td>
</tr>
<tr>
<td></td>
<td>$4\text{HI} (aq) + \text{O}_2 \leftrightarrow 2\text{I}_2 (aq) + \text{H}_2\text{O}$</td>
<td>(iii)</td>
</tr>
<tr>
<td></td>
<td>$2\text{HI} + \text{hv} \rightarrow \text{H}_2(g) + \text{I}_2$</td>
<td>(iv)</td>
</tr>
<tr>
<td></td>
<td>$2\text{I}^- + \text{hv} \leftrightarrow \text{I}_2 + 2\text{e}^-$</td>
<td>(v)</td>
</tr>
<tr>
<td>UV</td>
<td>$3\text{CH}_3\text{NH}_2^+ (s) + \text{hv} \leftrightarrow 3\text{CH}_3\text{NH}_2(g) + 3\text{H}^+$</td>
<td>(vi)</td>
</tr>
<tr>
<td></td>
<td>$\text{I}^- + \text{I}_2 + 3\text{H}^- + 2\text{e}^- \leftrightarrow \text{HI}(g)$</td>
<td>(vii)</td>
</tr>
<tr>
<td>Thermal</td>
<td>$\text{CH}_3\text{NH}_3\text{PbI}_3(s) \rightarrow \text{CH}_3\text{NH}_2(g) + \text{HI}(g) + \text{PbI}_2(s)$</td>
<td>(viii)</td>
</tr>
<tr>
<td>AgI</td>
<td>$\text{Ag} + \text{I}^- \rightarrow \text{AgI} + \text{e}^-$</td>
<td>(ix)</td>
</tr>
</tbody>
</table>

In addition to degradation, there is also a loss in PCE when PSCs are scaled from small to large area devices. For most solar cells, the absolute PCE value decreases by 0.8% as the area increases by an order of magnitude. However, this has not been the case with perovskites where the rate of PCE loss has been significantly higher (Figure 1.7). The expected PCE loss is due to increasing series resistance caused by the linear relationship between the sheet resistance of the transparent electrode and increasing area. For this reason, researchers focused on record performance have produced an abundance of small area devices (<0.1cm²). To address this concern, coating uniformity over large areas need to improve, internal defects at grain boundaries and CTL interfaces need to be reduced, and
the various degradation pathways need to be prevented.\textsuperscript{71} Additive engineering, fast solvent evaporation, and evaporation assistance via heating or air flow are methods being explored to address these shortcomings.\textsuperscript{50, 71, 72}

![Figure 1.7. Certified PCE records for champion PSC and perovskite solar modules Lab cells (≈0.01 cm\textsuperscript{2}); large lab cells (≈1.0 cm\textsuperscript{2}); lab modules (10–200 cm\textsuperscript{2}); small modules (800–6500 cm\textsuperscript{2}).\textsuperscript{70}](image)

1.9 Charge Transport Layers

This section expands on the explanation of the effects of CTL’s on PSCs. A brief comment is given on why traditional space charge layer model do not accurately model the perovskite CTL interfaces followed by a review of both ETL and HTL materials with a focus on scalable processing of metal oxides.

1.9.1 Space Charge Layer

As discussed in section 1.8.2, CTLs play a key role in the p-i-n junction of the perovskite and is compositionally dependent. When the p-type and n-type semiconductors are brought into contact with each other they immediately induce charge carrier gradients at the boundary forming an electrostatic field. At equilibrium this region is described as a
space charge layer. Ideally the space charge layer would extend uniformly across the entire perovskite, however, the further from the junction the weaker the carrier gradient is as defined by the depletion width ($x_0$). The depletion width at the p-n heterojunction can be defined as follows: \[^{48}\]

$$x_n = \sqrt{\frac{2\varepsilon_n\varepsilon_p n_p V_0}{\varepsilon_p (\varepsilon_n n_n + \varepsilon_p n_p)}}$$ (1.8)

$$x_p = \sqrt{\frac{2\varepsilon_n\varepsilon_p n_n V_0}{\varepsilon_p (\varepsilon_n n_n + \varepsilon_p n_p)}}$$ (1.9)

$$x_0 = x_n + x_p = \sqrt{\frac{2\varepsilon_n\varepsilon_p V_0 (n_n + n_p)^2}{\varepsilon_p n_p (\varepsilon_n n_n + \varepsilon_p n_p)}}$$ (1.10)

where $x_n$ and $x_p$ are the depletion widths in n-type and p-type, respectively. $V_0$ is the difference in Fermi levels, $\varepsilon_n$ and $\varepsilon_p$ stand for the static permittivity of n-type and p-type, respectively, $e$ is the elementary charge, $n_n$ and $n_p$ refer to the doping density of n-type and p-type, respectively. From this relationship we can see that the depletion width is inversely proportional to the level of p and n doping in the semiconductor. However, this relationship only holds true when both the electrostatic potential and electric field at $x = 0$ are continuous.

In perovskite devices the p-i-n junction still forms the space charge layer across the perovskite but, is complicated by the polycrystalline nature of perovskite and ion migration in the film. \[^{73}\] Due to the polycrystallinity of perovskites, boundaries between crystal grains and CTL interfaces are highly prone to defects and trap state formations. These defects cause charge extraction to be in competition with recombination processes along the HTL/perovskite and ETL/perovskite interfaces. A full derivation of the depletion width
accounting for these issues is well outside the scope of this work. It is sufficient for our purpose to understand the basic effect of doping concentration and work function has on charge carrier extraction. There is growing evidence that the band alignment of the CTLs with the perovskite have a larger effect on improved charge extraction then the difference in work function between the ETL and HTL. Work by Ompong et al. when analyzing the effect of HTL on $V_{oc}$ found that higher $V_{oc}$ occurs, the lower the valance band of the HTL. Using the difference between the conduction band of the perovskite and the valance band of the HTL as the effective band gap they show a good match between theoretical and experimentally reported values for $V_{oc}$ over several common HTL materials. The increases in $V_{oc}$ are attributed to the long carrier life inside the perovskite leading to low internal recombination and effective charge extraction to the HTL. This leads to an increase in the hole concentration in the perovskite, reducing charge recombination and increased quasi-Fermi level splitting. For these reasons, CTL materials should be selected that are aligned with the conduction band (ETL) and valance band (HTL) of the perovskite to reduce interfacial recombination, have high charge carrier density and high carrier mobility to improve overall device performance.

1.9.2 Electron Transport Layers

For an ETL material to be effective it needs to have a conduction band that is slightly lower than that of the perovskite, while also having a deep valence band to prevent electron-hole recombination. This wide band gap is also important for insuring high transparency and maximum light adsorption by the perovskite layer. Additionally, the selected material needs to have high electron mobility to reduce internal series resistance and increase charge extraction.
The ETL also acts as a protective barrier between the perovskite and the electrode, mitigating the degradation of the perovskite layer due to contact with the metal electrode. Various binary and ternary metal oxides, including TiO₂, ZnO, SnO₂, WO₃, In₂O₃, Nb₂O₅, Fe₂O₃, Cr₂O₃, CeO, BaSnO₃, SrSnO₃, BaTiO₃, SrTiO₃, Zn₂SO₄, Nb₂O₅, and BaSnO₃, have been explored as ETLs in n−i−p configurations.⁷⁶-⁷⁸ Of these TiO₂, ZnO and SnO₂ have been demonstrated as effective inorganic ETLs. Organic nanomaterials, such as C₆₀, C₇₀, PC₆₁BM, and PC₇₁BM, as well as a variety of fullerene derivatives and their corresponding different isomeric functionalized fullerene structures, have been investigated in p−i−n configurations, where the ETL is deposited directly on the perovskite thin film.⁷⁹,⁸⁰

1.9.2.1 Organic ETLs

Fullerene derivatives are favored due to their facilitation of low-temperature processing via solution or physical vapor deposition, superior electron mobility, and tunable LUMO energy levels, which match well with the energy band of perovskite, and high reproducibility.⁸¹ They are also often employed in bilayer structures with additional metal oxide ETLs (fullerene/MOₓ ETL), a common approach taken to enhance the performance of PSCs. The improvement in efficiency is primarily attributed to the defect passivation properties of fullerenes, which in turn improves stability.⁸²,⁸³ However, a significant impediment to the widespread adoption of these materials in commercial applications is the extremely high production costs associated with fullerenes. As such, the development of cost-effective alternatives to these ETL materials for inverted perovskite solar cells is critical for facilitating broader commercialization of this promising technology.
1.9.2.2 Inorganic ETLs

Developed initially in dye-sensitized solar cells, TiO$_2$ was the first ETL material used in a perovskite sensitized solar cell during the pioneering work of Miyasaka’s team in 2009.$^{31}$ Since then, the application and optimization of TiO$_2$ have progressively evolved, and improved with it playing a major role in the development of mesoporous perovskite architectures. TiO$_2$ has been the dominate ETL material used for mesoporous architectures that are effective, but complex requiring time-consuming methods and high-temperature sintering. This renders mesoporous structures unsuitable for scaling up perovskite solar cells for commercial use.

Transitioning from the complex mesoporous scaffold to a simpler planar structure was demonstrated as feasible by Snaith et al. in 2013. Their initial report on planar PSCs employed TiO$_2$ as a compact layer and achieved a power conversion efficiency (PCE) of 4.9%.$^{84}$ Snaith et al. followed this initial result with a vapor phase deposited perovskite on compact TiO$_2$ resulting in a PCE of over 15% accompanied by an open circuit voltage of 1.07 V.$^{85}$ This research signified a paradigm shift in perovskite solar cell research, with a simplified planar structure being sufficient to achieve highly efficient perovskite solar cells.

Following this innovation, researchers began to investigate other low-temperature processable ETLs such as ZnO, PCBM, and SnO$_2$ as potential alternatives to TiO$_2$ for use in simple planar structures. Currently, tin(IV) oxide (SnO$_2$) has emerged as a prominent ETL alternative to titanium dioxide (TiO$_2$) and zinc oxide (ZnO) in PSCs, with the highest reported PCE of 25.7% in single-junction planar structures.$^{86}$ SnO$_2$ is a wide bandgap n-type semiconductor (3.5-4.0 eV) that aligns with the conduction band of the perovskites.
and is transparent to most visible and UV light. It also has been reported to have high electron mobility (200 to 250 cm$^2$/V•S) while being able to be processed at low temperatures.$^{87}$

SnO$_2$ exhibits superior photostability compared to TiO$_2$, particularly towards ultraviolet (UV) light. This increased photostability addresses the issue of light-induced degradation, a significant problem reported for TiO$_2$ based PSCs.$^{88}$ Chemically, SnO$_2$ exhibits good stability in the presence of moisture and oxygen and its hygroscopic nature is less pronounced compared to TiO$_2$ and ZnO, making it less prone to degradation in ambient environments.$^{89}$ When compared to fullerene derivatives, SnO$_2$, displays superior thermal and chemical stability. This enhanced stability can potentially lead to improved long-term performance and reduced degradation of PSCs.

The processing temperature requirements for SnO$_2$ are also lower than those for TiO$_2$, broadening the range of viable substrates for PSCs fabrication, to include flexible and temperature-sensitive polyethylene terephthalate (PET) based substrates. SnO$_2$ as an ETL is amenable to a wide variety of deposition methods, such as spin-coating, spray coating, blade coating, and slot die coating. This adaptability introduces greater flexibility into the fabrication process, but most work with SnO$_2$ uses the n-i-p configuration as the deposition of SnO$_2$ on top of a perovskite is challenging. Finally, SnO$_2$ is non-toxic and environmentally friendly, characteristics that enhance its suitability as an ETL material for large-scale production and application of PSCs.

The low-temperature fabrication methodologies of SnO$_2$ have provided its suitability for the development of flexible PSCs on low temperature substrates.$^{90, 91}$
Standard flexible plastic substrates like PET (Tg: 70–110 °C) and polyethylene naphthalate (PEN) (Tg: 120–155 °C) are capable of withstanding limited heating, but are incompatible with higher temperature precursor or mesoporous annealing conditions. Low temperature work by Song et al. and Qi Jiang et al. have demonstrated up to 21.6% PCE using commercially available SnO₂ nanoparticles. As flexible modules and roll-to-roll processing become more common, colloidal SnO₂ nanoparticles have been deemed a promising route to formulate the ETL for flexible PSCs. The utilization of nanoparticles circumvents the high-temperature sintering process, which would otherwise be integral in the transition from precursors to SnO₂ films. Additionally, pre-synthesized nanoparticles can be suspended in an array of solvents that are compatible with perovskite enabling direct coating on the perovskite layer to serve as an upper CTL. Consequently, the utilization of pre-synthesized SnO₂ nanoparticles simplifies the process and holds the potential to shorten the total fabrication time.

The synthesis of SnO₂ nanoparticles is generally achieved through precipitation, solvothermal, hot injection, and the inverse micelle-water injection methods. These processes result in the formation of pre-synthesized SnO₂ nanoparticles, which are subsequently deposited onto a substrate to form a film. A distinct advantage of synthesized nanoparticles is the ability to engineer surface ligands and solubility to fit a desired application (Table 1.3). An example of this is the work of Xie et al. where they developed highly crystalline SnO₂ nanoparticles with superior dispersibility in non-polar solvents utilizing a solvothermal method. Using spin-coating they were able to deposit a high quality SnO₂ film on ITO-PEN that had a PCE of 13.90%. Park et al. engineered ultrafine SnO₂ quantum dots (QD) capped with a liable ligand where the ligands spontaneously
exchanged with halides in a perovskite solution as part of the coating process, leading to an appropriate SnO2 QD–halide junction resulting in a PCE of 17.7% with a short current density ($J_{sc}$) of 19.7 mA cm$^{-2}$, $V_{oc}$ of 1.13 V, and a fill factor (FF) of 79.0%. $^90$

Along with ligands and solubility, the electrical properties of nanoparticles can be tuned by the introduction of dopants to the crystal lattice. Doping of semiconducting metal oxides (MO$_x$) effectively modulates electrical properties such as carrier concentration and electron mobility, in addition to altering optical and structural properties. Common doping methodologies can be categorized as equivalent cation doping in which the material is doped with an ion of the same oxidation state, and nonequivalent cation doping in which the material is doped with an ion of higher or lower oxidation state. Equivalent cation doping improves defect densities, improves carrier mobility, and induces alterations in the energy band structure, which can lead to diminished trap-state density and promoted energy band alignment with perovskite. Noh et al. demonstrated Zr doping in SnO$_2$ that resulted in a conduction band up shift which increased the built in potential and improved the band alignment with the perovskite with a champion device achieving a PCE of 19.54%. $^97$
Table 1.3. Survey of recent works using SnO$_2$ nanoparticles as the ETL. SC: Spin-coating.

<table>
<thead>
<tr>
<th>Device architecture</th>
<th>Deposition</th>
<th>Processing</th>
<th>$J_{sc}$ mA/cm$^2$</th>
<th>$V_{oc}$ V</th>
<th>FF %</th>
<th>PCE %</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb:SnO$_2$/MAPbI$_3$/ spiro-OMeTAD/ Au</td>
<td>SC</td>
<td>100°C, 30 min</td>
<td>22.6</td>
<td>1.06</td>
<td>72.0</td>
<td>17.2</td>
<td>98</td>
</tr>
<tr>
<td>PEN/ITO/MAPbI$_3$/ spiro-OMeTAD/ Au</td>
<td>SC</td>
<td>80°C, 15 min</td>
<td>19.7</td>
<td>1.13</td>
<td>79.0</td>
<td>17.7</td>
<td>90</td>
</tr>
<tr>
<td>ITO/SnO$_2$/(FAPbI)$_x$ (MAPbBr$<em>3$)$</em>{1-x}$/ Spiro-OMeTAD/ Au</td>
<td>SC</td>
<td>150°C, 30 min</td>
<td>24.87</td>
<td>1.09</td>
<td>74.77</td>
<td>20.2</td>
<td>93</td>
</tr>
<tr>
<td>ITO/SnO$_2$/(FAPbI)$_x$ (MAPbBr$<em>3$)$</em>{1-x}$/Spiro-OMeTAD/ Au</td>
<td>SC</td>
<td>150°C, 30 min</td>
<td>25.2</td>
<td>1.18</td>
<td>78.4</td>
<td>23.32</td>
<td>99</td>
</tr>
<tr>
<td>ITO/SnO$_2$/ MAPbI$_3$/Spiro-OMeTAD/ MoOx/Ag</td>
<td>Slot-die</td>
<td>Air-knife, IPL</td>
<td>23.70</td>
<td>0.91</td>
<td>52.0</td>
<td>11.24</td>
<td>55</td>
</tr>
<tr>
<td>ITO/SnO$_2$/ MAPbI$_3$/Spiro-OMeTAD/ Au</td>
<td>Blade</td>
<td>100°C</td>
<td>22.86</td>
<td>1.124</td>
<td>76.17</td>
<td>19.6</td>
<td>100</td>
</tr>
<tr>
<td>ITO/SnO$<em>2$/ Cs$</em>{0.05}$FA$<em>{0.85}$ MA$</em>{0.15}$Pb$<em>{1.85}$ Br$</em>{0.15}$/ Spiro-OMeTAD/Au</td>
<td>Spray</td>
<td>150°C, 30 min</td>
<td>23.35</td>
<td>1.14</td>
<td>66.6</td>
<td>17.78</td>
<td>101</td>
</tr>
</tbody>
</table>

| Glass/ ITO/ NiO$_x$/ MAPbI$_3$/ ZnO/ Al | SC | N/A | 21.0 | 1.01 | 76 | 16.1 | 102 |
| Glass- ITO/ PTAA/PFN/ MAPbI$_3$/ SnO$_2$-A/Ag. | Blade | 100°C, 10 min | 22.6 | 1.02 | 61.0 | 14.1 | 103 |
| PET/ ITO/ PTAA/ PFN/MAPbI$_3$/ Y:SnO$_2$-A/ BCP/Ag | Blade | 100°C 2 min | 22.38 | 1.08 | 68.4 | 16.5 | 104 |
| PET/ITO/ PTAA/PFN/ FAMAPbIBr/ Y:SnO$_2$-A/ BCP/Ag | Blade | IPL | 23.7 | 1.09 | 65.7 | 16.9 | 105 |
Nonequivalent doping directly effects the electron density of the conduction band. Specifically, the incorporation of lower valence cations such as Li$^+$, Mg$^{2+}$, Zn$^{2+}$, Y$^{3+}$, and Al$^{3+}$ into the crystal lattice of tetravalent Sn$^{4+}$ or Ti$^{4+}$ results in p-type doping, while the incorporation of higher valence cations like Nb$^{5+}$, and W$^{6+}$ yields n-type doping. The incorporation of higher valence cations, n-type doping, enhances the electron density causing a more positive shift in the conduction band. Together the shifted conduction band and increased electron density increase film conductivity. Ren and associates report a 2.44% increase in PCE using Nb-doped SnO$_2$. P-type doping decreases the electron density of the conduction band while upshifting the Fermi level and decreasing the oxygen vacancies. This promotes electron transport while impeding charge recombination at the ETL/perovskite interface. Yang et al. reported the Y doping led to a more positive conduction band minimum in Y-SnO$_2$ improving conductivity and charge extraction.

