Ligand-stabilized SnO2 as a high-performance and scalable electron transport material for inverted perovskite solar cells.

Sashil Chapagain
University of Louisville

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LIGAND-STABILIZED SnO₂ AS A HIGH-PERFORMANCE AND SCALABLE ELECTRON TRANSPORT MATERIAL FOR INVERTED PEROVSKITE SOLAR CELLS

By

Sashil Chapagain
M.S., Middle Tennessee State University, 2018
M.S., University of Louisville, 2021

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in Chemistry

Department of Chemistry
University of Louisville
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To my family, friends, and mentors
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ABSTRACT

LIGAND-STABILIZED SnO$_2$ AS A HIGH-PERFORMANCE AND SCALABLE ELECTRON TRANSPORT MATERIAL FOR INVERTED PEROVSKITE SOLAR CELLS

Sashil Chapagain

March 15, 2024

Over the past decade, perovskite solar cell (PSC) technology has attracted significant attention for its low material costs, simple fabrication processes, and impressive photovoltaic performance, with recent power conversion efficiencies (PCEs) surpassing 26%. This advancement marks PSCs as strong competitors to traditional silicon-based photovoltaics. Despite the high efficiency of PSCs, the path to commercialization is hindered by challenges in stability, scalability, and module efficiency. The stability and scalability of PSCs are primarily dependent on the successive charge transfer layers (CTLs) that are interfaced with the perovskite layer. Among CTLs, metal oxide (MO$_x$) CTLs are preferred for their cost-effectiveness, high stability, and scalability, facilitated by solution processing. Nonetheless, their application is mainly confined to being deposited beneath the perovskite layer due to solvent incompatibility of typical metal oxide dispersion mediums with the perovskite layer and high-temperature requirements to process metal oxide thin films. This dissertation proposes a novel approach for depositing tin (IV) oxide
(SnO$_2$) as an electron transport layer (ETL) directly onto the perovskite layer, aiming to fabricate large area, inverted flexible PSCs. SnO$_2$ is recognized for its excellent optoelectronic properties, low-temperature processability, and superior photo and chemical stability, yet its integration into inverted (p-i-n) architectures has been challenging due to solvent incompatibility and high processing temperature demands. We address these challenges by functionalizing pre-synthesized SnO$_2$ nanoparticles with acetate through ligand exchange, allowing their dispersion in anhydrous ethanol and enabling direct blade coating onto the perovskite without damage. The integrity of the perovskite layer after the deposition of the solution processed SnO$_2$ was confirmed through X-ray diffraction and scanning electron microscopy analysis.

The resulting SnO$_2$ nanoparticle dispersions performed well as an ETL in inverted perovskite solar cells and demonstrated excellent compatibility with diverse perovskite compositions. Furthermore, the performance of SnO$_2$ as an ETL was enhanced by doping the SnO$_2$ nanoparticles with yttrium during the synthesis process. The yttrium doped SnO$_2$ dispersion significantly improved performance in inverted flexible PSCs. Flexible PSCs on PET-ITO substrates, fabricated using blade coating methods, exhibited a champion PCE of 20.41\% with an open-circuit voltage ($V_{oc}$) of 1.17V for the triple cation perovskite composition. This study highlights the potential of fully solution-processed metal oxide charge transfer materials as a cost-effective and efficient alternative to fullerene-based organic ETLs in inverted perovskite solar cells, leading to efficient large-area flexible PSCs.
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CHAPTER 1 – INTRODUCTION

1.1 Lay Summary

The sun has been giving us energy for billions of years and is free wherever there is sunlight. If we could capture even a small part of this energy, we could reduce our dependence on fossil fuels, which are harmful to the environment. Solar energy can be turned directly into electricity using devices called solar cells. Currently, most solar cells are made from silicon because it works well and is reliable. However, these cells are relatively expensive and not very environmentally friendly, which is why researchers are looking for better solutions. One of these is a technology called perovskite photovoltaics.

Perovskite solar cells, which are solution-processable, offer a cost-effective and scalable alternative to traditional solar cell technologies, enabling large-scale production through methods such as roll-to-roll processing. They are made up of a material called halide perovskite, which is sandwiched between two layers that help move the electric charge around. These cells also have contacts at the front and back. One of the materials used for these layers is metal oxides, which are affordable and stable. But they are usually only used underneath the perovskite layer because they do not disperse in perovskite compatible solvents and need high temperatures to be applied. This dissertation presents a new way of applying tin (IV) oxide (SnO₂) as a metal oxide directly onto the perovskite layer. This could help make inexpensive and large area flexible perovskite solar cells.
SnO$_2$ is known for its great properties, it can be processed at low temperatures, and it is very stable. The research in this dissertation addresses the solvent incompatibilities and processing temperatures that have previously limited the application of SnO$_2$ in perovskite devices. By modifying SnO$_2$ particles with acetate the particles can be dispersed in ethanol and applied directly onto the perovskite without causing any damage.

The modified SnO$_2$ particles worked well in the perovskite solar cells and were compatible with different types of perovskites. The performance of the SnO$_2$ was improved by adding yttrium during the preparation of the SnO$_2$ particles. This led to a significant improvement in the performance of the flexible perovskite solar cells. The flexible perovskite solar cells fabricated on PET-ITO substrate using blade coating method achieved an efficiency of 20.41% with a voltage of 1.17V. This study shows that metal oxide materials processed in solution could be a cheap and efficient alternative to organic materials leading to efficient and large area flexible perovskite solar cells.