A recent significant achievement by Chapagain et al. has led to the development of a SnO$_2$ nano dispersion compatible with solution coating on the perovskite surface. Synthesized via a sol-gel technique and subsequently functionalized with acetic acid, the resulting nanoparticles were functionalized with acetate ligands (SnO$_2$-A). This functionalization permitted the formation of a stable colloidal dispersion of SnO$_2$-A in anhydrous ethanol. The photovoltaic performance of devices fabricated using this approach attained a maximum PCE of 14.1%. Device efficiency was impeded by a relatively high series resistance, a consequence of insufficient crystallinity associated with the lower-temperature annealing employed for the solution-processed SnO$_2$ nanoparticles in contrast to the high-temperature annealed SnO$_2$. To enhance the performance of the low-temperature synthesized SnO$_2$, yttrium was incorporated into the SnO$_2$ crystal lattice at an optimized
concentration of 2 mol%. After the yttrium doping, the performance of the low-temperature processed flexible PSCs on PET-ITO substrates increased from 14.3% to 16.5%.\(^{104}\)

The extended annealing time required by different layers constitutes a significant limiting factor for the rapid, scalable production of PSCs on flexible substrates utilizing high-throughput printing techniques such as the roll-to-roll method. To address this area, Martin et al. implemented intense pulsed light (IPL) for rapid annealing of the perovskite absorber layer.\(^{105}\) Utilizing rapid IPL annealing of the perovskite active layer and top coated Y:SnO\(_2\)-A a PCE of 16.7% was achieved for blade-coated, flexible, mixed-cation PSCs on ITO-PET substrates in a p-i-n structure.\(^{105}\) Annealing of the SnO\(_2\) was facilitated by the perovskite absorbing the photonic energy of the IPL and super heating at the surface.

Bu et al. demonstrated an interface passivation strategy with potassium treatments for SnO\(_2\) ETLs to obtain high-efficiency and hysteresis-free low-temperature fabricated PSCs. After the treatment of pre-synthesized SnO\(_2\) with potassium, they were able to achieve a PCE of 20.50% for rigid PSCs and a PCE of 17.18% for flexible PSCs on a small area device of 0.16 cm\(^2\). Additionally, they also obtained a high PCE of 15.22% for flexible PSCs based on slot-die-coated commercial SnO\(_2\) and a PCE of 14.89% with their synthesized SnO\(_2\) nanoparticles. The addition of the K ions in the interface forms KBr that thus passivates the surface defects of the perovskite to promote high performance and hysteresis-free properties.\(^{112}\)

Dou et al. demonstrated blade coating of a commercial SnO\(_2\) nanoparticle dispersion achieving a PCE up to 19.6% with an \(V_{oc}\) of 1.124 V. Using a slot-die coating on glass-ITO/SnO\(_2\), they achieved a PCE of 17.31% and \(V_{oc}\) of 1.111 V, and FF of 69.5%.\(^{100}\)
Taheri et al. developed a simple and scalable deposition approach based on automated spray-coating to prepare uniform and dense SnO$_2$ ETLs achieving a PCE of 15.3% on a flexible substrate with reduced device hysteresis.$^{113}$

Overall, pre-synthesized SnO$_2$ nanoparticle dispersions are emerging as an ideal material for the ETL in PSCs. The employment of nanoparticles circumvents the need for a high-temperature sintering process, typically obligatory in the conversion from precursor to SnO$_2$ nanoparticles. The low-temperature fabrication methodologies associated with SnO$_2$ emphasize its suitability for the development of flexible PSCs on substrates comprised of low-melting PET. Nevertheless, the use of SnO$_2$ nanoparticles as an ETL in PSCs has predominantly been as a base layer directly on the substrate.

The main challenges in the adoption of SnO$_2$ as an ETL in p-i-n devices are solvent incompatibility with the perovskite layer and annealing conditions. Solvent incompatibility can be addressed through ligand design as demonstrated with SnO$_2$-A. Annealing is a major issue as SnO$_2$ nanoparticles that are either left unannealed or annealed at low temperatures tend to suffer from poor conductivity and overall diminished performance. Thus, future research endeavors should prioritize the enhancement of the performance of these nanoparticle. One possible avenue for such improvement could involve modifying the electronic properties through elemental doping or by annealing low temperature processed SnO$_2$ ETL. The traditional method of hotplate annealing proves ineffective for annealing SnO$_2$ on the perovskite layer due to the degradation of perovskite at high temperatures. Thus, it becomes necessary to explore alternate annealing techniques apart from hotplate annealing, such as the IPL method.
Annealing of the SnO$_2$ layer is also critical for device durability as incomplete annealing can exhibit porous characteristics, potentially falling short of providing an adequate barrier to prevent interaction between the top metal contact and perovskite. Hence, further studies are needed to understand the possible interaction at the perovskite/SnO$_2$/silver interface. The potential interaction can be circumvented by engineering an appropriate interface between either the perovskite and SnO$_2$, or the SnO$_2$ and Ag. Lastly, a critical area of study is the long-term stability of PSCs when using SnO$_2$ as the top layer. This investigation is vital to ensure the extended functionality and viability of these solar cells.

1.9.3 Hole Transport Layers

HTL materials face many of the same considerations as ETLs but with the electronics targeting hole transport instead of electron transport.

1.9.3.1 Types of HTL Materials

Favored for their stability over organic alternatives and good band alignment with the valence band of the perovskites; NiO$_x$, Cu$_x$O, Cul, CuSCN, and CuS, have been explored as HTLs through a variety of methods. Inorganic copper salts such as CuSCN, CuI, and CuS have shown promise as inorganic options for devices of n-i-p configuration.\textsuperscript{114} However, they struggle with conductivity and reactivity with deposited metal contacts. Copper oxide nanoparticles are also an active field of work with delafossite like composition (CuM$^{3+}$O$_2$) recently emerging as a promising solution to the instability of Cu$_2$O.\textsuperscript{115} To date, copper oxide nanoparticles trail nickel oxide (NiO$_x$) in terms of conductivity and device performance, which has been the most successful inorganic HTL
to date. Due to its natural self-doping p-type character NiO\textsubscript{x} has shown high hole carrier densities, conductivity, and good band alignment with perovskites. NiO\textsubscript{x} has a tunable valence band that sits at 5.2 eV which is just above the valence band of MAPbI\textsubscript{3} which sits at ~5.4 eV the ideal location for proper p-type conduction.\textsuperscript{116} The band gap of NiO\textsubscript{x} is also large at 3.5 eV which places the NiO\textsubscript{x} conduction band well above that of the perovskites thus providing a blocking layer for reverse flow of electrons to the electrode.\textsuperscript{116} These properties make it a natural choice for use as an HTL.

There are several organic alternatives available for the HTL, such as 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS), polytriarylamine (PTAA), and polythiophene (PT).\textsuperscript{116-119} For devices of n-i-p configuration spiro-OMeTAD and PEDOT-PSS are the most commonly used. However, both struggle with charge carrier concentrations and require doping with Li salts to improve conductivity. The addition of Li\textsuperscript{+} increases the already hydroscopic nature of the perovskite accelerating its degradation.\textsuperscript{116} While highly effective, the natural instability of the organic HTLs makes them unappealing for longer term solar applications. As such, NiO\textsubscript{x} is widely used in perovskite research; often as independent HTLs or in conjunction with an organic polymers like PTAA.\textsuperscript{120} Coated primarily by spin-coating, many devices using NiO\textsubscript{x} have exceed 20% on both glass and flexible substrates.\textsuperscript{120-126}

1.9.3.2 NiO\textsubscript{x}

From a fabrication perspective, controlling film formation to ensure a uniform surface for perovskite growth is highly important in reducing propagation of defects, such as pinholes. Defects in the HTL can result in drops in the $V_{oc}$ and shunt resistance and
significant increases in series resistance. This is especially a challenge for the fabrication of NiO$_x$ HTLs from nanoparticle solutions using blade coating or slot die coating, which to date have not surpassed spin-coated devices in performance. However, progress is being made and Yang et al. reported in 2022 a PCE of 19.87% on a fully blade coated flexible stack. Thus developing methods to optimize the NiO$_x$/perovskite interface, improve film uniformity, control band alignment and conductivity are all active areas of NiO$_x$ research.

While our focus will be on nanoparticles, we would be remiss to ignore work that has been done with precursor deposition methods. Precursor deposition is a popular method for NiO$_x$ film formation as it bypasses the often-tedious cleaning process and directly forms the NiO$_x$ film on the desired substrate. This has the advantage of being able to form highly uniform films with few defects. However, this method has a high thermal cost (300-600 °C) and long annealing time (1-3 hours) that make it incompatible with flexible substrates. Work with photonic curing by Piper et al. has presented some promising results by reducing the annealing time to several seconds instead of hours. However, there is still space for significant development from their work as they were only able to produce devices with about 12% PCE. A recent example of work done using precursor inks, is the work of Li et al. with utilizing urea to passivate surface defects on the NiO$_x$ surface. Their resulting devices achieved a champion PCE of 23.61% and a FF of 85.4%.

While precursor-based inks have demonstrated remarkable efficiency, so to have nanoparticle-based inks without the high thermal cost. An advantage of working with nanoparticles is the versatility they offer as composite coatings with other HTL materials or by functionalization of the particle surface. An active area of current research is in the
passivation of defects at the NiOx/perovskite interface. Whether by doping or introducing a passivator into the NiOx ink prior to coating, nanoparticles can be customized to address the specific needs of the application.

The most common method for synthesizing NiOx nanoparticles is the low temperature precipitation method. In general a nickel salt is dissolved in water then precipitated by the addition of base to form Ni(OH)2. The cleaned Ni(OH)2 is then annealed at >270 °C to convert to the oxide, and suspended in water for coating. Controlling the particle surface through selection of the counter anions or introduction of ligands to the reaction mixture is critical for forming small, stable particles. In 2021, Guo et al. demonstrated an average 2% PCE increase when using nitrate vs chloride. Their further analysis shows a direct relationship between ink stability and the identity of the initial counter anion. Addition of ligands prior to precipitation has also been shown to effectively control particle growth. Cui et al. has taken this one step further by using alkylammonium hydroxides as the base to introduce alkylammonium ligands during precipitation. The resulting particles were tunable within a couple of nm in size and had a valence band maximum downshift of 0.26 eV. Their champion devices reached a PCE of 22%, with a dual NiOx/PTAA HTL layer.

An alternative synthetic method, solvothermal synthesis, offers more control to the synthesis conditions. Usually centered around decomposing or reducing an oxygen containing metallo-organic salt, reactions are carried out at high temperatures and often in the presence of secondary reducing agents. The added control comes from the organics acting as coordinated ligands controlling particle growth. While solvothermal synthesis can provide control over particle morphology and properties, the poor atom
economy, high energy costs and often poor yields make this synthesis route undesirable for larger applications and its use for future perovskite development is limited.

An additional property that is important to control in the particles during synthesis is the Ni\textsuperscript{2+}/Ni\textsuperscript{3+} ratio, which produces the innate p-type character of NiO\textsubscript{x}.\textsuperscript{118, 136-138} Doping with transition metals such as Co,\textsuperscript{139} V,\textsuperscript{140} and Cu,\textsuperscript{123, 137} have been found to induce changes in the Ni\textsuperscript{2+}/Ni\textsuperscript{3+} ratio while also improving conductivity.\textsuperscript{138} A seminal investigation by Chen et al. in 2018 revealed important insights into the mechanism of Cu doping.\textsuperscript{137} Utilizing DFT to calculate the density of states, they found a shift in gap state positions of NiO\textsubscript{x} from 1.3 eV to 0.7eV in Cu:NiO\textsubscript{x}. This shift resulted in shallower acceptor levels which would likely lead to improvements in conductivity and the work function. Investigations by XPS showed no significant change in the Ni\textsuperscript{2+}/Ni\textsuperscript{3+} peak ratio, which was observed in prior studies, but did confirm the presence of both Cu\textsuperscript{2+} and Cu\textsuperscript{+} indicating that the change in conductivity is likely related to the copper oxidation state.\textsuperscript{141} The exact mechanism for increasing conductivity from transition metal doping is still debated but studies like Zhang et al. on Li doped films in 2018 help to identify contributing features for alkali metal doping. They found that the addition of Li increased hole type carriers while shifting the valence band maximum towards the Fermi energy.\textsuperscript{142}

While optimizing the ratio of Ni\textsuperscript{2+}/Ni\textsuperscript{3+} is important for high charge carrier density and conductivity, Ni\textsuperscript{3+} at the perovskite interface has been found to induce device degradation. First reported by Boyd et al. in 2020, the presence of Ni\textsuperscript{3+} sites at the film surface are highly reactive oxidants that can degrade the perovskite rapidly.\textsuperscript{143} A similar report by Hsu et al. in 2020 also demonstrated this degradation by tracking reaction
byproducts by MS-FTIR. Boyd and Hsu both found that degradation is taking place through the A site cation with reactions being localized at the perovskite surface.

To date spin-coated films have made up the majority of NiO\textsubscript{x} coatings (Table 1.4). While spin-coating is effective at forming uniform coatings, this method limits scalability and the results are often difficult to translate to larger area deposition methods. Other methods being explored are spray pyrolysis, blade/meniscus coating, and slot die roll-to-roll. Improving the uniformity and speed of these methods are major targets for the research community.

While annealing free devices have been known for decades using particles prepared by precipitation, the addition of ligands or solvothermal based ligands require thermal annealing following deposition. Annealing plays an important role in controlling the Ni\textsuperscript{2+}/Ni\textsuperscript{3+} ratio. One drawback of the post treatment free approach is the lack of control of this ratio. To address this challenge, the use of UV-O\textsubscript{3} post treatment is being explored in solgel systems. In 2017 Islam et al. studied the effects of UV-O\textsubscript{3} treatment on NiO\textsubscript{x} films in which they analyzed the change in resistance and XPS peak intensity in relation to treatment duration. They found a 10-fold reduction in resistance after 10 min of UV-O\textsubscript{3} treatment, then 10-fold again after 60 min of treatment. They also reported a significant shift in the Ni\textsuperscript{2+}/Ni\textsuperscript{3+} ratio with increasing Ni\textsuperscript{3+} species found. Using glancing angle XPS they identified that the Ni\textsuperscript{3+} is predominantly generated at the film surface, but that it penetrates the film bulk as well. Taking note of these results and applying similar methods to nanoparticles based films could be advantages for continued improvements.
1.10 Summary

Perovskites are an emerging solar technology that has the potential to rapidly increase solar production as a low cost, effective alternative to traditional crystalline silicon. To reach these goals development of solvent systems for large scale coating applications that maintain control of film formation while reducing processing time is necessary. In this dissertation these goals are approached for the application of NiO$_x$ as a hole transport layer. Emphasis is placed on film quality as interfacial defects are among the leading causes of charge recombination and performance loss.
### Table 14. Survey of recent works using NiOx as the HTL. SC: Spin-coating.

<table>
<thead>
<tr>
<th>Device architecture</th>
<th>HTL</th>
<th>Deposition</th>
<th>Processing</th>
<th>$J_{sc}$ mA/cm²</th>
<th>$V_{oc}$ V</th>
<th>FF %</th>
<th>PCE %</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass/ ITO/ NiOx-Urea/ CsFAMAPbI/Br2-MIM Br/ C60/ BCP/ Ag</td>
<td>Precursor</td>
<td>Spray Pyrolysis</td>
<td>400C, 20 min</td>
<td>24.04</td>
<td>1.15</td>
<td>85.4</td>
<td>23.61</td>
<td>129</td>
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<tr>
<td>glass/ ITO/ NiOx/ triple-cation perovskite/ PCD6BM/ ZnO NPs/ Ag</td>
<td>Precipitation, Precursor</td>
<td>SC</td>
<td>350C, 30 min or 300C, 45 min</td>
<td>24.34</td>
<td>1.06</td>
<td>79.18</td>
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<td>157</td>
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<tr>
<td>Glass/ NiOx/ CsFAMAPbIBr/ PCBM:C60/ BCP/ Au</td>
<td>Precipitation</td>
<td>SC</td>
<td>100C, 10 min</td>
<td>23.49</td>
<td>1.15</td>
<td>84.68</td>
<td>22.81</td>
<td>153</td>
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<td>Glass/ ITO/ NiOx/ PTAA/ CsFAMAPbIBr/ PCBM/ Ag</td>
<td>Precipitation</td>
<td>SC</td>
<td>150C, 20 min</td>
<td>24.52</td>
<td>1.13</td>
<td>82</td>
<td>22.71</td>
<td>120</td>
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<tr>
<td>Glass/ ITO/ NiOx/ CsFAMAPbIBr/ C60/ BCP/ Cu</td>
<td>Precipitation</td>
<td>SC</td>
<td>180C, 10 min + 400C, 45 min or UV lamp 10min</td>
<td>24.25</td>
<td>1.126</td>
<td>82.19</td>
<td>22.45</td>
<td>156</td>
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<tr>
<td>Glass/ ITO/ NiOx/ CBSA/ CsFAMAPbIBr/ PCBM/ BCP/ Ag</td>
<td>Precipitation</td>
<td>SC</td>
<td>130C, 20 min</td>
<td>23.72</td>
<td>1.11</td>
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<td>21.8</td>
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<td>Glass/ ITO/ NiOx/ TMPA/ MAPbI/ PCBM/ BCP/ Ag</td>
<td>Precipitated</td>
<td>SC</td>
<td>No Anneal</td>
<td>23.7</td>
<td>1.07</td>
<td>80.4</td>
<td>20.4</td>
<td>154</td>
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<td>PEN/ hc-PEDOT:PSS/ NiOx/Cs0.05Fa0.85Ma0.10Pb(I0.97Br0.03)3/ PCBM/ Ag</td>
<td>Precipitation</td>
<td>Blade Coated</td>
<td>130 C, 30 min</td>
<td>23.74</td>
<td>1.12</td>
<td>74.7</td>
<td>19.87</td>
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<tr>
<td>Glass/ ITO/ Li:NiOx/ NiOx/ FAMAPbIBr/ PCBM/ BCP/ Ag</td>
<td>Precipicator</td>
<td>SC</td>
<td>120 C, 10 min + 2nd coat 450 C, 1h</td>
<td>23.22</td>
<td>0.99</td>
<td>82.83</td>
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<td>Glass/ ITO/ V:NiOx/ MAPbI/ PCBM/ BCP/ Ag</td>
<td>Solvothermal</td>
<td>SC</td>
<td>25C, 15 min + UV-Vis 20min</td>
<td>19.81</td>
<td>1.04</td>
<td>75</td>
<td>15.45</td>
<td>140</td>
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<td>Glass or PET/ ITO/ NiOx/ MAPbI3,Clx/ PCBM-C60/ Zracac/ Ag</td>
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<td>SC</td>
<td>No Anneal</td>
<td>23.16/ 22.02</td>
<td>1.11/ 1.06</td>
<td>81/ 78</td>
<td>20.8/ 18.16</td>
<td>123</td>
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<td>Glass/ ITO/ NiOx/ Cs0.05Ma0.16Fa0.87Pb1.03(Br0.16I0.86)3/ LiF/ C60/ BCP/ Ag</td>
<td>Precipicator, Sputtered, Precipitation</td>
<td>SC</td>
<td>400C, 50 min; Particles: No Anneal</td>
<td>19.56</td>
<td>1.15</td>
<td>84.7</td>
<td>19.06</td>
<td>143</td>
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</table>

#### Inverted (N-I-P) architecture

<table>
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<tr>
<th>Device architecture</th>
<th>HTL</th>
<th>Deposition</th>
<th>Processing</th>
<th>$J_{sc}$ mA/cm²</th>
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<th>FF %</th>
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</thead>
<tbody>
<tr>
<td>Glass/ ITO/ TiO2/ MAPbI/ NiOx/ Au</td>
<td>Precipitation</td>
<td>SC</td>
<td>100C, 5 min</td>
<td>23.59</td>
<td>0.885</td>
<td>60.1</td>
<td>12.57</td>
<td>131</td>
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</tbody>
</table>
CHAPTER 2.0 EXPERIMENTAL METHODS

2.1 Experimental Methods for Chapter 3

This section describes methods of synthesis and sample preparation used in “Solvation of NiOₓ for hole transport layer deposition in perovskite solar cells” by Armstrong et al.¹⁵¹

Physical characterization methods are described in section 2.4.

2.1.1 Synthesis

This section describes methods of synthesis for Xanthates, Carbonates, NiOₓ nanoparticles, and associated inks.

2.1.1.1. Xanthate

The potassium xanthates salts were prepared from potassium hydroxide, carbon disulfide, and the appropriate alcohol using reported methods. Xanthates with 4- and 12-carbon chains were isolated as yellow solids as described by Carta.¹⁵⁹ The 18-carbon chain xanthates was prepared as reported by Sawant as white solids.¹⁶⁰

4X. Butanol (25 mmol, 1.85g) and potassium hydroxide (25 mmol, 1.40 g) were mixed in diethyl ether (10mL) and stirred for 1.5 hours. Carbon disulfide (27.5 mmol, 2.06g) was added dropwise inducing precipitation. Resulting slurry was allowed to stir for 2 hours prior to filtering and washing with cold diethyl ether. Yield of C₄H₉CS₂K = 72.2% (18.0 mmol, 3.397 g).
12X. Dodecanol (25 mmol, 4.66g) and potassium hydroxide (25 mmol, 1.40 g) were mixed in toluene (10mL) and stirred for 30 min. Carbon disulfide (27.5 mmol, 2.06g) was added dropwise inducing precipitation. Resulting slurry was allowed to stir for 2 hours prior to filtering and washing with by alternating hexane and water washes. Yield of C₁₂H₂₅CS₂K = 65.7% (16.4 mmol, 4.939 g).

18X. Octadecanol (6.6 mmol, 1.83g) and potassium hydroxide (6.6 mmol, 0.41 g) were heated to 150°C until fully melted and mixed. The mixture was then cooled to 100 °C before adding toluene (4mL). Carbon disulfide (9.8 mmol, 0.74g) was added dropwise inducing precipitation. Resulting slurry was allowed to stir for overnight prior to filtering and washing with hexane. Yield of C₁₈H₃₇CS₂K = 32.7% (3.2 mmol, 1.25 g).

2.1.1.2. Carbonates

The sodium carbonate salts were prepared as flaky, white solids from sodium phenoxide, carbon dioxide, and the appropriate alcohol according to the method reported by Ichiro. Sodium alkyl carbonate salts were prepared through the nucleophilic attack of n-butyl alcohol (4C), n-dodecyl alcohol (12C), and n-octadecyl alcohol (18C) on carbon dioxide. Addition of the carbonates to the 0X suspension results in a clear, colorless suspension following filtration.

4C. Butanol (40 mmol, 3.71g) and sodium phenoxide (30 mmol, 3.48g) were mixed in tetrahydrofuran (10mL) and stirred until dissolved. Carbon dioxide was purged through the solution immediately inducing precipitation. Solid was collected by filtering and washing with diethyl ether. Yield of C₄H₉CO₂Na = 29.6% (11.8 mmol, 1.67 g).
12C. Dodecanol (40 mmol, 7.38 g) and sodium phenoxide (20 mmol, 2.32 g) were mixed in toluene (20 mL) and stirred until dissolved. Carbon dioxide was purged through the solution immediately inducing precipitation. Solid was collected by filtering and washing with diethyl ether. Yield of C_{12}H_{25}CO_2Na = 24.6% (9.87 mmol, 2.5 g).

18C. Octadecanol (6 mmol, 1.62 g) and sodium phenoxide (3 mmol, 0.35 g) were mixed in acetone (10 mL) and stirred until dissolved. Carbon dioxide was purged through the solution immediately inducing precipitation. Solid was collected by filtering and washing with cold diethyl ether and acetone. Yield of C_{18}H_{37}CO_2Na = 43.7% (1.3 mmol, 0.443 g).

2.1.1.3. Solvothermal decomposition NiO_x

NiO_x particles were synthesized using the solvothermal method reported by Beach et al.\textsuperscript{135} as described below.

NiO_x. Nickel acetylacetonate (Ni(acac)\textsubscript{2}) was dissolved in methyl ethyl ketone (MEK) to form a 0.1 M solution. The resulting solution was sparged with N\textsubscript{2} gas for 30 minutes and then sealed in a Teflon lined Parr reactor. The reactor was heated at 225 °C for 16 – 18 hours. The reactor was cooled to room temperature and the resulting product isolated from the solution by centrifugation for 15 minutes. The crude NiO_x product was cleaned by repeated suspension/isolation with MEK and isopropanol. After cleaning the collected NiO_x was dried in a vacuum oven at 80 °C overnight. Yield of NiO_x = 0.104 g, 9.3%
2.1.1.4. Ink preparation

The NiO\textsubscript{x} inks were prepared by sonication of NiO\textsubscript{x} particles (20 mg) in 200 µL of a 3:1 (v/v) Et\textsubscript{3}N/EtOH mixture for 60 minutes at 65 °C in a closed vial. The resulting suspension was diluted with 700 µL chlorobenzene (CB) and 100 µL EtOH to make a 20 mg/mL NiO\textsubscript{x} solution. For NiO\textsubscript{x} inks containing xanthate ligands, 0.125 eq. of ligand was added to the CB in the dilution step. After dilution, the suspensions were sonicated with heating at 65°C. During this step, inks containing xanthate ligands underwent a color change from tan to dark brown. The hot ink suspensions were filtered through 0.2 µm PTFE prior to blade coating. The perovskite ink was prepared by dissolving PbI\textsubscript{2} and MAI in dimethyl sulfoxide (DMSO, 7%), N-methyl-2-pyrrolidone (NMP, 2%), and dimethylformamide (DMF, 91%) to make a 1.2 M solution by gentle stirring\textsuperscript{162}.

2.1.2 Device Fabrication

Films were deposited using an air knife equipped Zehntner ZAA 2300 Automatic film applicator and ZUA 2000 Universal Applicator.

Devices with p-i-n architecture Glass/ITO/NiO\textsubscript{x}/PFN/MAPbI\textsubscript{3}/C60/BCP/Ag where PFN and BCP are poly[(9,9-bis(3’-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] and bathocuproine, respectively, were prepared. The ITO coated glass was cut into 1” x 2” substrates that were cleaned by N\textsubscript{2} flush, followed by UV-O\textsubscript{3} treatment for 15 minutes and a second N\textsubscript{2} flush. No further steps were taken to clean the ITO substrates. The cleaned ITO substrates were immediately used for sequential deposition of NiO\textsubscript{x}, PFN, and MAPbI\textsubscript{3} by blade coating.
40 µL inch⁻² of the NiOₓ inks were deposited by blade coating using an optimized blade gap of 225 µm at a speed of 5 mm sec⁻¹ followed by annealing on a hotplate at 300 °C for 20 minutes. Next, a layer of PFN (4 mg/mL in methanol) was deposited by blade coating with a blade gap of 100 µm at a speed of 7.5 mm sec⁻¹. The perovskite was deposited by blade coating with a blade gap of 100 µm at a speed of 7.5 mm sec⁻¹ with an air knife set to 40 psi. The air knife was passed multiple 4-5 times across the sample before transferring to a hotplate for annealing at 140 °C for 2 min. Devices were completed by thermally evaporating C60 (20 nm), BCP (5 nm), and Ag (100nm) followed by mechanical scribing into an active area of 0.25 or 1 cm² cells.

The n-i-p devices with a glass/ITO/SnO₂/MAPbI₃/NiOₓ/Ag architecture were constructed using 20 µL inch⁻² of 3% (wt%) commercial SnO₂ nanoparticles as the ETL. Optimized SnO₂ films were deposited using blade coating with a blade gap of 100 µm blade gap at 5 mm sec⁻¹ on a 100°C heated stage followed by annealing at 150 °C for 1 hour. All other layers were deposited in the same manner as for p-i-n devices.

2.2 Experimental Methods for Chapter 4

This section describes methods of synthesis and sample preparation used in “Scalable Solution Processing of Cu:NiOₓ Nanoparticles for Perovskite Solar Cells” by Armstrong et al.

2.2.1 Synthesis

This section describes methods of synthesis for copper doped NiOₓ (Cu:NiOₓ) nanoparticles, and yttium doped SnO₂ (Y:SnO₂) and associated inks
2.2.1.1 Copper doped NiO$_x$

Cu: NiO$_x$ particles were prepared via a classical precipitation method. Briefly a solution of Ni(NO$_3$)$_2$ (0.5 M) with 5 mol% Cu(NO$_3$)$_2$ was titrated with NaOH (1M) until a pH of 10 was reached. The resulting precipitation of Cu:Ni(OH)$_2$ was then collected by centrifuge and washed by repeatedly resuspending and collecting from water. After washing, the precipitate was dried overnight in an oven at 80 °C. The dried Cu:Ni(OH)$_2$ was then converted to the oxide by annealing in a 270 °C furnace for 20 min. The resulting Cu: NiO$_x$ particles were then suspended in solution by sonication.

2.2.1.2. Y:SnO$_2$

The Y:SnO$_2$ was synthesized according to reported procedures$^{104}$ as described below.

Y:SnO$_2$ nanoparticles were synthesized by neutralizing 1M aqueous tin (IV) chloride solution with 5M sodium hydroxide solution. The yttrium doping was accomplished by adding 2 mol% yttrium (III) chloride hydrate to the tin (IV) chloride solution prior to neutralization. The sodium hydroxide solution was added dropwise until a pH of 10 was reached. The resulting white precipitate of Y:SnO$_2$ was collected by centrifugation. The collected Y:SnO$_2$ was washed by repeated redispersion in DI water and collecting by centrifugation. This process was then repeated using a 50% ethanol solution until the supernatant passed a silver nitrate test for chloride. The washed Y:SnO$_2$ nanoparticles were dried at room temperature.

To functionalize the Y:SnO$_2$ was mixed with glacial acetic acid in a 1:1.2 mass by volume ratio. The mixture was then heated at 110°C for 1hr in a closed container fitted with a condenser and thermometer. The mixture initially forms milky white colloidal
dispersion which becomes transparent upon the completion of functionalization. Any unreacted Y:SnO$_2$ was then extracted by centrifuge leaving a clear thick suspension.

2.2.1.3. Ink Preparation

The Cu:NiO$_x$ inks were prepared by sonication of Cu:NiO$_x$ particles (20 mg/mL) in H$_2$O for 1 hour through a closed loop flow sonication cell. The sonicator was set to max amplitude and 30 sec pulses. The Cu:NiO$_x$ was then filtered through a 1.0 µm Nylon filter. The amount of pressure required to filter was used as an early indicator for the quality of the ink. The resulting suspension were diluted down to 10 mg/mL using the different alcohols studied. Prior to diluting the concentration of the ink was found using thermal gravimetric analysis. The perovskite ink was prepared by dissolving methylammonium iodide, methylammonium bromide and lead iodide in a mixture of DMF/DMSO/NMP at a ratio of 0.91:0.07:0.02 for a final concentration of 1.2 M. Y:SnO$_2$ inks were prepared by diluting the 42wt% concentrate into anhydrous ethanol to a final concentration of 1.6% then stirring.

2.2.2 Device Fabrication

Films were deposited using an air knife equipped house-built blade coater with vacuum stage and ZUA 2000 Universal Applicator. Slot die coatings were done on a house-built roll-to-roll system with line width of 6 in and line length of 3 meters. Devices with the p-i-n architecture were fabricated: PET/ITO/Cu:NiO$_x$/MAPbI$_3$/Y:SnO$_2$/Ag. ITO-PET substrates were cut into 3 x 8 in. pieces then washed by layering acetone, EtOH and $i$-PrOH than blown drying from top to bottom with an air gun. The cleaned PET substrates were then treated with UV-Ozone for 15 minutes prior to coating. The cleaned ITO substrates
were then used immediately used for sequential deposition of Cu:NiO\text{x}, MAPbI\text{3}, and Y:SnO\text{2} by blade coating.

Cu:NiO\text{x} was blade coated using 4 µL/inch\text{2} an optimized blade gap of 150 µm at a speed of 30 mm/s. 20 seconds after coating a 5-10 psi air knife was turned on to accelerate drying. Turning the air knife on to earlier results in streaking of the film. After coating films were heat treated by placing on a 100 °C hotplate for 2 minutes, or by IPL (3 pulses at 1940 V power for 1000 µsec with 200 msec delay between pulses). Films coated by slot die were coated at 1.8m/min, with a slot gap of 50 µm, flow rate of 1.7 mL/min, and 20 psi of air knife. 40 µL of PVSK solution was coated using a 150 µm blade gap at 10 mm/sec and a dry air knife. After initial coating, the air knife was then passed back across the coating 3-4 times before transferring to a 140 °C hotplate for 2 minutes. 40 µL of solution of a 1.6 wt% suspension of Y:SnO\text{2} in ethanol was coated using a blade gap of 100 µm at 10 mm/sec followed by heating for 5 minutes at 100 °C. For slot die coated devices C60 and bathocuproine (BCP) where thermal evaporated at 20 nm and 3nm respectively in place of Y:SnO\text{2}. Devices were completed with thermal evaporation of 100 nm of silver.

2.2.3 Hansen solubility modeling

The HSP sphere was calculated using the HSP Excel solver developed by Manuel Diaz De Lox Rios.\textsuperscript{163} To survey solvent compatibility with Cu:NiO\text{x} 10 mg/mL of Cu:NiO\text{x} nanoparticles were added to the selected solvent and sonicated for 1 hour through a closed loop flow sonication cell. The sonicator was set to max amplitude and 30 sec pulses, if the solvent was unable to carry the particles through the sonicator it was considered a failure. Solvents that were able to sonicate successfully were then left on the counter and observed
for 48 hours. At which point any separation of the ink and precipitation accumulated on the vial bottom was considered a failure. Inks that passed these tests were scored a 1, all failures scored a 0. Table 2.1 summarizes the results for the tested solvents.