1.2 Scope of Dissertation

This dissertation investigates efficient and straightforward methods for depositing fully solution-processed tin oxide (SnO$_2$) onto perovskite as an electron transport layer (ETL), aiming to enhance the fabrication of lightweight and efficient flexible perovskite solar cells. It encompasses a series of studies, including the synthesis and functionalization of SnO$_2$ nanoparticles, formulation of perovskite compatible SnO$_2$ nanoparticle dispersions, investigation of the SnO$_2$ dispersions’ impact on perovskite, evaluation of SnO$_2$ performance as an ETL, performance enhancement of SnO$_2$ ETL through doping, and exploration of the compatibility of the SnO$_2$ dispersion with various perovskite compositions.
Following their synthesis, both pristine and functionalized SnO$_2$ nanoparticles were characterized using X-ray diffraction (XRD) and Fourier-transform infrared (FT-IR) spectroscopy. The coatings of SnO$_2$ and perovskite were also examined via scanning electron microscopy (SEM) to assess microscopic imperfections and film uniformity. The compatibility of SnO$_2$ dispersion with perovskite was evaluated using XRD, UV-visible spectroscopy, and SEM. Additionally, the electronic properties of SnO$_2$ nanoparticles as an ETL were assessed through photoluminescence (PL), time-resolved photoluminescence spectroscopy (TRPL), and electrochemical impedance spectroscopy (EIS). The performance of the PSCs was characterized using current density-voltage ($J-V$) analysis.

Chapters 1 to 3 provide background and experimental methods for the dissertation. Chapter 1 provides an overview of the dissertation, an introduction to perovskite solar cells (PSCs), and a discussion on current global energy and solar issues, setting the stage for the research on perovskites. Chapter 2 delves into the unique properties of SnO$_2$ as an ideal ETL material, its developmental history as an ETL material in PSCs, SnO$_2$ thin film fabrication methods, performance improvement strategies, and challenges for depositing solution processed SnO$_2$ directly on the perovskites. Chapter 3 outlines the experimental procedures for synthesizing and characterizing SnO$_2$ nanoparticles, including their functionalization with acetate ligands, fabrication of perovskite devices, and characterization methodologies.

Chapters 4 to 7 present research results and a summary. Chapter 4 discusses performance enhancement of solution processed SnO$_2$ nanoparticles as an ETL through elemental doping with yttrium, detailing the synthesis process, functionalization, and evaluation of photovoltaic performance in inverted flexible PSCs. Chapter 5 examines the compatibility of fully solution processed SnO$_2$ dispersions with various perovskite
compositions in an inverted architecture, highlighting the broader compatibility with commonly used perovskite compositions. Chapter 6 offers concluding remarks on the potential of fully solution processed SnO$_2$ for large-scale applications in inverted device architecture and future directions for perovskite and metal oxide coatings. A summary of the work is provided in Chapter 7.

1.3 Solar Energy Potential

Global energy consumption has steadily risen, particularly in emerging markets and developing economies. These areas face a surge in energy demands due to expanding populations, growing transportation, burgeoning industries, and technological advancements. Between 2009 and 2021, worldwide energy consumption rose from 482.82 exajoules to 595.15 exajoules.$^{1,2}$ Notably, nonrenewable fossil fuels such as oil, natural gas, and coal have been the primary sources, accounting for roughly 84% of the total energy consumption. Consequently, greenhouse gas emissions, specifically CO$_2$, surged from 26.98 gigatons to 30.74 gigatons during this period.$^{1,2}$ The burning of fossil fuels exacerbates the greenhouse effect, leading to a phenomenon commonly known as global warming. Moreover, fossil fuels are nonrenewable and finite. Once used up, they cannot be regenerated within human lifespans. Adding to the complexity, their distribution worldwide is uneven, making their prices susceptible to availability and geopolitical influences. Recent geopolitical events have led to a sharp spike in fossil fuel prices, triggering energy crises in various regions.$^3$ Further, electricity represents roughly 20% of the globe’s total final energy consumption. In 2022, about 70% of the global electricity generation relied on fossil fuels. The escalating fuel prices are responsible for a rapid hike in average electricity generation costs worldwide.$^4$ To mitigate the severe implications of
global warming and the looming energy crisis, a swift transition from nonrenewable fossil fuels to renewable alternatives is imperative.

Solar energy, characterized as the radiant light and heat from the sun, is a vast and readily available renewable energy source on Earth. The sun provides our planet with $1.4 \times 10^5$ TW of power, of which approximately $3.6 \times 10^4$ TW is harnessable.\(^5\) Remarkably, the energy Earth receives from the sun every hour equates to the annual consumption of an entire civilization.\(^6\) Solar energy utilization has ancient roots, evidenced by early technologies like sundials. However, it was only in the last century that we began harnessing solar energy for power generation. Solar energy, being a renewable and inexhaustible resource, holds significant importance due to its sustainability. Embracing it reduces our reliance on fossil fuels, leading to decreased greenhouse gas emissions that exacerbate climate change. If even a tiny fraction of this sunlight were to be harnessed by photovoltaic (PV) cells, which directly convert it into electricity, we could significantly reduce the need for greenhouse gas-emitting power plants.\(^6\)

Moreover, the universal availability of solar energy promotes decentralized power distribution, fostering energy independence worldwide. Unlike many other technologies, PV provides a direct and efficient method to transform solar energy into electricity, presenting an environmentally friendly and sustainable approach to address the ever-growing global energy demand.