**Table 2.1.** Experimental data on the solubility of Cu:NiOₓ.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>δ₄ (MPa)¹/₂</th>
<th>δ₅ (MPa)¹/₂</th>
<th>δ₆ (MPa)¹/₂</th>
<th>Score</th>
</tr>
</thead>
<tbody>
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<td>26</td>
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</tr>
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<td>Methanol</td>
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</tr>
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<td>Ethanol</td>
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<td>8.8</td>
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<td>5.1</td>
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<tr>
<td>Sec-Butanol</td>
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<td>Toluene</td>
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2.3 Experimental Methods for Chapter 5

This section describes methods of sample preparation and testing used in “Evaluation of Imidazole Blocking Layers for Perovskite Stability” by Armstrong et al.

2.3.1. Ink Preparation

The perovskite ink was prepared by dissolving methylammonium iodide, methylammonium bromide and lead iodide in a mixture of DMF/DMSO/NMP at a ratio of 0.91:0.07:0.02 for a final concentration of 1.2 M. Imidazole suspensions where prepared by dissolving 1.8mg/mL of imidazole in EtOH then stirring until dissolved.

2.3.2 Device Fabrication

Films were deposited using an air knife equipped house-built blade coater with vacuum stage and ZUA 2000 Universal Applicator. Films with architecture PET/ITO/MAPbI3/IM/Y:SnO2/Ag were fabricated for stability evaluation. Devices with the p-i-n architecture PET/ITO/PTAA/PFN/MAPbI3/ Y:SnO2/Ag were fabricated for device testing and EIS characterization. ITO-PET substrates were cut into 3 x 8 in. pieces then washed by layering acetone, EtOH and i-PrOH than blown drying from top to bottom with an air gun. The cleaned PET substrates were then treated with UV-Ozone for 15 minutes prior to coating. The cleaned ITO substrates were then used immediately used for sequential deposition of Cu:NiOx, MAPbI3, and Y:SnO2 by blade coating. A minimum of 6 cells were measured for statistical comparison.

40 µL of an 8 mg/mL solution of PTAA was coated from toluene using a 100 µm blade gap at 10 mm/sec followed by annealing for 10 min at 100 °C. PFN was coated using the same parameters as the PTAA using a 0.4 mg/mL solution in methanol. 40 µL of PVSK
solution was coated using a 150 µm blade gap at 10 mm/sec and a dry air knife. After initial coating, the air knife was then passed back across the coating 3-4 times before transferring to a 140 °C hotplate for 2 minutes. 40 µL of solution of a 1.6 wt% suspension of Y:SnO₂ in ethanol was coated using a blade gap of 100 µm at 10 mm/sec followed by heating for 5 minutes at 100 °C. Devices were completed with thermal evaporation of 100 nm of silver. 1.8 mg/mL solutions of each tested imidazole were coated from ethanol using a 100 µm blade gap at 10 mm/sec followed by annealing at 100 °C for 5 minutes. The same coating parameters were used regardless of whether they were coated on the perovskite or the Y:SnO₂ layer.

2.3.3 Stability testing

Degradation mechanism testing: PET/ITO/PVSK/Y:SnO₂/Ag films were placed in ambient environment (25-30 °C, 50-60% RH, Dark), in an inert environment (Dark, 25 °C, N₂ glovebox) under thermal strain in inert environment (80 °C, Dark, N₂ glovebox) under illumination with or without heating in an N₂ glovebox). Material screening and long-term stability testing: Illuminated by 1 sun LED source while held at short circuit in a N₂ glovebox fan cooled to maintain 35 °C. A minimum of 10 devices were used per test sample for device stability. Samples were tested at time zero, after 24 hours, and again at 72 hours.

2.4 Characterization Methods

Physical characterization methods are here in described with an explanation of JV curve measurements and general procedures for other measurements.
2.4.1 *J-V* Characteristics

The current density–voltage (*J-V*) characteristics of devices were measured using a Class AAA solar simulator having a xenon arc lamp under 1 sun condition (AM1.5G, 100 mW/cm²). Prior to the device measurements, the solar simulator was calibrated using an NREL-certified Si reference cell and a KG3 filter to adjust for spectral mismatch. Devices were tested from 1.2 to 0 V at a scan rate of 100 mV/s with a step size of 10 mV. A representative *J-V* curve highlighting the key parameters discussed below is provided in Figure 2.1.

![Cell diagram with an example of a J-V curve for a solar cell undertest. Highlighted are the primary values of interest namely, *V*<sub>oc</sub>, *J*<sub>sc</sub>, *V*<sub>mp</sub>, and *J*<sub>mp</sub>, using these values we can calculate the FF and PCE using the equations shown on the right.](image)

**Figure 2.1.** Cell diagram with an example of a *J-V* curve for a solar cell undertest. Highlighted are the primary values of interest namely, *V*<sub>oc</sub>, *J*<sub>sc</sub>, *V*<sub>mp</sub>, and *J*<sub>mp</sub>, using these values we can calculate the FF and PCE using the equations shown on the right.

Linear sweep voltammetry is the primary method of characterizing solar cells. Measurements proceed by applying a voltage bias and stepwise scanning while recording the current response. Under dark conditions this scan gives induces reverse flow of current to photocurrent and presents as a diode. Under illuminated conditions and correcting for area this measures the photocurrent density. The difference between the maximum...
photocurrent at zero bias ($J_{sc}$) and the dark current gives the total device current, which can be expressed as:

$$J = J_{sc} - J_0 (e^{qV/k_BT} - 1)$$  \hspace{1cm} (2.1)$$

where $J_0$ is a constant, $q$ is charge, $V$ is voltage, $k_B$ is Boltzmann’s constant, and $T$ is temperature. For an ideal solar cell with moderate or less resistive losses this relationship should equal zero. When the electrodes are isolated the potential difference between has the maximum value, this is the open circuit voltage ($V_{oc}$). The $V_{oc}$ can be expressed in relation to the current using the following equation:

$$V_{oc} = \frac{kT}{q} \ln \left( \frac{J_{sc}}{J_0} + 1 \right)$$  \hspace{1cm} (2.2)$$

Multiplying current density by potential gives the power density. At the maximum power output, we find the $V_{mp}$ and $J_{mp}$. As shown in Figure 2.1 this point can be used to define a square area which would represent the ideal diode at that current and potential. By taking the ratio of the square defined by the max power point with the square defined by the $V_{oc}$ and $J_{sc}$ an ideality factor can be calculated. This is the FF and defines the “squareness” of the J-V curve. The primary features that contribute to decreased FF are increased series resistance and decreased shunt resistance.

$$FF = \frac{J_{mp}V_{mp}}{J_{sc}V_{oc}}$$  \hspace{1cm} (2.3)$$

To find the overall performance of the solar cell the efficiency ($\eta$) is calculated by dividing the max power point by the incident light power density ($P_s$). Expressed in terms of $V_{oc}$ and $J_{sc}$ that relationship looks like this:
\[ \eta = \frac{I_{mp}V_{mp}FF}{P_s} \]  

These values serve as the primary identifiers for photovoltaic performance. The Standard Test Conditions for solar cells is the Air Mass 1.5 spectrum, an incident power of 1000 W/m² at 25 °C. For the best results scan speed should emulate max power point steady state response. Accelerated scan speeds do not allow sufficient time for ion response and can build capacitive response in the perovskite.¹⁶⁴

### 2.4.2 X-Ray Diffraction (XRD)

NiOₓ powders and perovskite films were measured XRD for crystallinity and phase purity. Measurement was done using a Bruker Discovery D8 High resolution X-ray diffractometer with Cu Kα radiation (1.54Å, 40 KV, at a step speed of 0.7 sec/step, and 2θ ranging from 7.5° - 85°.

### 2.4.3 Scanning electron microscopy (SEM)

Film morphology was characterized using a top-view scanning electron microscope. Instruments used include a FEI Nova NanoSEM 600 with an accelerating voltage of 1.5 kV and a working distance of 5-6 mm; a Thermo-Fisher Scientific Apreo C LoVac FESEM with an accelerating voltage of 1.5 kV and working distance of 5-10 mm.

### 2.4.4 UV-Vis

Absorption spectra NiOₓ were measured using a UV-visible spectrophotometer (Agilent 8453).
2.4.5 Thermogravimetric Analysis

Thermal decomposition of xanthates and associated inks was identified by TGA, using a Differential Scanning Calorimeter Q20 scanning from 30 – 800 °C, at a rate of 20 °C/min under oxygen atmosphere.

2.4.6 FT-IR

Infrared spectra of organics and inks were collected using a Thermo Nicolet Avatar 360 FT-IR with Smart iTR.

2.4.7 Zeta potential and Dynamic Light Scattering (DLS)

The stability and particle size of NiO₃ inks were characterized by performing DLS and Zeta potential measurements on a Brookhaven Instrument Corporation 90Plus Particle Size Analyzer. To prepare a solution for DLS all glassware and fluorescent cuvettes were washed in triplicate with the selected solvent system that will be used for the measurement then capped. Particle solutions were prepared at 0.1mg/mL or lower prior to measurement. Prior to Zeta potential measurement the particle size must be measured. For accurate measurement input the solvent viscosity and refractive index and turn on dust filter. Once the average particle size is measured input that value into the Zeta potential scan options as well as refractive index, viscosity, and dielectric.

2.4.8 Electrochemical Impedance Spectroscopy

Impedance measurements were carried out under 1 sun illumination (AM1.5G, 100 mW/cm²) at short circuit potential. The semicircle at a high-frequency region represents charge transfer resistance and the semicircle present at a low-frequency region represents
the impedance of recombination, ion diffusion, and interface phenomenon. The circuit used for simulation is shown below in Figure 2.2.

![Figure 2.2. Electro impedance spectroscopy equivalent circuit.](image)

2.4.9 Profilometer

Film thickness and roughness were measured using a Veeco Dektak 8M Profilometer.
CHAPTER 3.0 SOLVATION OF NiO$_x$ FOR HOLE TRANSPORT LAYER DEPOSITION IN PEROVSKITE SOLAR CELLS

3.1 Introduction

This chapter describes the development of soluble NiO$_x$ particles for the solution phase deposition of inorganic HTLs for use in scalable PSCs. The work described in this chapter is included in the publication “Solvation of NiO$_x$ for hole transport layer deposition in perovskite solar cells” by Armstrong et al.$^{151}$

As described in Chapter 1, Among the inorganic HTLs, NiO$_x$ has great potential due to its wide band gap (>3.50 eV), high optical transmittance, high carrier mobility for rapid extraction and transportation of charge carriers, and favorable energy alignment with the photoactive perovskite layer.$^{165, 166}$ In addition, NiO$_x$ has superior thermal and chemical stabilities.$^{102, 167}$ Deposition of NiO$_x$ HTLs has been reported using various methods such as spin coating, pulsed laser deposition, electron beam evaporation, spray pyrolysis, co-sputtering, and atomic layer deposition.$^{168-172}$ While these methods have produced highly efficient devices, they are not scalable methods. Scalable, solution processes such as blade coating or slot die coating of NiO$_x$ are limited to aqueous NiO$_x$ solutions for bottom layers deposition in p-i-n devices,$^{173}$ which are incompatible with perovskite surfaces preventing their deposition on top of perovskite for n-i-p devices. Icli et al. using an isopropanol solution of NiO$_x$ were able to deposit on top of perovskite by spin coating but they still
expressed concern for perovskite degradation from exposure to isopropanol. Alternatively, Liang et al. developed NiO$_x$ particles with an 18-carbon chain stearate protecting group that could be suspended in a chlorobenzene (CB) for deposition by spin coating. The drawback of this approach is the residual presence of the long chain alkyl ligands in the NiO$_x$ film, which lowers PCE and requires treatment by UV-O$_3$ for removal.

In this chapter, the development of CB compatible NiO$_x$ nanoparticles is explored using ligands with variable alkyl chain lengths to obtain NiO$_x$ films with a reduced presence of residual organic ligands. Specifically, a series of inks with alkyl xanthates (ROCS$^2$-) with various chain lengths and triethylamine (Et$_3$N) have been prepared (Figure 3.1). Xanthates were selected as an alternate to carboxylates, which have been extensively studied, due to their excepted enhanced lability, while still being structurally comparable with carboxylates, and ease of preparation from low-cost materials. The Et$_3$N additive was included as it was found to promote stability of the dispersion. The overall goal of the study was to identify the shortest possible alkyl chain length required to obtain CB stable inks for the fabrication of functional PSCs by blade coating.

3.2 Results and Discussion

To simplify the discussion results have been broken in to three parts. ink formulation and characterization, deposition of inks, and device performance.

3.2.1 Ink Formulation and Characterization

A series of NiO$_x$ nanoparticles have been prepared that can be readily suspended in CB as inks for the preparation of hole transport layers with perovskite photovoltaics. The
NiO$_x$ particles were initially ligated with the Lewis base triethylamine (Et$_3$N) to which alkyl xanthate (ROCS$^{2-}$) ligands were added (Figure 3.1). The alkyl substituent on the xanthate was varied to evaluate the effect of carbon chain length on the ink properties and device performance. The various NiO$_x$ particles are identified based on the length of the alkyl chain as follows: 0X (no xanthate), 4X (n-butyl xanthate), 12X (n-dodecyl xanthate), 18X (n-octadecyl xanthate).

The initial NiO$_x$ particles were prepared by solvothermal synthesis as described by Beach et al.$^{135}$ The identity and purity of the synthesized nanoparticles was confirmed by powder x-ray Diffraction (PXRD) studies, which showed the expected peaks at 36.8° (111), 42.8° (200), 62.3° (220), 74.7° (311), 78.8° (222) (Figure 3.2a). From the PXRD, the crystal size was estimated to be approximately 8 nm based on the Scherrer equation (Equation 3.1)$^{175}$.

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (3.1)

![Figure 3.1. Preparation of xanthate functionalized NiO$_x$](image)
Where \( \tau \) is the mean size of ordered crystal domain, \( K \) is a dimensionless shape factor, \( \lambda \) is the x-ray wavelength, \( \beta \) is the line broadening at half the maximum intensity after subtraction of the instrumental line broadening, and \( \theta \) is the Bragg angle. These small particles tend to agglomerate and form large aggregates in the solid phase as shown in the SEM image in Figure 3.2b. The initially prepared NiO\(_x\) nanoparticles were dispersed in a 3:1 (v/v) Et\(_3\)N/EtOH solution and subjected to sonication for one hour at 65 °C. The Et\(_3\)N, a Lewis base with a high donor number and entropic alkyl groups,\(^{176}\) was added as a weakly coordinating ligand to help break up the agglomerate and prevent re-aggregation by changing the particle surface energies and steric.\(^{177}\) After sonication, the dispersion was diluted with a 7:1 (v/v) CB/EtOH solution to which the xanthate salt, if used, was added. The resulting ink suspensions were then filtered through a 0.2 \( \mu \)m PTFE filter resulting in transparent suspension (Figure 3.1). The SEM image of a film prepared using the 0X ink showed the formation of a uniform film (Figure 3.2c) confirming the breakdown of NiO\(_x\) aggregates into smaller nanoparticles by the Et\(_3\)N. Dynamic light scattering on the sonicated 0X ink found the particle size to be 8.3 ± 2.1 nm, which is consistent with the PXRD size estimates.

To quantify the effect of Et\(_3\)N on the dispersion stability of the NiO\(_x\) particles, the \( \zeta \)-potential was measured for the 0X solution. The \( \zeta \)-potential measures the potential difference between the dispersed particle and the medium with stable suspensions generally having values of at ±30 mV.\(^{178,179}\) The \( \zeta \)-potential is strongly dependent on the composition of the particles and their chemical environment.\(^{180}\) Prior to the addition of Et\(_3\)N, the \( \zeta \)-potential of the initially prepared NiO\(_x\) particles was 6.19 ± 3.0 mV consistent with their observed agglomeration. Addition of 15% Et\(_3\)N to yield the 0X particles increased the \( \zeta \)-
potential to 27.29 ±3.9 mV. The results clearly indicate that Et₃N, even in the absence of additional alkyl xanthate ligands, is sufficient to stabilize the suspension of NiOₓ in CB.

![Figure 3.2. a) PXRD of as synthesized NiOₓ particles. SEM images of NiOₓ particles. b) As prepared NiOₓ powder showing particle agglomeration. c) NiOₓ films prepared using the 0X ink showing uniform dispersion of small particles. Scale bars are 1 µm.

A series of sodium alkyl carbonate salts were prepared through the nucleophilic attack of n-butyl alcohol (4C), n-dodecyl alcohol (12C), and n-octadecyl alcohol (18C) on carbon dioxide as described in Chapter 2. Addition of the carbonates to the 0X suspension results in a clear, colorless suspension following filtration. Characterization by UV-Vis shows loss of the sharp peak at 290 nm and the formation of the broad low intensity 0X peak centered on 300 nm indicating ligand decomposition (Figure 3.3). Further characterization by FT-IR showed the loss of the carbonate structure and reversion to the starting alcohol (Figure 3.4). Together this indicates that the carbonates are not stable enough to effectively coordinate to the NiOₓ and act as ligands.
Figure 3.3. UV-V is of n-butyl carbonate, and n-octaldecyl carbonate showing carbonate decomposition and return to 0X ink.

Figure 3.4. a) FT-IR of 18C ink and solvated n-octaldecyl carbonate, b) octadecyl alcohol showing loss of carbonate peak at 1600 cm\(^{-1}\) and reversion of the carbonate to the starting alcohol.

Addition of alkyl xanthate to the 0X ink results in a ligand exchange process with coordination of xanthate to the NiO\(_x\) particles as observed by UV-Visible spectroscopy. The 0X ink has a primary excitonic peak centered at 300 nm and the ink is visually a light tan in CB. Addition of alkyl xanthates to the NiO\(_x\) particles yields deep brown suspensions.
after heating and filtration (Figure 3.1). A comparison of the UV-visible spectra of the alkyl xanthates and their corresponding inks confirms the color changes are associated with coordination of the alkyl xanthates to the NiOx particles. The UV-visible spectra of the 12X alkyl xanthate salt in CB shows a ligand-to-ligand band at 380 nm that shifts to 420 nm upon addition of NiOx (Figure 3.5a). Additionally, there is a new band at 480 nm in the ink associated with a ligand-to-metal charge transfer from the xanthate to the nickel. Similar bands are observed at 476 and 414 nm in molecular nickel xanthate complexes.\textsuperscript{181, 182} The UV-visible spectra for the 4X and 18X xanthate salts and their respective inks show similar features (see Figure 3.5b). The coordination of the alkyl xanthate ligands to the NiO\textsubscript{x} particles was further confirmed by FT-IR spectroscopy. The spectrum of the 12X alkyl xanthate shows a C=S stretch at 1070 cm\textsuperscript{-1} that shifts to 1030 cm\textsuperscript{-1} in the ink and a C-O-C stretch at 1120 cm\textsuperscript{-1} to 1230 cm\textsuperscript{-1} upon addition of the NiO\textsubscript{x} (See Figure 3.6), additionally indicating coordination.\textsuperscript{183}

Figure 3.5. a) UV-Vis of the 12X ligand, 12X ink and 0X ink in the same solvent system in a 1 mm quartz cell showing coordination of 12X to NiO\textsubscript{x} in the ink. b) UV-Vis of 18X and 4X ligands and inks confirming ligand coordination.
Thermal gravimetric analysis (TGA) was performed on the alkyl xanthate ligands and their corresponding inks to determine their stability under annealing conditions. Since residual long-chain compounds in the NiO\textsubscript{x} layer have been shown to lower the PCE of PSCs\textsuperscript{174} ligands that decompose during annealing may offer an advantage. TGA studies by Beach et al. on as synthesized NiO\textsubscript{x} particles without additional ligands yielded an annealing temperature of 300 °C\textsuperscript{135} The TGA of the 12X salt, as a powder, shows an initial, small mass loss due to dehydration followed by a sharp, substantial mass loss associated with xanthate decomposition from 210 to 315 °C (Figure 3.7a). The TGA of films prepared from 12X inks show a similar decomposition feature between 135 and 350 °C (Figure 3.7a). Results for the 4X and 18X ligands and inks are similar with xanthate decomposition occurring from 210 -320° C (Figure 3.8). Notably, all the xanthates decompose at or below NiO\textsubscript{x} particle annealing temperature of 300 ° C indicating that under our current conditions the xanthates are fully removed from the NiO\textsubscript{x} films.

Figure 3.6. FT-IR of the 12X ligand as a powder and the 12X ink as a film showing coordination of 12X to NiO\textsubscript{x} in the ink.
Figure 3.7. a) TGA of 12X ligand as a solid and the 12X ink as a thick film confirming degradation of the xanthate at temperatures above 300 °C. b-d) SEM images of 0X, 12X, and 18X films prepared by blade coating showing changes in film uniformity in the presence of xanthate ligands. Scale bars are 5 µm.

Figure 3.8. TGA of 4X, 12X, and 18X inks and solid ligands under O₂ flow showing major decomposition by 300 °C
3.2.2 Film Deposition

The 0X – 18X inks were deposited as thin films on ITO glass by blade coating with a blade gap of 225 µm at a speed of 5 mm sec⁻¹. The films were annealed at 300 °C for 20 minutes. Using these parameters film thicknesses of approximately 40 nm, as determined with a Dektak surface profilometer, were reproducibly obtained. The roughness of the 0X film is measured to be 5.9 nm by Dektak. SEM imaging of the 0X film shows a tightly packed film with no visible pinholes (Figure 3.7b). The tight packing of the film is attributed to the presence of the volatile Et₃N in the ink. The Et₃N coordinates to the NiOₓ particles in the ink to stabilize the suspension. Once the ink is deposited, evaporation of Et₃N would allow NiOₓ particles to pack closely together in the film.

For inks containing xanthate ligands, the film quality is dependent on the length of the carbon chain. The SEM image of the 18X film shows uniform coverage with the presence of some pinholes (Figure 3.7d). Surface roughness is found to be about 6.5 nm. Imaging of the 12X film shows a film with significant pinholes and the presence of agglomerating particles (Figure 3.7c). These defects result in a roughness of 12.9 nm. The 4X inks failed to yield a uniform film and only a few agglomerates were observed on the surface (Figure 3.9). The uniform coverage of the long chain xanthate ligand (18X) is attributed to strong dispersion forces that induce alignment of the hydrophobic alkyl chains allowing tighter packing of the NiOₓ particles. Removal of the xanthate ligands during annealing results in the formation of some pinholes as the xanthates decomposes to gaseous products. It is envisioned that the short chain xanthate ligand (4X) is unable to induce film formation resulting in a random distribution of NiOₓ particles on the surface leading to poor film quality and significant agglomeration upon annealing. Films formed with the
intermediate length xanthates (12X) as a result show both pinholes and some particle agglomeration while still being able to form a film.

![SEM image of 4X film showing particle aggregates. Scale bar is 5 µm.](image)

**Figure 3.9.** SEM image of 4X film showing particle aggregates. Scale bar is 5 µm.

### 3.2.3 Device Performance

To evaluate the effect of xanthate ligands on PSC performance, a series of devices having an architecture of glass/ITO/NiOx/PFN/MAPbI3/C60/BCP/Ag\textsuperscript{116} were constructed by blade coating of the NiOx, PFN, and MAPbI3 and thermal evaporation of C60, BCP, and Ag. Cells were mechanically scribed into an active area of 0.25 cm\(^2\) and tested under 1 sun condition. PFN was incorporated to improve the surface wetting of the perovskite deposition using known blade coating parameters.\textsuperscript{162} Figure 3.10 shows the distribution of device performance parameters across multiple samples of the different ligand conditions investigated. The device performance results show that 0X clearly outperforms the xanthate coated particles. However, for devices containing xanthates performance decreases with decreasing xanthate chain length. Figure 3.11 shows the light and dark current-voltage (J-V) curves of the champion devices, and their corresponding photovoltaic
parameters are summarized in Table 3.1. The highest 0X device exhibited a PCE of 14.47%, with $J_{sc}$ of 19.23 mA/cm$^2$, $V_{oc}$ of 1049.32 mV, and FF of 71.72%.

Figure 3.10. a-d) Statistical comparison of photovoltaic parameters for 0.25 cm$^2$ cells prepared with 0X – 18X inks. e) Schematic illustration of p-i-n device stack with expected energy alignment in eV.
Figure 3.11. J-V curves of champion 0.25 cm$^2$ PSCs.

Table 3.1. Photovoltaic parameters of champion devices.

<table>
<thead>
<tr>
<th>Ink</th>
<th>PCE</th>
<th>$V_{oc}$</th>
<th>$J_{sc}$</th>
<th>FF</th>
<th>$R_s$</th>
<th>$R_{sh}$</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>mV</td>
<td>mA/cm$^2$</td>
<td>%</td>
<td>Ω cm$^2$</td>
<td>Ω cm$^2$</td>
<td>cm$^2$</td>
</tr>
<tr>
<td>0X</td>
<td>14.47</td>
<td>1049.32</td>
<td>19.23</td>
<td>71.72</td>
<td>8.0</td>
<td>728.7</td>
<td>0.25</td>
</tr>
<tr>
<td>18X</td>
<td>7.61</td>
<td>891.80</td>
<td>16.22</td>
<td>52.61</td>
<td>6.9</td>
<td>316.6</td>
<td>0.25</td>
</tr>
<tr>
<td>12X</td>
<td>4.86</td>
<td>817.16</td>
<td>12.44</td>
<td>47.84</td>
<td>11.9</td>
<td>326.9</td>
<td>0.25</td>
</tr>
<tr>
<td>4X</td>
<td>0.19</td>
<td>89.99</td>
<td>8.64</td>
<td>25.03</td>
<td>10.3</td>
<td>11.2</td>
<td>0.25</td>
</tr>
<tr>
<td>0X</td>
<td>9.96</td>
<td>970.45</td>
<td>17.81</td>
<td>57.61</td>
<td>8.5</td>
<td>615.9</td>
<td>1.00</td>
</tr>
<tr>
<td>18X</td>
<td>7.51</td>
<td>968.89</td>
<td>13.95</td>
<td>55.58</td>
<td>8.4</td>
<td>573.9</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The relative values of $J_{sc}$ are consistent with the differences in NiO$_x$ film quality observed in the SEM images, which directly affects the quality of the perovskite layer. The
$J_{sc}$ value is highest for 0X and decreases in films containing xanthate ligand as the chain length decrease. This is consistent with previous reports by Agarwal that show a decrease in $J_{sc}$ with an increasing size and density of pinholes in the HTL.\textsuperscript{184} As further noted in that study, $V_{oc}$ is dependent on total surface coverage with a nearly constant value when there is at least 80% surface coverage. In the present study, the $V_{oc}$ decreases from 0X to 18X to 12X consistent with decreasing surface coverage within this series, followed by a substantial drop for 4X, which performed as a photo-resistor, due to its poor film quality. Overall, the high $V_{oc}$ and $J_{sc}$ of the 0X device indicate a high level of uniformity in the HTL and subsequently the perovskite depositions. Variations in the $J_{sc}$ being due to small variations in the perovskite itself but having no overall effect on the trends observed.

Further confirming the significant effects of the film quality, the FF shows a nearly 20% drop from the 0X to the 18X devices. The FF is dependent on the shunt ($R_{sh}$) and series ($R_s$) resistance of the device. Where $R_{sh}$ is the prevention of contact between the top and bottom contacts and $R_s$ is a measure of internal resistance to charge migration. The series resistance in these two films is similar (0X: 8.0 Ω cm$^2$ vs 18X: 6.9 Ω cm$^2$) despite the inclusion of a long chain xanthate ligand in the 18X ink. This is attributed to removal of the xanthate ligand during the annealing step. However, the shunt resistance of the 0X film is more than twice that of the 18X film (0X: 728 Ω cm$^2$ vs 18X: 316 Ω cm$^2$) resulting in the improved FF in the 0X device. The lower shunt resistance in the 18X device is consistent with the greater presence of pinholes noted above. The shunt resistance for our champion 0X device is significantly below the value 2635 Ω cm$^2$ obtained by Li et al. for a NiO$_x$/MAPbI$_3$/C60 device.\textsuperscript{185} In that example, the NiO$_x$ layer was deposited by spin-
coating suggesting that further refinement of our blade coating method could substantially improve device performance.

Next, 0X and 18X were evaluated as 1 cm$^2$ devices to test their applicability for large scale production. The J-V curves are shown in Figure 3.12 and the data is summarized in Table 3.1. Notably, in the 1 cm$^2$ devices 0X and 18X have similar $V_{oc}$, FF, $R_s$, and $R_{sh}$ values. There is, however a nearly 4 mA/cm$^2$ difference in $J_{sc}$, between the 18X and 0X samples resulting in a greater PCE for the 0X device. The higher $J_{sc}$ of the 0X device was also observed in the 0.25 cm$^2$ devices and can be attributed to increased presence of pinholes in the 18X film. A comparison of 0X performance in the 0.25 cm$^2$ and 1 cm$^2$ cells shows a 4.9 ± 0.3 percent decrease in PCE due to largely due to decreases in $J_{sc}$ and $R_{sh}$ attributed to the presence of more pinholes over the larger area.

![Figure 3.12. J-V curves for 1 cm$^2$ devices prepared with 0X and 18X inks.](Image)

The long-term stability of a 0X and 18X device was evaluated following storage in a nitrogen flow box for 100 days exposed to lab lighting. Device performance is summarized in Table 3.2 with the corresponding J-V curves shown in Figure 3.13. The 18X
device shows a general degradation in quality with decreases in $J_{sc}$, $R_{sh}$, and FF resulting in a drop in PCE after 100 days. The 0X device shows greater stability. There is a decrease in $V_{oc}$ and FF over 100 days, but there is also an unexpected increase in $J_{sc}$ and $R_{sh}$ resulting in no statistical change in PCE. It is suggested by reviewers that this increase could be due to the further removal of Et$_3$N from the device interface. Et$_3$N having a vapor pressure of 7.2 kPa at 20 °C would further evaporate with aging of the device. Due to the limited sample set further testing over more samples and under illuminated conditions is needed to confirm if the observed increases in $J_{sc}$ and $R_{sh}$. The higher stability of the 0X device compared to the 18X device is attributed to the quality of the NiO$_x$ film and the quality of the resulting perovskite to have less trap states that would lead to film degradation.

![Figure 3.13. J-V curves of 0X and 18X 0.25 cm$^2$ PSCs before and after 100 day in nitrogen flow box](image)
Table 3.2. Photovoltaic parameters for 0.25 cm$^2$ devices before and after storage in nitrogen flow box for 100 days.

<table>
<thead>
<tr>
<th>Ink</th>
<th>PCE</th>
<th>$V_{oc}$</th>
<th>$J_{sc}$</th>
<th>FF</th>
<th>$R_s$</th>
<th>$R_{sh}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>mV</td>
<td>mA/cm$^2$</td>
<td>%</td>
<td>Ω cm$^2$</td>
<td>Ω cm$^2$</td>
</tr>
<tr>
<td>0X Initial</td>
<td>10.00</td>
<td>988.01</td>
<td>14.41</td>
<td>70.25</td>
<td>3.3</td>
<td>990.7</td>
</tr>
<tr>
<td>0X 100 day</td>
<td>11.16</td>
<td>956.53</td>
<td>18.11</td>
<td>64.41</td>
<td>7.3</td>
<td>1306.5</td>
</tr>
<tr>
<td>18X Initial</td>
<td>7.61</td>
<td>891.80</td>
<td>16.22</td>
<td>52.61</td>
<td>6.9</td>
<td>316.6</td>
</tr>
<tr>
<td>18X 100 day</td>
<td>5.06</td>
<td>884.13</td>
<td>14.13</td>
<td>40.57</td>
<td>6.4</td>
<td>103.0</td>
</tr>
</tbody>
</table>

Given the performance of p-i-n devices using the 0X ink, construction of a n-i-p device was undertaken with a glass/ITO/SnO$_2$/MAPbI$_3$/NiO$_x$/Ag architecture (Figure 3.14a). The ETL, HTL, and perovskite layer were deposited by blade coating using the parameters described in Chapter 2. Upon deposition of NiO$_x$ atop the perovskite the appearance of the stack shifted from a black mirror finish to a metallic blue with retention of its reflective nature (Figure 3.14b and c). However, no functional devices were found upon solar testing. Evaluation of the MAPbI$_3$-NiO$_x$ interface by PXRD shows the appearance of a peak at 9.5° (Figure 3.14d) upon deposition of the 0X ink on the perovskite. The same peak is observed when the ink solvent mixture (CB, EtOH, Et$_3$N) is deposited on the perovskite (Figure 3.15). This suggests the formation of a Et$_3$N adduct peak with the perovskite similar to that observed with DMSO.$^{186}$ Notably, no peak is observed at 12.7 indicating that MAPbI$_3$ is not degraded to PbI$_2$. Further work is ongoing to study this interface interaction and develop functional n-i-p devices.
3.3 Conclusions

A series of ink formulations have been developed that successfully suspend NiO$_x$ nanoparticles in the perovskite antisolvent CB in mixtures containing EtOH with Et$_3$N (0X) or Et$_3$N/alkyl xanthates (4X, 12X, 18X). The carbon chain length of the alkyl xanthate was
varied to probe its effect on ink performance. Although hydrophobic chelating ligands were previously used to solubilize NiOₓ for fabrication of PSCs, we found that Et₃N alone was sufficient to stabilize NiOₓ nanoparticles in solution and disperse aggregates upon sonication. In fact, the 0X ink yielded the best film quality and device performance with champion PCEs of 14.47% (0.25 cm²) and 9.96% (1 cm²). The 0X cells were stable for 100 days in a nitrogen flow box with no significant change in PCE. For PSCs containing alkyl xanthate ligands, the best film quality and device performance was obtained for 18X. This is attributed to preferential ordering of the NiOₓ on the surface due to dispersion interactions of the long carbon chain and the degradation of the alkyl xanthate during thermal annealing. However, the 18X inks led to more pinholes than the 0X ink resulting in a decrease in PCE. Shorter chain alkyl xanthates had lower performance with 4X inks failing to form films. Overall, our results provide a new formulation for the preparation of NiOₓ inks in the perovskite antisolvent CB based on the volatile and weakly coordinating Et₃N ligand. This provides several advantages over non-volatile charged ligands with long carbon chains.
CHAPTER 4.0 SCALABLE SOLUTION PROCESSING OF Cu:NiOₓ NANOPARTICLES FOR PEROVSKITE SOLAR CELLS

4.1 Introduction

In the previous chapter we discussed the use of organic ligands to stabilize NiOₓ in a chlorobenzene-based ink. We found that the long ligands were not necessary to stabilize the nanoparticles and that they were obstructive to effective charge extraction. It was demonstrated that solvent engineering can be used to stabilize the nanoparticles in place of the long ligands. In this chapter we will continue the investigation solvent engineering to stabilize and coat metal oxides over large areas. For this study we will start with a NiOₓ nanoparticle ink formulation commonly used for spin coating and modify it for blade coating and slot die coating. The work described in this chapter is included in the submitted manuscript “Scalable Solution Processing of Cu:NiOₓ Nanoparticles for Perovskite Solar Cells” by Armstrong et al.

In 2022 Chandrasekhar et al. reported a 1 cm² PSC devices with a SnO₂ layer that was fabricated using slot die coating of a water-based ink at 2.0 m/min. In those devices annealing of the SnO₂ was accomplished using a rapid thermal process. To ensure proper wetting at speed, a Triton-X 100 surfactant was utilized. The resulting devices had an average PCE of 10.6%. Using NiOₓ on a blade coating system, Chen et al. used a heated
stage to ensure proper wetting while coating at 10 mm/s. On a fully blade coated device they were able to achieve a champion PCE of 19.04% on a flexible device. Using the same methodology, Yang et al. reported a PCE of 19.87% a year later. These works relied on coating at slow speeds with a heated stage or supporting ligands to stabilize the particles and direct uniform film formation when coated at higher speeds.