1.4 Solar Radiant Energy and Photovoltaic Technology

The sun can be closely modeled as a blackbody emitter, characterized by a temperature of approximately 5800 K. Solar radiation refers to the electromagnetic radiation...
radiation emitted by the sun. Electromagnetic radiation can be understood as electromagnetic waves composed of massless energy quanta photons. Each photon is characterized by its wavelength ($\lambda$) or energy ($E$). The energy of a photon ($E$) and the wavelength of the light ($\lambda$) share an inverse relationship, which is expressed by equation 1.1:

$$E = \frac{hc}{\lambda}$$

where: $h$ is Planck’s constant ($h = 6.626 \times 10^{-34}$ J·s), $c$ is the speed of light ($c = 2.998 \times 10^8$ m/s), and $\lambda$ is the wavelength of the photon. The product of $h$ and $c$ is $1.99 \times 10^{-25}$ J m, which is more commonly represented in units of the electron-volt (eV) as shown in equation 1.2:

$$E(eV) = \frac{1240}{\lambda(nm)}$$

where 1 eV = $1.602 \times 10^{-19}$ J and 1 m = $10^9$ nm. This inverse relationship implies that high-energy photons are associated with short wavelengths, while low-energy photons correspond to longer wavelengths.

The spectral irradiance earth receives is not always uniform. It is influenced by the distance between earth and the sun and the angle at which sunlight hits the Earth's atmosphere. Additionally, solar radiation inside of the atmosphere differs from that outside due to the absorption, scattering, and reflection of solar radiation by atmospheric components (Figure 1.1). The non-uniformity of spectral irradiance is a critical factor to consider in evaluating the potential performance of photovoltaic devices in different geographic locations at different time cycles.
Solar cells convert solar energy into electrical energy through the photovoltaic effect, fundamentally operating on solid-state semiconductor principles. When a semiconductor absorbs a photon with energy ($E$) equal to or greater than its band gap energy ($E_g$), electrons are excited from its valence band to the conduction band, creating an electron-hole pair. Due to the built-in asymmetry in solar cells, an electrical potential is generated, which guides the electrons towards external circuits, separating the electron-hole pair (Figure 1.2a). The performance of a solar cell can be characterized by measuring its current density as a function of the biased voltage with variable loads and under light irradiation. The power conversion efficiency (PCE) of a solar cell is given by equation 1.3:

$$PCE = \frac{J_{sc}V_{oc}FF}{P_{in}}$$  \hspace{1cm} (1.3)$$

where $J_{sc}$ is the short-circuit current density, $V_{oc}$ is the open-circuit voltage, $FF$ is the fill factor, and $P_{in}$ is the incident power from solar irradiation.
The short-circuit current density ($J_{sc}$) signifies the maximum current across the solar cell when no potential difference exists (Figure 1.2a). The $J_{sc}$ value of a solar cell depends strongly on the band gap energy of the semiconductor ($E_g$). Given that photon energy ($E$) has an inverse relationship with radiation wavelength ($\lambda$), $J_{sc}$ typically increases with an increase in $\lambda$ across the visible and infrared regions of the solar spectrum whenever $E$ is greater than $E_g$.

![Figure 1.2. (a) Working principle of solar cells and (b) J-V curve of a solar cell identifying key J-V parameters.](image)

The open-circuit voltage ($V_{oc}$) is the potential difference across a solar cell when no current flows through it. Typically, there is a direct correlation between $V_{oc}$ and $E_g$ with a decrease in $E_g$ often results in a decrease in $V_{oc}$. On the other hand, as the bandgap of the semiconductor increases, the current density decreases. This is because the fraction of light with photon energy ($E$) greater than $E_g$ decreases. Although an increase in $J_{sc}$ can increase the power conversion efficiency (PCE), there is a trade-off involving $V_{oc}$, suggesting an optimal $E_g$ value for maximizing PCE. This balance gives rise to a fundamental efficiency limit for single-junction solar cells, known as the Shockley-Quiesser limit. Essentially, the Shockley-Quiesser limit underscores the fundamental role of the $E_g$ in photovoltaic
materials, showing how one can determine the maximum theoretical efficiency of a single-junction solar cell based on its band gap.\textsuperscript{14, 15} Based on the Shockley–Quiesser limit, we can get a maximum PCE of 33.7\% from a single p–n junction photovoltaic at the optimal bandgap of 1.34 eV (Figure 1.3a).\textsuperscript{14, 15} Additionally, photons with energies higher than the bandgap energy of semiconductor undergo thermalization and cannot be entirely converted to electrical energy. Thermalization reduces the efficiency of solar cells, so it is the primary loss mechanism in single-junction photovoltaics besides transmission and recombination losses, leading to a disparity between theoretical and actual device performance (Figure 1.3b).\textsuperscript{16} The value of FF in the solar cell is the ratio of $P_{\text{max}}$ ($J_{\text{max}}V_{\text{max}}$) to the product of $J_{\text{sc}}$ and $V_{\text{oc}}$ and is a measure of the squareness of the $J$-$V$ profile.