Coatings deposited at slower speeds were uniform, resulting in a high open circuit potential ($V_{oc}$) and fill factor (FF). At higher speeds, the addition of surfactants improved coating uniformity, but resulted in decreased FF due to high series resistance. Given the thin nature of these charge transport layers, the addition of bulky nonconductive ligands can obstruct charge transport resulting in lower performance. Attempting to avoid the use of surfactants or ligands, Watson et al. followed a limited flow model to identify the unstable coating regime of a SnO₂ ink. They were able to successfully coat uniform films at speeds up to 1 m/min from an alcohol-water mixture with an average PCE of 13.4% when finished by spin coating perovskite.

Alcohol water mixtures are ideal green solvents for large scale processing. The alcohols can disrupt the internal hydrogen bonding network of water thus improving wetting properties while also accelerating evaporation due to lowering the vapor pressure. For a given solvent system to be effective it needs to balance both the coating properties and the stability of the nanoparticle suspension. The Hansen Solubility Parameters (HSPs) provide a method of quantifying solvent characteristics. Traditionally, HSPs have used to quantify polymer and molecular solvation. Recent work by Süß et al. has applied HSP principles to nanoparticle suspensions, such as carbon black and ZnO.
particles. In 2014, Petersen et al. applied HSP to optimizing dispersive and rheological properties of silver nanoparticle inks for printed structures.

This chapter focuses on solvent engineering to stabilize and coat copper doped nickel oxide (Cu:NI\textsubscript{x}) nanoparticles. As noted in Chapter 1, NiO\textsubscript{x} is the leading inorganic hole transport material favored for its stability, large band gap, intrinsic p-type character and easy of doping. The HSP is used to help predict ink stability which must also be balanced with coating and annealing properties. To date there has been little work to transition NiO\textsubscript{x} from spin coating to more scalable methods. To address this gap, this chapter describes Cu:NI\textsubscript{x} films that were deposited by blade coating at speeds of 1.8 m/min. This work includes the roll-to-roll deposition of Cu:NI\textsubscript{x} nanoparticle films by slot die coating utilizing intense pulsed light (IPL) annealing to further reduce dwell time during annealing. IPL provides a rapid alternative to traditional thermal annealing methods reducing dwell time and energy loss during processing. A recent technoeconomic analysis of perovskite production on a roll to roll line showed that IPL can reduce energy cost by up to 80% compared to conventional ovens. These steps will help in the development of an effective low cost Ink for large area coating of NiO\textsubscript{x}.

4.2 Results and Discussion

The Cu:NI\textsubscript{x} nanoparticles were prepared by low temperature precipitation of Cu:NI(OH)\textsubscript{2} upon addition of NaOH to a mixture of Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and Cu(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, which was then annealed at 270 °C for 30 minutes. The Cu:NI\textsubscript{x} nanoparticles were readily dispersed in water with sonication yielding uniform, black inks. Similar Cu:NI\textsubscript{x} inks have been successfully employed for the fabrication of PSCs by spin-
coating of the hole transport layer with PCE up to 20.83%.\textsuperscript{123} To evaluate the suitability of a water-based Cu:NiO\textsubscript{x} ink for high-speed coating processes, we attempted blade coating of the inks. Suspensions were prepared by sonication of Cu:NiO\textsubscript{x} nanoparticles in water for 60 minutes followed by filtration and dilution to final concentration of 1 wt% Cu:NiO\textsubscript{x}. Inks were then applied to an ITO coated PET substrate by blade coating at the targeted speed of 30 mm/sec (1.8 m/min). The aqueous Cu:NiO\textsubscript{x} ink failed to adhere to the surface resulting in significant de-wetting and island formation across the coating. The addition of an air knife during coating increased streaking along the length of the coating, again producing an unusable film. These results are consistent with the high surface tension (72 dyns/cm\textsuperscript{2}) and moderately low vapor pressure (23.8 mm Hg) of water, which has poor adhesion to the ITO surface and slow evaporation kinetics.\textsuperscript{189}

**4.2.1 Ink stability**

Based on the poor performance of the aqueous inks for blade coating, the stability of unfunctionalized Cu:NiO\textsubscript{x} particles in 31 solvents was surveyed and a HSP sphere was constructed (Figure 4.1a). The HSP sphere is based on the Hansen parameters ($\delta_d$, $\delta_p$, $\delta_h$) and the stability of the ink, which is scored as 1 for “good stability” and 0 for “poor stability.”\textsuperscript{196} Ink stability was evaluated by visual inspection over 48 hours under ambient conditions. Inks that showed no apparent change over this period were classified as good, whereas inks that resulted in sedimentation, phase separation, or for which no suspension could be formed were classified as poor (Table 2.1). The HSP was calculated using the HSP Excel solver developed by Manuel Diaz De Lox Rios.\textsuperscript{163} The resulting sphere is centered at $\delta_d = 17.1$, $\delta_p = 15.2$ and $\delta_h = 8.0$ with a radius of 3.6. It is worth noting that water was not used
for the HSP evaluation as its hydrogen bonding component makes it an outlier during evaluation. Overall, solvents showing the best ink stability were found to be slow evaporating and strongly coordinating solvents such as DMSO and γ-butyrolactone (GBL). This is consistent with the good ink stability of Cu:NiOx in water. However, these solvents are not suitable for high-speed coating processes due to their long drying times and poor wettability (for water).

Figure 4.1. a) Calculated Cu:NiOx HSP sphere and surveyed solvents; alcohols are highlighted, b) 2D representation (looking down the hydrogen bonding axis) of the Cu:NiOx HSP sphere and HSP parameters of alcohol-water mixtures shown as colored blocks converging from pure alcohol to pure DMSO in increments of 10% v/v. c) 3D representation of the Cu:NiOx HSP sphere and HSP parameters of alcohol-DMSO mixtures shown as colored blocks converging from pure alcohol to pure DMSO in increments of 10% v/v.

The addition of high vapor pressure solvents, such as alcohols, with water decreases surface tension and accelerates drying rates. As shown in Figure 4.1a, pure alcohols fall far outside the HSP sphere for Cu:NiOx stability due to their relatively low polarity and strong hydrogen-bonding. The polarity of alcohol-water mixtures increases as a function of the water content. As shown in Figure 4.1b for a range of alcohols, when the volume of alcohol is below ~30% the polarity of the solvent mixtures enters the HSP sphere, with no significant effect on the dispersion parameter. The hydrogen-bonding parameter still lies
significantly above the HSP sphere, but given the good stability of Cu:NiO$_x$ in water this is not considered a reliable parameter for predicting ink stability in this case. Notably, the changes in polarity and dispersion parameters as a function of the alcohol chain length or chain branching were relatively small allowing for evaluation of a wide range of alcohol-water mixtures.

A series of Cu:NiO$_x$ inks were prepared using 30 v/v% alcohol-water mixtures. The images in Figure 4.2 show representative samples of freshly prepared Cu:NiO$_x$ inks and inks aged for 48 hrs. under ambient conditions. For straight chain alcohols (ethanol (EtOH), propanol (PrOH), and butanol (BuOH)), ink stability decreased with increasing chain length consistent with the slightly lower polarity of the solvent mixture. Dispersion of Cu:NiO$_x$ in 30% EtOH showed no differences after 48 hours while inks prepared in 30% PrOH were generally stable, but did begin to show signs of phase separation. Dispersions of Cu:NiO$_x$ in 30% BuOH were highly unstable with very poor mixing between the water and alcohol. Notably, both EtOH and PrOH are miscible with water, whereas BuOH is only partially soluble in water. For branching chains alcohols ($i$-PrOH) and tert-butanol ($t$-BuOH)), the Cu:NiO$_x$ inks were visually stable in 30% alcohol-water mixtures for at least 48 hours. The enhanced stability in $t$-BuOH mixtures versus BuOH-water may be attributed to the miscibility of the solvents in the former.

Encouraged by the success in stabilizing Cu:NiO$_x$ inks in the alcohol-water mixtures, a similar approach was employed with alcohol-DMSO mixtures. Unlike water, DMSO sits in the HSP sphere of Cu:NiO$_x$, but like water its moderate surface tension and low vapor pressure leads to relatively poor wetting in high-speed coating processes. As shown in Figure 4.1c, mixtures of alcohol and DMSO have increased polarity and
dispersion parameters relative to pure alcohols, with ~40% alcohol-DMSO mixtures and below in the HSP sphere of Cu: NiOx (Figure 4.3). Initial testing showed good ink stability over one week in 25% methanol (MeOH)-DMSO.

**Figure 4.2.** Representative digital images of ink stability tests after aging 48 hr. Stable suspension in 30% isopropanol (a) and unstable suspension in 30% propanol (b). The unstable solutions are highlighted with red boxes.
4.2.2 Blade Coating of Cu:NiO$_x$ Inks

A critical feature for high-speed coating processes is good wetting of the substrate. This requires sufficiently strong adhesive forces between the ink and surface to overcome the cohesive forces within the ink. This can be evaluated by comparison of the surface energies of the substrate and solvent as determined by contact angle measurements. The surface energy of oxygen plasma treated ITO surface has a surface energy of 64.5 dyn/cm$^2$, while water and DMSO have surface tensions of 72 and 43 dyn/cm, respectively. The high surface tension of water relative to the ITO surface energy results in the observed hydrophobic behavior and poor wetting. In contrast, the surface tension of the surveyed alcohols ranges from 21 to 23 dyn/cm with surfaces tensions below 30 dyn/cm for alcohol-water mixtures containing up to 80% water with $t$-BuOH, PrOH, and $i$-PrOH. EtOH and MeOH being smaller and more prone to hydrogen-bonding are not as effective at disrupting the internal adhesion forces of water and only maintain a surface tension below 30 dyn/cm in alcohol-water mixtures containing at least 50-60%...
alcohol. At concentrations less than 20% for most alcohols (50% EtOH, MeOH), the surface tension increases exponentially as the intermolecular forces of water dominate. Using this transition from water to alcohol dominated regimes as a cut off we targeted to stay below the 30dyn/cm threshold to optimize wetting properties.

To test their applicability for high-speed coating processes, Cu: NiO<sub>x</sub> inks prepared in 30% EtOH, 30% i-PrOH, and 30% t-BuOH and coated on ITO/PET by blade coating at 30 mm/min with no air flow. Good wetting was observed during the coating process with rapid solvent evaporation. The resulting films were inspected by SEM for uniformity (Figure 4.4). Films prepared using the EtOH ink were of marginal quality with some regions showing uniformity, but significant regions of exposed ITO. Pinholes were also observed in the more uniform sections. Films from the i-PrOH ink had larger sections of exposed ITO than the EtOH ink, but with less and smaller pinholes. The t-BuOH ink yielded the most uniform coverage with a dense layer of Cu: NiO<sub>x</sub> observed across the film surface. Small pinholes are uniformly dispersed across the surface. The superior performance of the t-BuOH ink can be attributed to its relatively low polarity and hydrogen-bond interactions of t-BuOH compared to the other alcohols, which allows for more favorable adhesion of the Cu: NiO<sub>x</sub> particles with the ITO surface. Additionally, the lower vapor pressure of the t-BuOH may help control evaporation rates providing for a more uniform coating.
The suitability of Cu:NiO$_x$ inks in alcohol-DMSO mixtures was also investigated. The addition of alcohol to DMSO decreases surface tension directly proportional to the alcohol content. As such, much higher alcohol volumes are needed to reduce the surface tension of the solvent mixture to values suitable for blade coating. Cu:NiO$_x$ inks prepared in 50% MeOH-DMSO were successfully coated on ITO with moderate air knife support (6 scfm). Overall, the resulting films displayed good coverage and uniformity. However, a significant increase in particle size was observed with the average particle size measuring 123.6 ± 42.2 nm by SEM (Figure 4.5). For comparison, SEM measurements of films deposited using the 30% i-PrOH-water ink showed an average particle size of 66.1 ± 28.3 nm. The doubling in size of particles indicates that the significant Ostwald ripening has taken place in the DMSO inks. While thick hole transport layers are advantageous for preventing shunting and increasing the $V_{oc}$, films over 100 nm are prone to losses in FF due to increasing series resistance and decreased short circuit current ($J_{sc}$) due to light absorption of the transport layer. For these reasons we focused on the alcohol-water based inks moving forward.
4.2.3 Device Performance and Optimization

A series of 0.25 cm² devices with the architecture PET/ITO/Cu:NiOₓ/MAPbI₃/Y:SnO₂/Ag were fabricated by blade coating using selected 30% alcohol-water Cu:NiOₓ inks to test device performance. Overall, device performance was poor (Table 4.1) with average PCE values between 3.79 and 6.96% for the three alcohol-water inks. The low PCEs are the result of a low fill factor associated with low shunt resistance, high series resistance and low current density (Figure 4.6). Of the three alcohol-water Cu:NiOₓ inks, the i-PrOH ink had the highest performance with an average PCE of 6.96 %, fill factor (FF) of 44.9%, $V_{oc}$ of 0.96 V and $J_{sc}$ of 16.06 mA/cm².

**Figure 4.5.** SEMs of Cu:NiOₓ coated from 25% methanol in DMSO (a) and 30% i-PrOH (b) for measuring particle size. Scale bar is 500nm.
**Figure 4.6.** JV-curves from 30% alcohol inks using EtOH, i-PrOH, and t-BuOH.

**Table 4.1.** Average and Champion device photovoltaic performance of 0.25 cm² f-PSCs using different alcohol-water inks Cu: NiOx coating.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-PrOH</td>
<td>16.20</td>
<td>1.02</td>
<td>53.6</td>
<td>8.83</td>
</tr>
<tr>
<td></td>
<td>16.06 ± 0.816</td>
<td>0.96 ± 0.037</td>
<td>44.9 ± 3.52</td>
<td>6.96 ± 0.75</td>
</tr>
<tr>
<td>EtOH</td>
<td>18.42</td>
<td>0.96</td>
<td>44.4</td>
<td>7.88</td>
</tr>
<tr>
<td></td>
<td>16.33 ± 0.97</td>
<td>0.92 ± 0.049</td>
<td>38.94 ± 3.56</td>
<td>5.89 ± 0.87</td>
</tr>
<tr>
<td>i-BuOH</td>
<td>12.55</td>
<td>0.89</td>
<td>39.90</td>
<td>4.45</td>
</tr>
<tr>
<td></td>
<td>11.26 ± 0.85</td>
<td>0.85 ± 0.026</td>
<td>39.43 ± 2.75</td>
<td>3.79 ± 0.38</td>
</tr>
<tr>
<td>IPL anneal of 20%</td>
<td>17.50</td>
<td>0.74</td>
<td>40.3</td>
<td>5.28</td>
</tr>
<tr>
<td>i-PrOH ink (0.1cm²)</td>
<td>14.76 ± 1.52</td>
<td>0.75 ± 0.04</td>
<td>38.1 ± 3.0</td>
<td>4.24 ± 0.66</td>
</tr>
</tbody>
</table>

To improve device performance, a series of Cu: NiOₙ inks were evaluated to optimize the percentage of i-PrOH. Decreasing the i-PrOH content from 30% to 15% improved film uniformity of the blade coated Cu: NiOₙ films (Figure 4.7). While decreasing the alcohol content will decrease the surface tension the higher water content will increase film dwell time allowing for increased Brownian motion and particle rearrangement. With
lower alcohol content (20%), the quality of the Cu:NiOₓ film transitions from dense
deposits of Cu:NiOₓ to a uniformly distributed film (Figure 4.7c). The improved uniformity
is reflected in a moderate increase in $V_{oc}$ of 0.05 mV, and significant increases of 4.7% and
2.4 mA/cm² in the average FF and $J_{sc}$ of the resulting 0.1cm² devices (Table 4.2). The
improvements in $J_{sc}$ and FF are reflective of improved perovskite growth on the Cu:NiOₓ
as the uniform film provides a better platform for crystal growth. Interestingly there is no
statistical difference in the performance of 25% and 20% $i$-PrOH inks indicating that there
is some flexibility in the alcohol concentration while still maintaining device performance.
While both the 30% and 15% had significantly lower PCE, the loss of performance is
almost exclusively in the $J_{sc}$ indicating poor charge extraction (Figure 4.8).

Figure 4.7. SEMs of Cu:NiOx coatings surveying the effect of varying the concentration
of isopropanol in water. 30% (a), 25% (b), 20% (c), 15% (d). Scale bars are 5 um.
Table 4.2. Average and Champion device photovoltaic performance of 0.1 cm$^2$ f-PSCs using with varying concentrations of i-PrOH.

<table>
<thead>
<tr>
<th>i-PrOH (v/v%)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30%</td>
<td>16.46</td>
<td>1.02</td>
<td>47.3</td>
<td>7.93</td>
</tr>
<tr>
<td></td>
<td>16.30 ±0.42</td>
<td>0.95 ±0.034</td>
<td>44.2 ±2.2</td>
<td>6.87 ± 0.46</td>
</tr>
<tr>
<td>25%</td>
<td>18.42</td>
<td>1.02</td>
<td>53.4</td>
<td>10.03</td>
</tr>
<tr>
<td></td>
<td>17.90 ± 0.51</td>
<td>1.00 ±0.01</td>
<td>48.7 ±2.2</td>
<td>8.73 ± 0.59</td>
</tr>
<tr>
<td>20%</td>
<td>19.67</td>
<td>1.03</td>
<td>51.9</td>
<td>10.46</td>
</tr>
<tr>
<td></td>
<td>18.71 ± 1.16</td>
<td>1.00 ± 0.01</td>
<td>48.9 ±3.0</td>
<td>9.20 ± 1.11</td>
</tr>
<tr>
<td>15%</td>
<td>17.57</td>
<td>1.02</td>
<td>52.9</td>
<td>9.51</td>
</tr>
<tr>
<td></td>
<td>16.10 ± 0.83</td>
<td>0.98 ± 0.03</td>
<td>47.3 ±3.3</td>
<td>7.52 ± 1.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>IPL Annealed</th>
<th>0.25 cm$^2$</th>
<th>21.06</th>
<th>1.03</th>
<th>58.3</th>
<th>12.58</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20.29 ± 1.00</td>
<td>0.99 ± 0.03</td>
<td>50.56 ± 4.4</td>
<td>10.2 ± 1.48</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R2R w/C60</th>
<th>0.25 cm$^2$</th>
<th>22.31</th>
<th>0.97</th>
<th>56.6</th>
<th>12.23</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>21.93 ± 0.51</td>
<td>0.93 ± 0.03</td>
<td>53.6 ± 2.3</td>
<td>10.92 ± 0.76</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.8. $J$-$V$ curves of f-PSC devices made with 30-15% i-PrOH-water inks.

In addition to being able to deposit rapidly, the annealing time can also be reduced using IPL annealing which can effectively reducing the annealing time from several
minutes to milliseconds. Chandrasekhar had chosen an IPL processing parameter for processing the SnO2 at 2.0 m/min, which was adopted for this work. Because of the significant reduction in annealing time evaporation and film formation kinetics change significantly when moving from a thermal hot plate anneal to an IPL anneal. For this reason, IPL annealing requires may not be applicable with the same alcohol concentration. As the nanoparticles are already in the desired oxidation state the IPL serves to sinter the film increasing film density instead of assisting in solvent removal. Initial attempts for IPL annealing with the 20% \(i\)-PrOH ink had significant decreases in performance from the champion of thermal annealing (Table 4.1). This is due to the limited time for complete evaporation of the solvents prior to the IPL processing. Increasing the alcohol concentration to 30% \(i\)-PrOH Using the same deposition and annealing conditions, we were able to fabricate 0.25 cm\(^2\) devices on a 15Ω ITO/PET that had a champion PCE of 12.58% and average PCE of 10.2 % (Figure 4.9a, Table 4.2). This was a significant improvement when compared with hot plate coated samples. While the 20% \(i\)-PrOH improved uniformity through increasing ink dwell time, 30% \(i\)-PrOH increases film density due to faster solvent evaporation. Upon annealing with IPL these dense deposits are sintered together removing particle boundaries. Due to the thermal limitations of PET, the hotplate treatments cannot reach high enough temperatures to induce these sintering effects while the rapid annealing of IPL can super heat the surface while the bulk is left unaffected. Encouraged by these results with IPL, we attempted to slot die coat on a roll-to-roll with IPL annealing again utilizing processing parameters adopted from Chandrasekhar.

The roll-to-roll system is equipped with a premier die slot die head followed by an air knife before entering a 34 in\(^2\) optical window for IPL annealing (as described by
The distance from the slot die head to the IPL is 1 meter which at 1.8 m/min gives the film 33 secs to fully dry prior to IPL. Utilizing the air knife and low vapor pressure of alcohol makes drying this rapidly possible. We coated Cu:NiO\textsubscript{x} in a 30\% \textit{i}-PrOH ink at 1.8m/min using slot die gap of 50\textmu m and flow rate of 1.7mL/min. The SEM of the slot die coated ink shows a dense film with good overall coverage (Figure 4.9b).

Utilizing C60, and BCP (bathocuproine), to simply the stack for this testing we finished devices by blade coated MAPb\textsubscript{3} on top of the slot die coated Cu:NiO\textsubscript{x} then finished with thermal evaporation of C60, BCP, and Ag. The resulting 0.25 cm\textsuperscript{2} devices had a champion PCE of 12.23\%, FF of 56.6\%, \textit{Voc} of 0.98 V and \textit{Jsc} of 22.31 mA/cm\textsuperscript{2} (Figure 4.9a, Table 4.2). These result demonstrate that Cu: NiO\textsubscript{x} can be coated at 1.8 m/min without the addition of surfactants or supporting ligand network. To the best of our knowledge, this is the first reported NiO\textsubscript{x} nanoparticle ink coated at speeds above 10 mm/s, and the first to report solution phase deposited metal oxides for both CTLs.

**Figure 4.9.** a) \textit{J-V} curves of 30\% \textit{i}-PrOH ink annealed with IPL and coated blade coating or roll to roll slot die. b) SEM of Cu: NiO\textsubscript{x} coated by slot die on a roll to roll using a 30\% \textit{i}-PrOH ink. Scale bars are 4 \textmu m.
4.3 Conclusion

Here in we have discussed the development of a Cu:NiO\textsubscript{x} ink compatible with coating speeds of 1.8 m/min on slot die and blade coating platforms. Utilizing HSP we identified a range of water alcohol mixtures in which Cu:NiO\textsubscript{x} nanoparticles is stable while simultaneously improving the surface wetting without the addition of surfactants. It was found that in this alcohol water system $\delta_\text{h}$ played a minor role to $\delta_\text{p}$ when calculating compatibility due to the significant hydrogen bonding of water. Highly coordinating solvents such as DMSO could also be diluted down with alcohols and showed great stability however significant Ostwald ripening was observed making the particles unusable for the targeted thin films of PSCs. By varying alcohol concentration, we were able to further improve film uniformity while maintaining the surface tension below 30 dyn/cm\textsuperscript{2}. There is a distinct difference between ink alcohol concentration and annealing times, where the IPL process requires a higher concentration of alcohol that pushes the formulation towards the edge of the HSP sphere to accelerate drying but maintains enough stability for deposition. The IPL processed films were further demonstrated on a roll-to-roll platform. The resulting devices had champion performance ranging from 10-12.5% on flexible substrates. To the best of our knowledge this is the first reported NiO\textsubscript{x} nanoparticle ink coated at speeds above 10 mm/s, and the first report of solution phase deposited metal oxides for both the hole transport and electron transport layers.
CHAPTER 5.0 EVALUATION OF IMIDAZOLE BLOCKING LAYERS FOR PEROVSKITE STABILITY

5.1 Introduction

In the previous chapter we investigated scalable solution coatings of Cu:NiOₓ nanoparticles. Coatings were successfully coated with reasonable performance using 20 and 30% i-PrOH inks. A specific feature of those devices was the coating of SnO₂ on top of the perovskite surface. Although device stability was not studied quantitatively in that chapter, those devices were observed to undergo rapid degradation of the top metal (Ag). In this chapter the causes of this degradation are investigated and several imidazoles are evaluated as potential blocking materials at the perovskite/SnO₂ and SnO₂/Ag interfaces. The work described in this chapter is included in the submitted manuscript “Evaluation of Imidazole Blocking Layers for Perovskite Stability” by Armstrong et al.²⁰⁶

As described in Chapter 1, lead halide perovskites (ABX₃) are comprised of a cation (A), Pb²⁺ (B), and a halide or mixture of halides (X) with iodide being the primary species. The loss of iodide in the crystal lattice via ion migration leads to phase segregation in mixed halide devices, structural deformation with the development of lead rich regions, and the formation of PbI₂ resulting in device hysteresis.⁴⁶, ⁴⁷, ⁶⁶, ²⁰⁷ The application of electric fields and thermal stress have specifically been associated with iodide migration.²⁰⁸-²¹⁰ Permeation of iodide through the CTL to the electrode materials can result in the formation
of degradation products, such as the p-type dopant AgI. Early works by Kato et al. proposed that the perovskite degradation was induced by pinholes in the spiro-OMeTAD HTL, which allowed for moisture penetration and ion migration from the perovskite to the silver back contact. Similar results have been observed by other researchers with attempts to reduce this degradation pathway ranging from ion doping, small molecule additives, and polymer additives. These methods passivate the perovskite grain boundaries by stabilizing iodide in the perovskite surface and preventing migration. An alternative to additive engineering is interface modification via interfacial coatings to provide a material barrier to prevent ion migration. These can have the added benefit of improving band alignment between the perovskite, CTL, and electrode.

As noted in prior chapters, metal oxide nanoparticles are attractive CTL materials as they are made from earth abundant sources, have suitable band alignment that can be varied by doping, are inherently more durable than organic CTLs, and are scalable when deposited as nanoparticle inks. However, a significant obstacle to device stability when using nanoparticle CTL inks in the fabrication process is the presence of pinholes. To date, nanoparticles CTLs have been primarily deposited as the base CTL underneath the perovskite due to solvent incompatibilities of the perovskite surface with typical nanoparticle inks. The recent development of SnO₂ inks that can be directly deposited on top of perovskites has expanded the potential for the use of metal oxide ETL materials in both n-i-p and p-i-n devices. The packing of nanoparticle spheres invariably leads to intersectional gaps between the tightly packed particles. This can be minimized by using smaller particles to increase packing density. Additionally, fillers or interfacial layers can be used to reduce these gaps. While working with a silver interlayer for a transparent
conductive electrode, Yun et al. observed iodide migration through their nanoparticle SnO$_2$ ETL resulting in decreased conductivity.$^{219}$ The addition of diethanolamine into the ETL prevented AgI formation and increased device efficiency and durability.

Imidazoles have recently been explored as additives and interfacial materials compatible with metal oxides and perovskites.$^{223-226}$ The base structure is a five-membered heterocyclic ring containing a pyrrole-like nitrogen and a non-adjacent pyridine-like nitrogen in an aromatic $\pi$-system. The basic pyridine nitrogen can be involved in coordination to films as well as passivation of defects. The three carbons and the pyrrole nitrogen can each be functionalized to increase desired properties such as hydrophobicity, coordinating groups, structural orientation, or aromaticity. This flexibility provides a platform for exploring how these different properties effect interfaces in PSCs. Groups such as amides$^{227}$ and nitro$^{228}$ introduce strong bidentate coordinating character, while amines$^{229, 230}$ and alcohols$^{231, 232}$ can engage in hydrogen bonding interactions or serve as weak Lewis base donors. The addition of sterically restrictive phenyl, cyclohexyl, or fused aromatic structures alter conductivity of the interfacial material as well as adding structural restriction, effecting molecule packing.$^{233-235}$

In this chapter, a series of imidazole compounds are investigated as potential interfacial passivators or blocking materials to prevent the formation of AgI in the back contact in p-i-n PSCs. Selected compounds were employed as interfacial layers between the perovskite and Y:SnO$_2$ or between the Y:SnO$_2$ and Ag electrode. For this work, a UV lamp was utilized to accelerate iodide migration through the Y:SnO$_2$ layer. From the surveyed imidazoles it was found that successful blocking layers to have planar packing orientation with dense $\pi$-stacking and supporting hydrogen bonding network. The
hydrogen bonding network improves charge conduction through the interface, while anchoring the imidazole to the Y:SnO₂ surface

5.2 Results and Discussion

The degradation of PSCs via iodide migration from the perovskite absorber, through the CTL, to the Ag electrode can be observed by the formation of AgI on the back contact. To demonstrate this, a series of stress tests were performed on half-cell devices consisting of MAPbI₃ as the perovskite absorber on a flexible ITO-PET substrate with Y:SnO₂ as the ETL and Ag as the back contact (Figure 5.1a). In these initial studies, no interfacial layers were employed. The half-cell devices were exposed to a range of conditions to identify the role of external forces including heat and UV exposure (Figure 5.1b-d). Samples left under dark, ambient conditions showed a rapid browning around the silver contacts overnight. These results are indicative of moisture induced degradation propagating from the outer edge of the contacts towards the center.²²⁰,²³⁶ Consistent with this observation, samples placed on a hotplate at 80 °C overnight in an inert environment and dark conditions showed no visible signs of degradation. However, samples that were exposed to full spectrum light or UV light while heating at 80 °C under inert environment and short circuit conditions showed significant degradation of the Ag contact. This can be attributed to iodide migration under the simulated operating conditions. Investigation by XRD confirmed that no PbI₂ had formed during the degradation while AgI was not able to be detected. (Figure 5.1e).
5.2.1 Initial Stress Tests with Interfacial Layers

A series of imidazoles were investigated as interfacial layers to evaluate their ability to prevent iodide migration and formation of AgI. The compounds include 1-methylimidazole (Me-IM), 2-methyl-5-nitro imidazole (Me,NO2-IM), 5-aminoimidazole-4-carboxamide (NH2,Am-IM), 1-phenylimidazole (Ph-IM), 4-(imidazol-1-yl)phenol (PhOH-IM), 1-methylbenzimidazole (Me-BIM), 2-(chloromethyl)-benzimidazole (Cl-BIM), 4,5-diphenylimidazole (diPh-IM), and 1,5-dicyclohexylimidazole (diCy-IM) (Figure 5.2). The compounds were selected to encompass a variety of functional groups that can influence packing interactions and binding modes as described below. The compounds were incorporated as a separate interfacial layer between the perovskite and Y:SnO2 layers in the half-cells (Figure 5.1a), which were exposed to accelerated stress tests.
of 1 sun illumination under short circuit conditions at an elevated operation temperature of 35°C for 24 hours in a nitrogen glove box.

**Figure 5.2.** Imidazoles tested as interfacial layers at the perovskite Y:SnO2 interface

During the initial stress-test, half-cells with Me-IM, NH₂,Am-IM, and Me,NO₂-IM interfacial layers suffered from critical failures with significant conversion of the Ag to AgI (Table 5.1). Of these, NH₂,Am-IM showed the most degradation of Ag to AgI with complete conversion occurring even prior to any illumination. This is attributed to the bidentate coordinating ability of NH₂,Am-IM, which can coordinate to Pb²⁺ and destabilize the PbI₆ octahedron leading to accelerated iodide migration. The Me-IM molecule is the smallest of the compounds tested and is a liquid at room temperature. Coating tests of varying Me-IM concentrations in ethanol on perovskite show solvation of the perovskite at Me-IM concentrations higher than 1 % (v/v) consistent with its poor performance as a blocking layer. The failure of the Me,NO₂-IM half-cell was unexpected as similar species have been used as additives with perovskites to stabilize PbI₆ and improve perovskite grain structure.²³⁷,²³⁸
Table 5.1. Digital images of half-cell devices (PET/ITO/MAPbI3/IM/Y:SnO2/Ag) showing initial appearance and after light soaking at short circuit for 24 hours. The lower half of each sample was covered to simulate dark conditions with the red line separating the two regions.

<table>
<thead>
<tr>
<th>Imidazole</th>
<th>0 hr</th>
<th>24 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Me-IM" /></td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td><img src="image" alt="Me,NO2-IM" /></td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td><img src="image" alt="NH2,Am-IM" /></td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td><img src="image" alt="Ph-IM" /></td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
</tr>
<tr>
<td>Imidazole</td>
<td>0 hr</td>
<td>24 hr</td>
</tr>
<tr>
<td>-----------</td>
<td>------</td>
<td>-------</td>
</tr>
<tr>
<td><img src="image1" alt="PhOH-IM" /></td>
<td>![image2]</td>
<td>![image3]</td>
</tr>
<tr>
<td><img src="image4" alt="Me-BIM" /></td>
<td>![image5]</td>
<td>![image6]</td>
</tr>
<tr>
<td><img src="image7" alt="Cl-BIM" /></td>
<td>![image8]</td>
<td>![image9]</td>
</tr>
<tr>
<td><img src="image10" alt="diPh-IM" /></td>
<td>![image11]</td>
<td>![image12]</td>
</tr>
<tr>
<td><img src="image13" alt="diCy-IM" /></td>
<td>![image14]</td>
<td>![image15]</td>
</tr>
<tr>
<td><strong>Control Device</strong>&lt;br&gt;(no interface)</td>
<td>![image16]</td>
<td>![image17]</td>
</tr>
</tbody>
</table>
Next, we evaluated a series of compounds with extended \( \pi \)-networks as interface layer materials. The benzimidazole derivatives Me-BIM and Cl-BIM have fused rings making the molecules rigidly planar. The imidazoles Ph-IM and PhOH-IM have an aromatic functional group on the pyrrole-like nitrogen of the imidazole ring, allowing for free rotation about the C-N bond. The compounds Me-BIM, Ph-IM, and PhOH-IM all successfully passed the stress test with no AgI formation over 24 hours illumination (Table 5.1). Interestingly, Cl-BIM did not pass the stress test with formation of AgI taking place even under dark conditions (Table 5.1). For the initial group of compounds, the observed stability can be attributed to weak \( \pi \)-coordination with the Pb\(^{2+} \) and \( \pi \)-stacking interactions that orient Me-BIM, Ph-IM, and PhOH-IM into sheets that cover the surface, similar to the \( \pi \)-stacking observed in the x-ray structures of 1-methylbenzimidazoles.\(^{233, 234, 239} \) For Cl-BIM, the Cl sits outside of the BIM plane disrupting \( \pi \)-stacking as observed in the structure of 2-chloromethylbenzimidazolium.\(^{240} \) Additionally, the phenolic -OH of PhOH-IM may also serve as a Lewis base or hydrogen-bonding site for interactions with the perovskite or Y:SnO\(_2\). The electron withdrawing effects of the aromatic ring make this group significantly less basic than the functional groups in NH\(_2\),Am-IM. This is consistent with strong chelating interactions leading to destabilization at the perovskite surface, whereas softer hydrogen bonding or weaker Lewis basic coordination does not.\(^{214} \)

The results above strongly suggest that molecular planarity and an extended \( \pi \)-interactions are essential for an effective interface layer. To further probe this, the pair of imidazoles diPh-IM and diCy-IM where selected to evaluate packing orientation and nonaromatic cyclic functional groups (Table 5.1). When tested these materials showed degradation after 24 hours and are unsuitable for use as blocking materials. This is
attributed to the high steric strain associated with adjacent bulky phenyl (or cyclohexyl) groups on the IM ring, which disrupt the planarity of the molecules and preclude extended $\pi$-stacking.\textsuperscript{241} Notably, the degradation in the presence of diPh-IM and diCy-IM was not as severe as NH$_2$Am-IM, which had chelating groups capable of strong coordination with Pb$^{2+}$. Overall, the initial stress testing indicates that interface materials should be planar, capable of extended $\pi$-interactions, and should not contain strongly donating groups capable of displacing iodide from the PbI$_6$ octahedron.