Figure 1.3. (a) Maximum achievable power conversion efficiency (PCE) as a function of the bandgap for single-junction photovoltaics according to the Shockley–Queisser theory\textsuperscript{17} and (b) occupied solar spectrum for Si solar cells.\textsuperscript{18}

1.5 Solar Cell Technologies

1.5.1 First Generation Solar Cells

First-generation solar cells are primarily comprised of silicon wafer-based solar cells, including monocrystalline silicon (c-Si) and polycrystalline silicon (p-Si). This is a mature technology with a well-established manufacturing process. Regarding efficiency,
these cells range from 15% to 20% for modules, with PCE values surpassing 26% under lab conditions.\textsuperscript{19-21} They have a long lifespan of 25 years and occupy above 80% of the current market share. However, their fabrication requires ultra-pure metallic silicon, derived by crystallizing melted Si in furnaces at temperatures exceeding 1400 °C. Moreover, silicon has a relatively low absorption coefficient due to its indirect band gap nature, which requires thicker silicon layers (often more than 100 µM) to absorb adequate light. Thus, the primary drawbacks of these cells are their high energy consumption during processing and the requirement for more material.\textsuperscript{21}

1.5.2 Second Generation Solar Cells

Second-generation solar cells encompass thin-film-based technologies such as amorphous silicon (a-Si), cadmium telluride (CdTe), and copper indium gallium selenide (CIGS). In contrast to the first-generation silicon wafer-based cells, these thin-film cells are advantageous due to their reduced material requirements and straightforward manufacturing processes. Their design allows flexibility, enabling diverse applications, fromrollable panels to building-integrated photovoltaics. Currently, CIGS and CdTe solar cells have reached above 20% efficiencies.\textsuperscript{19} However, they face challenges with device instability, material scarcity, and environmental toxicity.\textsuperscript{22}

1.5.3 Third Generation Solar Cells

The first and second-generation solar cells are known for their efficiency and stability. Nevertheless, challenges like slow and energy-intensive processing, high material costs, and environmental concerns have limited their potential as substitutes for fossil fuel-based energy sources, such as thermal power generation.\textsuperscript{23} These limitations prompted
researchers to seek more cost-effective solutions, leading to the emergence of third-generation photovoltaics.

Third-generation solar cells are based on semiconducting organic macromolecules, inorganic nanoparticles, or hybrids. Examples of these cells include dye-sensitized solar cells (DSSCs), organic photovoltaic cells (OPVs), perovskite solar cells (PSCs), and quantum dot solar cells. These third-generation solar cells are solution-processed, making them suitable for large-scale deployment through roll-to-roll production. Third-generation technologies aim to achieve higher efficiency and can potentially be manufactured more affordably and on a larger scale. However, many of these advanced technologies are still under development and have not been extensively commercialized. Furthermore, the durability and lifespan of these emerging technologies remain subjects of continuous research and development.\textsuperscript{13, 24}

1.6 Perovskite Solar Cells

Third-generation solar cells, which are solution-processible, offer the advantage of potentially being produced at a low cost. However, early members of this generation, such as DSSCs and OPVs, had a performance limited to around 10%.\textsuperscript{24} The lower photovoltaic performance of third-generation solar cells, compared to the first and second-generation, limited their commercialization prospects.\textsuperscript{24} To address these limitations and enhance performance, PSCs were evolved. Over the last decade, PSCs have gained significant interest from the scientific community due to their remarkable improvement in PCE as a single junction or as a tandem with other photovoltaic technologies (Figure 1.4).\textsuperscript{17} This is primarily due to their noteworthy improvement in PCE, which surged from 3.8% in 2009
to 26.1% in 2022.\textsuperscript{19, 24} Such figures are not only comparable to, but also surpass, the performance of the best-performing devices from the first and second generations.

PSCs operate similarly to solid-state p–n junction solar cells, where perovskite acts as an intrinsic semiconductor (i). In PSCs, halide perovskite is sandwiched between an electron-selective layer (n-type) and a hole-selective layer (p-type), with front and back contacts in place (Figure 1.5). The functionality of PSCs primarily involves light absorption by the perovskite materials, generation of excitons, separation of charge, and collection and transportation of charges.\textsuperscript{25}

When a halide perovskite in PSCs absorbs solar radiation with photon energy equal to or exceeding its bandgap, it excites electrons from their ground state to an excited state, forming excitons (electron-hole pairs). However, the exciton binding energy in halide perovskite is remarkably low, contributing to the spontaneous generation of free charge carriers (electrons and holes) from excitons.\textsuperscript{26}

![Figure 1.4. Chart of reported power conversion efficiencies (PCEs) against year for laboratory-scale perovskite PVs (including single-junction and multijunction configurations) and illustrates the rapid progress in device performance.\textsuperscript{17}](image)

\textsuperscript{12}
After generating free charge carriers, these electrons and holes exhibit ambipolar transport due to their small and similar effective masses.\textsuperscript{27} Before the recombination of electrons and holes occurs, the electron transport layer (ETL) captures the excited electrons, directing them to the cathode. Concurrently, the hole transport layer (HTL) extracts the holes and guides them to the anode. The band gap of the perovskite materials limits the maximum photocurrent density in PSCs. However, the open circuit voltage ($V_{OC}$) in PSCs is controlled by the splitting of quasi-fermi levels along and recombination within the perovskite.\textsuperscript{28, 29}