5.2.2 Device Performance with Interfacial Layers

The imidazole compounds that passed the stress test (Me-BIM, Ph-IM, and PhOH-IM) were then evaluated in full devices to determine their effect on device performance. A series of devices were prepared on a flexible ITO-PET substrate with the selected imidazoles as an interfacial layer between the perovskite and Y:SnO$_2$ ETL. The overall device structures were PET/ITO/PTAA/PFN/CH$_3$NH$_3$PbI$_3$/IM/Y:SnO$_2$/Ag where polytriarylamine (PTAA) was used as a hole transport layer (HTL), poly[(9,9-bis(3$^\prime$-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) as an interfacial layer, and IM as the imidazole interfacial layer.\textsuperscript{237} The devices were fabricated using blade coating for all layers, except the Ag back contact, which was deposited by evaporation. The fabricated f-PSCs were measured under AM 1.5G simulated sunlight. Before measurement, the solar simulator was calibrated using an NREL-calibrated silicon reference photodiode with a KG5 filter to minimize the spectral mismatch.

The $J$-$V$ curves and device performance statistics for PSC devices with Ph-IM, PhOH-IM, and Me-BIM interfaces are presented in Figure 5.3. The photovoltaic
performance statistics relative to a control device without an interfacial layer between the perovskite and Y:SnO₂ are summarized in Table 5.2. Of the imidazoles tested, only PhOH-IM maintained equal or better average performance compared to the control. In that case, slight increases in the $J_{sc}$ and $V_{oc}$ where offset by a significant decrease in FF due to increased series resistance. The highest performing device containing PhOH-IM had a PCE of 12.4% with $V_{oc}$ of 0.900 V, $J_{sc}$ of 21.97 mA/cm² and FF of 62.9%. The addition of Ph-IM and Me-BIM saw significant decreases in $J_{sc}$ and $V_{oc}$ resulting in the best devices only having PCE’s of 6.03% and 4.56%, respectively. Decreases in $J_{sc}$ and $V_{oc}$ have been associated with photogenerated charge build up at the interfaces indicating the Ph-IM and Me-BIM are acting as blocking layers with poor charge transfer and poor band alignment.²⁴²

**Table 5.2.** Average and champion device photovoltaic performance of 0.1 cm² f-PSCs with a imidazole blocking layer at the perovskite/Y:SnO₂ interface.

<table>
<thead>
<tr>
<th>IM Interfacial Layer</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>17.46 ± 2.30</td>
<td>0.811 ± 0.071</td>
<td>61.6 ± 7.9</td>
<td>8.76 ± 1.81</td>
</tr>
<tr>
<td>PhOH-IM</td>
<td>19.74 ± 1.16</td>
<td>0.873 ± 0.057</td>
<td>53.9 ± 7.5</td>
<td>9.28 ± 1.46</td>
</tr>
<tr>
<td>Ph-IM</td>
<td>15.06 ± 2.41</td>
<td>0.767 ± 0.091</td>
<td>51.9 ± 8.2</td>
<td>6.03 ± 1.72</td>
</tr>
<tr>
<td>Me-BIM</td>
<td>10.90 ± 1.36</td>
<td>0.719 ± 0.056</td>
<td>57.9 ± 13.2</td>
<td>4.56 ± 1.35</td>
</tr>
<tr>
<td></td>
<td>13.87</td>
<td>0.731</td>
<td>69.8</td>
<td>7.08</td>
</tr>
</tbody>
</table>
Figure 5.3. Performance and device characteristics. a) J-V curves of champion devices (0.1 cm²) with various IM layers at the perovskite/Y:SnO₂ interface; box plots of photovoltaic parameters (b) Jsc, (c) Voc, (d) FF, and (e) PCE.

To investigate if PhOH-IM is performing more as a material barrier or passivator layer, devices with the PhOH-IM layer between the perovskite/Y:SnO₂ interface versus the Y:SnO₂/Ag interface were fabricated. The resulting devices showed no significant difference in PCE, FF, \( J_{sc} \) or \( V_{oc} \) (Figure 5.4). Further investigation by electron impedance spectroscopy (EIS) showed a slight improvement in shunt resistance when PhOH-IM was coated on top of the Y:SnO₂ layer versus directly on the perovskite surface (Figure 5.5a, Figure 2.2).\(^{243, 244}\) This would indicate that PhOH-IM is acting as a barrier to iodide migration, and not passivating the surface.
Figure 5.4. Device performance characteristics of with PhOH-IM as an interfacial layer at the perovskite/SnO2 (PhOH-IM/SnO2) and SnO2/Ag (SnO2/PhOH-IM) interfaces as box plots of photovoltaic parameters (a) Jsc, (b) Voc, (c) FF, and (d) PCE.

Figure 5.5. a) EIS of devices with PhOH-IM at the perovskite/Y:SnO2 (PhOH-IM/Y:SnO2) and Y:SnO2/Ag (Y:SnO2/PhOH-IM) ) interfaces relative to a control with no PhOH-IM interfacial layer; Normalized stability metrics over 70 hours of continuous illumination under short circuit conditions at 40 °C for devices with: b) PhOH-IM at the Y:SnO2/Ag interface, and c) no PhOH-IM interfacial layer.
5.2.3 Device Stability with Interfacial Layers

To test the effect of the imidazole interfacial layer on device stability, devices with a PhOH-IM layer at the Y:SnO₂/Ag interface and control devices with no interfacial layer were placed under illumination at short circuit conditions for aging in a N₂ glovebox. Samples were tested until control failure to establish a baseline performance of the PhOH-IM interface. Figure 5.5b,c shows normalized stability data over 70 hours of testing. After 24 hours of illumination, the control lost 50% of its initial PCE with a further drop in PCE over the next 48 hours resulting in a final performance drop of 80% after 70 hours. Over that same testing period PhOH-IM lost 20% of its initial PCE and then maintained its performance for the next 46 hours. This is a 60% improvement in stability verse the control. Performance loss in the control is associated with significant decreases in the $J_{sc}$ associated with perovskite degradation and observable electrode degradation. In contrast, when PhOH-IM is present at the Y:SnO₂/Ag interface this same loss is not observed as $J_{sc}$ is maintained and $V_{oc}$ is slightly improved after the initial break in period.²⁴⁵ Consistent with the initial screening tests no degradation of the electrodes was observed. This initial screening is a promising indicator but longer and more strenuous testing will be necessary to fully evaluate the effectiveness of PhOH-IM as a blocking layer.

5.3 Conclusions

In this chapter a series of imidazoles were evaluated as interfacial layers to prevent iodide migration from the perovskite to the Ag back contact through a solution phase deposited Y:SnO₂. It was found that iodide migration through the Y:SnO₂ layer was driven by UV light. The addition of an interfacial barrier was able to successfully prevent ion migration from causing electrode degradation and device failure. It was found that
imidazoles with strong coordinating groups such as nitro or amides accelerated film degradation. Imidazoles with conjugated planar systems were able to prevent ion migration, but proper anchoring to the film surface was necessary to prevent reduced charge extraction and decreased band alignment. Of the materials evaluated, PhOH-IM had the best performance with a 60% increase in stability versus the control. The improved stability is attributed to the dense \( \pi \)-stacking and hydrogen bonding network formed through the phenol oxygen and imidazole’s pyridine-like nitrogen (Figure 5.6). The hydrogen bonding network improves charge conduction through the interface, while anchoring the imidazole to the Y:SnO\(_2\) surface. This work helps to identify materials properties necessary to improve device stability. Long term stability testing and further development are necessary to further improve this novel interface.

Figure 5.6. Diagram of proposed PhOH-IM packing orientation as an interfacial layer.
CHAPTER 6.0 CONCLUSIONS

The future of NiO$_x$ nanoparticle CTLs is optimistic but is still facing several material and process challenges. First, material challenges that need to be addressed include improving film conductivity while not accelerating degradation of the perovskite by over exposure to Ni$^{3+}$. Doping has shown promise in addressing this issue but has fallen short of expectations with secondary organic passivators still being required to improve device stability. Incorporation of Lewis basic moieties such as amines and thiols on interfacial layers has proven effective at coordinating to the NiO$_x$ surface and providing a bridge to the perovskite. Furthermore, organic HTLs with internal molecular dipoles have shown to increase $V_{oc}$ while reducing hysteresis. Incorporating internal dipoles into ligand design could further improve the NiO$_x$/perovskite interface. Based on our own observations as discussed in Chapter 3, bulky nonconductive ligands need to be removed for effective device performance. For ligand coated nanoparticles to be viable low temperature option any organic incorporated will need to be volatile after deposition or be incorporated into the NiO$_x$ layer. Ligands design needs to incorporate highly conductive groups that promote charge extraction and coordination between layers/nanoparticles.

While conventional thermal annealing is compatible with glass-based substrates, flexible plastic substrates for high throughput processing are incompatible with temperatures over 150 °C. To work around this temperature threshold using oxidative methods such as UV-O$_3$ or O$_3$-plasma can be used to remove organics and increase Ni$^{3+}$
sites. As we demonstrated in Chapter 4, the addition of IPL annealing resulted in a 30% increase in overall PCE when compared to the hotplate treated samples. IPL is a viable alternative for rapid annealing of nanoparticles with our results showing significant improvements to $J_{sc}$ and FF. This work will need to be expanded upon to understand the effect of different IPL conditions on NiO$_x$ surface morphology and conductivity.

The annealing challenge is further compounded when looking to apply NiO$_x$ in the n-i-p configuration, which is another material challenge. While p-i-n is the default stack for NiO$_x$, there are some examples with an inverted n-i-p stack. To date, effective devices have only been demonstrated using vacuum methods such as sputtering or thermal evaporation to deposit NiO$_x$ on top of the perovskite layer. Attempts utilizing long chain ligands to disperse NiO$_x$ in perovskite compatible organic solvents have failed to result in high performing devices with best champion device reported by Pirzad et al. with a champion PCE of 12.6%. In that study, they were unable to get higher efficiency due to low $V_{oc}$ (0.88V) and FF (60%) that resulted from the incorporation of oleic acid in their ink formulation.$^{131}$ IPL annealing could also be utilized to help address this challenge by using a gradient pulsing pattern or lower energy pulses to allow surface heating but preventing perovskite degradation.$^{247}$ Instead of trying to suspend the extremely hydrophilic NiO$_x$ in chlorobenzene-based solutions, we propose looking at more polar options such as short chain alcohols. In Chapters 4 and 5 we used an ethanol based SnO$_2$, which was compatible with the perovskite surface. Targeting a similar solvent system by shifting the particle solvation sphere of NiO$_x$ to be compatible with an alcohol-based ink would require significantly shorter ligands than the nonpolar chlorobenzene system discussed in Chapter 3.
The second process challenge is transitioning away from spin coating to more scalable methods, like slot die coating. In Chapter 4 findings were presented that demonstrate the use of alcohols to address this challenge with moderate success. However, film uniformity requires further improvement, and significant series resistance was observed indicating the interface was nonideal. The addition of ligands during particle synthesis to better control particle formation could help to address this issue but as mentioned above accounting for the ligand post deposition is a major consideration. For this reason, the use of interfacial films will likely be required to address these issues.

The work in Chapter 5 describing the effects of various functional groups on a core imidazole structure is valuable for selecting materials for on the perovskite/SnO$_2$ or SnO$_2$/Ag interfaces. A more in depth understanding of the NiO$_x$ particle surface and reactive sites would aid in developing effective ligands and interfacial materials that could both improve band alignment while reducing Ni$^{3+}$ induced degradation. Despite the shortcoming listed here, NiO$_x$ remains the hole transport material best suited for large, scale roll out.
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Education

May 2021 – Present  
University of Louisville, Louisville, KY, Pursuing PhD in Chemistry  
Department of Chemistry  
Advisors: Craig Grapperhaus, PhD, Thad Druffel, PhD  
GPA 3.903

Aug 2018 – May 2021  
University of Louisville, Louisville, KY, Master of Science in Chemistry

Aug 2014 – May 2018  
Utah State University, Logan, UT, Bachelor of Science in Chemistry

Research Experience

Aug 2018 – Present  
Graduate Research Assistant University of Louisville, Louisville, KY  
• Develop methods for the deposition of NiOx for blade and slot die coating methods for applications in perovskite solar cells  
• Developed ligands to functionalize NiOx nanoparticles  
• Investigated perovskite stability and interfacial degradation  
• Work in interdisciplinary environment with heavy cross disciplinary activities.
Jan 2020 – Aug 2020  **Visiting Research Scientist, National Renewable Energy Laboratory, Golden, CO**
- Conducted research on solution phase deposition of NiOx nanoparticles
- Worked extensively with solar simulator, 2D glass scribe, blade coater, glove boxes, and thermal evaporator systems

Sept 2017 – July 2018 **Undergraduate Research Asst. Utah State University Logan, UT**
- Investigated the kinetics and by products of CO release from small molecule enzyme mimic of dioxygenase on methionine
- Synthesis of organic ligands for catalysis studies and crystal growth

March 2015-Aug 2017  **Forage-Livestock Research Asst. Utah State University Logan, UT**
- Conducted the collection and processing of plant, animal byproduct, and methane samples to support research in eco-friendly alternative feed development.
- Trained and assisted team members in bioassays and other specific job duties.
- Managed and supervised a team of 3-5 employees.
- Supervised pastures management and animal care for two separate 3-month periods with up to 30 animals during intensive grazing studies.
- Utilized animal handling skills to train livestock in halter use and leading.
- Coordinated with other research teams for shared work equipment and animal care.

July 2016- Aug 2017  **Field Technician Utah State University Logan, UT**
- Collected plant, feces, methane, and urine samples for use in feed selection and greenhouse gas reduction research.
- Collected field data for use in greenhouse gas reduction research.
- Assisted in the care of 24 - 42 animals.

**Awards**

- **University Fellowship Award Aug 2018– May 2020:** The most prestigious award granted by the University of Louisville to graduate students that covers a stipend, health insurance and fringe benefits for two years.
- **Dorothy H Gibson Memorial Fellowship Award Jan 2022:** Awarded by the Department of Chemistry, University of Louisville to honor the memory of Professor Dorothy Gibson
- **Graduate School Council Travel Award Nov 2022:** Awarded by the graduate school to cover costs associated with traveling to a conference.

**Publications/Conferences/Workshops**

**Publications**


**Conferences**


Workshops
Sep 2022 – Oct 2022   LaunchIt: Product Innovation Bootcamp

Patent

Instrumentation:
Experienced in operating the following instruments and interpretation of the corresponding data:

- **X-Ray Diffraction:** BRUKER Discovery D8 HR-XRD
- **Thermal Gravimetric Analysis:** Q600 SDT
- **Ultraviolet -Visible Spectroscopy:** Agilent 8463 UV-Vis
- **Photoluminescent:** Renishaw inVia confocal Raman/PL microscope system
- **Infrared Spectroscopy:** ThermoNicolet 360 IR
- **Scanning Electron Microscope:** Apreo C LoVac FESEM by ThermoScientific; FEI Nova600 FEG-SEM; TESCAN Vega3 SEM
- **Dynamic Light Scattering:** Brookhaven Instrument Corporation 90Plus
- **X-ray Photoelectron Spectroscopy:** VG Scientific MultiLab 3000

Technical Experience

Glove Box System
- Train new users for glove box system
- Conduct routine checks & refill consumable components in glove box system (pump fluids, air filters, solvent trap systems)
- Facilitate hazardous waste removal from system & collection through coordination with Department of Environmental Health & Safety at the University of Louisville
- Coordinate with local compressed gas supplier to regularly deliver and install N₂ feed line into glove box system
- Disassembled and Reassembled gloveboxes for cleaning and repurposing followed by reestablishing of atmospheric conditions.
- Carry out catalyst regeneration protocol by regulating regeneration gas flow using repurposed flowmeter

Roll-to-Roll printing machine
- Careful, precise instrument installation as optimized slot-die gap equals 100 μm with little margin for error
- Operation of Roll to Roll coater in conjunction with Slot die coating, Corona Discharger and IPL for the fabrication
Blade Coater

- Fabrication of perovskite solar cells on glass and plastic substrates. Requiring precious control of coating conditions and blade care.

Intense Pulse Light

- Operation of IPL machine within the Roll-to-Roll housing to allow inline annealing during coating.

Solar Simulator

- Constructed enclosure for long term solar simulator lamp that simultaneously allows ease of access and protection of user from harmful light exposure.
- Measuring photovoltaic response from photovoltaic devices.

Thermal evaporation

- Maintained and cleaned the interior of the evaporator system, ensuring optimal efficiency and consistent performance.
- Executed precise and controlled operations of the thermal evaporator, specializing in the evaporation of diverse materials including C60, BCP, Ag, Au, In, etc.

Leadership/Teaching Experience

Aug 2022 – Present
Cofounder of SoFab Inks LLC

Nov 2021 – May 2022
Secretary, Chemistry Graduate Student Association, University of Louisville, Louisville, KY

Aug 2019– May 2022
Department Representative, Graduate Student Council, University of Louisville, Louisville, KY

Jan 2022 – May 2022
Mechanical Engineering Capstone Team Mentor

Jan 2020 – May 2021
Undergraduate Researcher Mentor

Affiliations

Member of the American Chemical Society, Inorganic Chemistry Division
Member of Material Research Society

Certifications

- Certified through LabelMaster Services