![Figure 1.5. Working principle of perovskite solar cells.](image)

1.6.1 Architectures of Perovskite Solar Cells

1.6.1.1 Mesoporous Perovskite Solar Cells

Early advancements in the efficiency of PSCs utilized a mesoporous configuration. In this architecture, a very thin layer of electron transport material, often TiO$_2$, is applied to a conductive glass substrate as a compact layer. Over the compact layer, a scaffold layer of metal oxide or nonmetal oxide nanoparticles such as TiO$_2$, Al$_2$O$_3$, ZrO$_2$, or SiO$_2$ sintered
at elevated temperatures is present, into which the perovskite material is introduced. The mesoporous design offers increased surface area and better light scattering. However, its need for high-temperature processing and a complex fabrication process makes it expensive and unsuitable for flexible PSCs on low melting substrates.

1.6.1.2 Planar Perovskite Solar Cells

Planar PSCs have a direct interface between the active layer and flat hole-transporting and electron-transporting layers, eliminating the need for a mesoporous scaffold (Figure 1.6a). This design is potentially more cost-effective due to simpler fabrication techniques and compatibility with flexible substrates since high-temperature sintering steps are not required. Uniform films are easier to achieve in planar configurations, which allows efficient charge extraction and minimizes recombination. Planar designs are more aligned with large-scale manufacturing methods. There are two main configurations for planar architecture depending on which transport layer light first passes through.

Figure 1.6. Different architectures of perovskite solar cells.
The n-i-p structure, also referred to as the regular planar structure, starts with an ETL on a transparent conductive oxide (TCO), followed by the intrinsic perovskite layer with a HTL on top (Figure 1.6b). Light enters through the ETL, and materials like TiO$_2$, SnO$_2$, or ZnO are used for ETLs, with spiro-OMeTAD as a common HTL.$^{24}$

The p-i-n, or inverted planar structure, begins with a HTL on a substrate coated with TCO, followed by the intrinsic perovskite and then the ETL (Figure 1.6c). Light enters through the HTL. This "inverted" configuration uses materials like NiO$_x$, PTAA, and PEDOT:PSS for the HTL and fullerene derivatives, SnO$_2$, and ZnO for the ETL.$^{24}$ See sections 1.9 and 1.10 for more detailed descriptions of ETL and HTL materials, respectively.

1.7 Halide Perovskite Materials

1.7.1 Structure and Composition

Perovskite materials are characterized by a crystal structure analogous to CaTiO$_3$ and can be described by the chemical formula ABX$_3$, where A and B are cations, and X is an anion (Figure 1.7). In halide perovskite the X-site is occupied by halide anions such as I$^-$, Br$^-$, and Cl$^-$. The A-site typically hosts monovalent cations like methylammonium [CH$_3$NH$_3$]$^+$, formamidinium [CH(NH$_2$)$_2$]$^+$, and cesium (Cs$^+$) or combinations of two or more of these. Meanwhile, bivalent metal cations like Pb$^{2+}$ and Sn$^{2+}$ predominantly occupy the B-site.$^{24,31}$ In the ideal cubic structure of halide perovskites, the larger A-site cation occupies space inside the eight corners-sharing octahedra [BX$_6$]$^{2+}$ and coordinates with twelve X anions, resulting in 12-fold cuboctahedral coordination. The smaller B-site cation
has sixfold coordination, stabilized within an octahedral site that it shares with six X anions.

![Perovskite Crystal Structure](image)

Figure 1.7. ABX₃ perovskite crystal structure showing BX₆ octahedral (left). A-site cation occupying space inside the eight corners-sharing octahdra [BX₆]⁴⁺ and coordinating with twelve X anions in cuboctahedral coordination (right).³²

Within the cubic unit cell, larger A cations occupy corner positions, B cations occupy body-center positions, and X anions are placed at the face-centered positions.³¹

The crystal structures of halide perovskites are often subject to distortions. These distortions arise from factors such as variations in ionic size, electrostatic interactions, and external conditions like temperature and pressure.³³⁻³⁵ The structural stability of halide perovskites can be empirically determined using the Goldschmidt tolerance factor (t) as shown in equation 1.4. This factor is calculated using the radii of the A-site cation, B-site cation, and X-anion.³⁶

\[
t = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}}
\]  (1.4)

Typically, a tolerance factor in the range of 0.8 < t < 1.0 suggests that the perovskite structure is stable.³⁷ However, the tolerance factor alone is not a sufficient condition to predict the formation and stability of the perovskite structure. The combination of octahedral factor (μ) (equation 1.5) with tolerance factor provides much accurate
information about the formation of perovskite structure.\textsuperscript{38} For halide perovskite, the empirical value of the octahedral factor adopts within $0.44 < \mu < 0.90$.

$$Octahedral \ factor \ (\mu) = \frac{r_B}{r_A}$$ \hspace{1cm} (1.5)

The halide perovskites adopt the tolerance factor ($t$) and octahedral factor ($\mu$) values in the ranges of $0.81 < t < 1.11$ and $0.44 < \mu < 0.90$, with the ideal cubic crystal structure restricted to $0.9 < t < 1.0$.\textsuperscript{39} Based on the calculated values of tolerance factor ($t$) and octahedral factor ($\mu$), it is possible to engineer stable perovskites with diverse compositions and varying band gaps using different combinations of the A-site, B-site, and X-site ions. Table 1.1 lists ions for the A-site, B-site, and X-site, along with their respective sizes, suitable for creating specific perovskite structures.\textsuperscript{24, 40} In the development of PSCs, a significant enhancement in both efficiency and stability has been observed with the incorporation of different cations in the A-Site and various halides in the B-Site. Over time, most of the champion efficiencies in PSCs have been achieved with mixed cation perovskites, either with single or mixed halides.\textsuperscript{41} The literature reports various combinations of A-site cations, including MA, FA, and Cs$^+$, as well as anions like iodide, bromide, and chloride. Among these, combinations like FA/MA, Cs/FA, and triple cations such as MA/FA/Cs, paired with different halide compositions, are particularly popular due to their enhanced performance.\textsuperscript{24}
Table 1.1. Ionic radii of some common A-site cations, B-site cations, and X-site anions used in metal halide perovskites.\textsuperscript{24,40}

<table>
<thead>
<tr>
<th>A-site</th>
<th>radius (pm)</th>
<th>B-site</th>
<th>radius (pm)</th>
<th>X-site</th>
<th>radius (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH\textsubscript{4}\textsuperscript{+}</td>
<td>146</td>
<td>Pb\textsuperscript{2+}</td>
<td>119</td>
<td>F\textsuperscript{−}</td>
<td>129</td>
</tr>
<tr>
<td>methylammonium [CH\textsubscript{3}NH\textsubscript{3}]\textsuperscript{+}</td>
<td>217</td>
<td>Sn\textsuperscript{2+}</td>
<td>110</td>
<td>Cl\textsuperscript{−}</td>
<td>181</td>
</tr>
<tr>
<td>formamidinium, [CH(NH\textsubscript{2})\textsubscript{2}]\textsuperscript{+}</td>
<td>253</td>
<td>Ge\textsuperscript{2+}</td>
<td>73</td>
<td>Br\textsuperscript{−}</td>
<td>196</td>
</tr>
<tr>
<td>hydrazinium, [NH\textsubscript{3}NH\textsubscript{2}]\textsuperscript{+}</td>
<td>217</td>
<td>Mg\textsuperscript{2+}</td>
<td>72</td>
<td>I\textsuperscript{−}</td>
<td>220</td>
</tr>
<tr>
<td>azetidinium, [(CH\textsubscript{2})\textsubscript{3}NH\textsubscript{2}]\textsuperscript{+}</td>
<td>250</td>
<td>Ca\textsuperscript{2+}</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydroxylammonium, [NH\textsubscript{3}OH]\textsuperscript{+}</td>
<td>216</td>
<td>Sr\textsuperscript{2+}</td>
<td>118</td>
<td></td>
<td></td>
</tr>
<tr>
<td>imidazolium, [C\textsubscript{3}N\textsubscript{2}H\textsubscript{3}]\textsuperscript{+}</td>
<td>258</td>
<td>Ba\textsuperscript{2+}</td>
<td>135</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethylammonium, [(CH\textsubscript{3}CH\textsubscript{2})NH\textsubscript{3}]\textsuperscript{+}</td>
<td>274</td>
<td>Cu\textsuperscript{2+}</td>
<td>73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dimethylammonium, [(CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2}]\textsuperscript{+}</td>
<td>272</td>
<td>Fe\textsuperscript{2+}</td>
<td>78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>guanidinium, [(NH\textsubscript{2})\textsubscript{3}C]\textsuperscript{+}</td>
<td>278</td>
<td>Pd\textsuperscript{2+}</td>
<td>86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetramethylammonium, [(CH\textsubscript{3})\textsubscript{4}N]\textsuperscript{+}</td>
<td>292</td>
<td>Eu\textsuperscript{2+}</td>
<td>117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>thiazolium, [C\textsubscript{3}H\textsubscript{4}NS]\textsuperscript{+}</td>
<td>320</td>
<td>Bi\textsuperscript{3+}</td>
<td>103</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-pyrrolinium, [NC\textsubscript{4}H\textsubscript{8}]\textsuperscript{+}</td>
<td>272</td>
<td>Sb\textsuperscript{3+}</td>
<td>76</td>
<td></td>
<td></td>
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<td>tropylium, [C\textsubscript{7}H\textsubscript{7}]\textsuperscript{+}</td>
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<tr>
<td>K\textsuperscript{+}</td>
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<td></td>
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</tr>
<tr>
<td>Rb\textsuperscript{+}</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs\textsuperscript{+}</td>
<td>188</td>
<td></td>
<td></td>
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</tbody>
</table>

1.7.2 Electronic Band Structure and Semiconducting Properties

The halide perovskite is recognized as a direct band gap semiconductor. Its electronic band structure is derived from the atomic orbitals of the B-site cation and the X-
site anion. Specifically, the valence band maximum (VBM) primarily comprises sigma antibonding orbitals (σ*), formed by the interaction between the B-s and X-p orbitals. On the other hand, the conduction band minimum (CBM) consists of a nonbonding hybrid state created by the B-p and X-p orbitals.\(^{35}\)

In MAPbI\(_3\) perovskite, the VBM comprises σ-antibonding orbitals (σ*) from the combination of Pb 6s and I 5p orbitals. In contrast, the CBM predominantly features the vacant Pb 6p orbitals, with a slight antibonding contribution from the I 5s orbitals (Figure 1.8).\(^{31}\)

![Figure 1.8. Schematic representation of the formation of bonding and antibonding orbitals in lead iodide perovskite through the hybridization of lead and iodide atomic orbitals.\(^{42}\)](image)

Interestingly, the A-site cation (MA in MAPbI\(_3\)) forms a sigma bond deep inside the VB and CB. This signifies that the contribution of A-site cation to energy band structures is relatively insignificant, with the primary determinants of the energy band structure emerging from the BX\(_6\) octahedra.\(^{43}\) The substitution of MA with other organic or inorganic cations leads to subtle changes in the electronic states, mainly attributed to
size effects. However, A-site cations are crucial for the stability of the perovskite crystal and the overall charge compensation of [BX₆]⁴⁻ octahedra. Different A-site cations interact differently with the surrounding octahedra, influencing their orientation, B-X bond lengths, and bond character (ionic and covalent). Such interactions are reported to influence the overall band gap of the perovskite materials. However, the halide component's substitution significantly affects the electronic states. As we transition from Cl to Br to I, there is a corresponding VB transition from 3p to 4p to 5p, which in turn reduces the ionization potential or binding energy.

1.8 Properties of Halide Perovskites as an Ideal Photovoltaic Material

The halide perovskite materials are direct band gap semiconductors with a high structural symmetry in which there is a p-p electronic transition from VB to CB, enabled by a pair of Pb s orbital electrons. This electronic transition results in very high optical absorption in halide perovskite with an absorption coefficient of 10⁵ cm⁻¹. Consequently, the high optical absorption ensures that even a thin film of halide perovskite, under 500 nm, can absorb nearly all visible light. Furthermore, halide perovskites have very low exciton binding energy, estimated at around 16 ± 2 meV for MAPbI₃. This minimal binding energy is fundamental as it facilitates the spontaneous generation of a substantial number of free-charge carriers.

The halide perovskite materials have remarkably high defect tolerance properties. The defect tolerance properties of halide perovskite originate from its energy band structure. In MAPbI₃, a weak antibonding interaction between Pb p orbital and I p orbitals results in a CBM close to the Pb p orbitals. Meanwhile, a stronger antibonding interaction between Pb s and I p orbitals lowers the VBM, drawing it closer to the I p orbital. Such
energy band structures prefer the formation of shallow vacancy defects created by removing I⁻ and Pb⁺ species.²³

The longer diffusion length and suppressed recombination are direct consequences of the high defect tolerance properties of halide perovskite. As estimated by the PL lifetime, the charge carrier diffusion length in halide perovskite ranges from 1 µm in polycrystalline film to above 100 µm in a single crystal.⁴⁴ In a halide perovskite, photogenerated carriers behave as free carriers and can migrate without recombination for hundreds of nanoseconds, similar to inorganic photovoltaic semiconductors such as Si and GaAs.²³ So, the generation of high voltage in PSCs originates from the high defect-tolerant nature of halide perovskite, and the high PCE of PSCs results from high photovoltage rather than the amplitude of the photocurrent.⁴⁵

1.9 Electron Transport Layer Materials in Perovskite Solar Cells

The ETLs are n-type semiconductors that collect photogenerated electrons from the perovskite layer and carry them to the electrode while blocking holes to reduce the likelihood of charge recombination. Key considerations for ETL design include proper energy band alignment with the perovskite to enable smooth electron flow with minimal energy loss (Figure 1.9). High electron mobility is crucial for rapid electron transport and minimizing recombination losses. The ETL must exhibit good environmental, photochemical, and thermal stability. Additionally, a wide band gap and high transparency are critical to reduce parasitic absorption by the ETLs, ensuring that light can effectively pass through the ETL and be absorbed by the perovskite layer. The uniform surface coverage without pinholes and the good quality film are essential to avoid unwanted
contact with the hole transport layer that could cause recombination and device failure. The commonly used ETLs are divided into inorganic ETLs and organic ETLs.

1.9.1 Inorganic Electron Transport Layer Materials

Inorganic transparent conductive metal oxide (TCO) with wide band gap and n-type semiconducting characters are excellent candidates for the ETL in PSCs. Due to their superior optoelectronic properties, cost-effectiveness, and simple fabrication methods, titanium dioxide (TiO$_2$), zinc oxide (ZnO), and tin(IV) oxide (SnO$_2$) are commonly used inorganic ETLs in PSCs.$^{46}$

TiO$_2$ is a well-established ETL material in PSCs, building upon its extensive development in dye-sensitized solar cells (DSSCs). In the preliminary stages of PSC development, TiO$_2$ was rapidly adopted due to its suitable band alignment with perovskite materials and high transmittance. The majority of the highest-efficiency PSCs previously reported utilized a mesoporous TiO$_2$ structure.$^{30}$ However, the need for high-temperature processing (around 500 °C), combined with low charge mobility in TiO$_2$ and high photocatalytic activity under UV radiation, has severely limited its potential for commercial application.$^{47,48}$

To address the issues associated with TiO$_2$, ZnO has been proposed as an alternative ETL. ZnO has high electron mobility, high transparency, and energy levels well matched with those of perovskite materials. Moreover, ZnO can be processed at low temperatures, typically below 150 °C, which makes it a promising candidate for lightweight and flexible PSCs (f-PSCs) on PET-based substrates. However, ZnO processed at low temperatures often contains hydroxyl groups that impart a basic characteristic to the material. This basic
nature of ZnO can lead to the deprotonation of the perovskite layer, resulting in the decomposition of the perovskite into its constituent materials. 

Currently, tin (IV) oxide (SnO\textsubscript{2}) has emerged as a prominent ETL alternative to TiO\textsubscript{2} and ZnO in PSCs. It has been involved in devices that have reported PCEs above 25.7\% in single-junction planar structures. A detailed introduction to SnO\textsubscript{2} ETLs is provided in Chapter 2. In short, SnO\textsubscript{2} is a wide bandgap n-type semiconductor with a band gap of approximately 3.5 - 4.0 eV, allowing most of the visible light spectrum to pass through. It has demonstrated high electron mobility, with values reported from 200 to 250 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}, which can lead to enhanced charge extraction in PSCs and reduce the need for high temperature processed mesoporous layers.

In addition to its favorable electronic properties, SnO\textsubscript{2} exhibits superior photostability compared to TiO\textsubscript{2}, especially regarding UV light exposure. This improved photostability helps mitigate light-induced degradation, a significant issue for TiO\textsubscript{2}-based PSCs. Chemically, SnO\textsubscript{2} is stable in the presence of moisture and oxygen, and its hygroscopic nature is less pronounced than that of TiO\textsubscript{2} and ZnO. This attribute makes SnO\textsubscript{2} less susceptible to degradation under ambient conditions, further endorsing its use in PSCs.

1.9.2 Organic Electron Transport Layer Materials

Fullerene derivatives, including C\textsubscript{60}, C\textsubscript{70}, PC\textsubscript{61}BM (Phenyl-C61-butyric acid methyl ester), and PC\textsubscript{71}BM (Phenyl-C71-butyric acid methyl ester) are prominent components in the ETL of inverted PSCs.\textsuperscript{51, 52} They are preferred for their ability to enable low-temperature processing, superior electron mobility, and tunable lowest unoccupied molecular orbital (LUMO) energy levels that are well-matched with the perovskite energy band.\textsuperscript{53} These
attributes make them suitable for inverted PSCs, which have achieved PCEs exceeding 26% in single-junction planar structures.\textsuperscript{54} The application of these materials onto the perovskite layer can be accomplished through physical vapor deposition (PVD) or solution-based deposition techniques using solvents that do not degrade perovskite. In many instances, fullerenes and their derivatives are used in a bilayer configuration alongside metal oxide ETLs (forming a fullerene/MOx ETL structure) to improve PSC performance and enhance stability. This bilayer technique takes advantage of the defect passivation properties of fullerenes, which contribute to enhanced device stability and efficiency.\textsuperscript{30, 55}

Despite their benefits, a notable barrier to the wider adoption of fullerene derivatives in commercial applications is their high production costs, energy-intensive deposition methods, poor wettability, and mechanical failure. To overcome this challenge, future research needs to prioritize the development of cost-effective alternatives to fullerenes for ETLs, which will be key in advancing the commercial viability of perovskite solar technology.

1.10 Hole Transport Layer Material in Perovskite Solar Cells

HTL materials are p-type semiconductors responsible for extracting photogenerated holes from the perovskite layer and transporting them to the anode. This function is vital for preventing electron/hole recombination and is essential across nearly all PSC architectures, whether mesoporous or planar. HTL requires certain qualities to be successfully utilized in PSCs. These include proper energy band alignment with the perovskite materials, high hole mobility, high transparency, and a wider band gap. Additionally, it should have long-term environmental stability and good photochemical and thermal stability.\textsuperscript{56}
The commonly used HTLs are divided into two categories: organic and inorganic. Organic HTLs, such as 2,2′,7,7′-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene (spiro-OMeTAD) spiro-OMeTAD, poly[bis(4-phenyl) (2,4,6-trimethylphenyl)amine] (PTAA), poly(3-hexylthiophene-2,5-diyl) (P3HT), and poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) are common in PSCs. Among organic HTL, PTAA, and spiro-OMeTAD are commonly used for highly efficient PSCs due to their superior performance. However, the charge carrier mobility PTAA and spiro-OMeTAD is inherently low. To address this, they are often doped with ionic salts containing Li⁺, which can improve mobility but at the cost of stability. Additionally, organic HTLs are costly, and their multistep synthesis complicates scalability.

In contrast, inorganic HTLs such as nickel oxide (NiOₓ), cuprous oxide (Cu₂O), cupric oxide (CuO), and copper thiocyanate (CuSCN) are less expensive and more straightforward to synthesize, making them more amenable to scaling up. Despite these
advantages, they typically offer lower efficiency than their organic counterparts. It is necessary to weigh the benefits of high performance offered by organic HTLs against the ease of production and cost-effectiveness of inorganic HTLs to find the optimal solution for practical commercial applications.
2.1 Background

Currently, SnO₂ has emerged as a prominent ETL alternative to TiO₂ and ZnO in PSCs with PCEs exceeding 25% in single-junction planar structures (Figure 2.1). SnO₂ as an ETL has several advantages over other ETLs. As a wide bandgap n-type semiconductor, the excellent optoelectronic properties of SnO₂ offer significant advantages as an ETL material for PSCs. Its wide bandgap of approximately 3.5-4.0 eV and low refractive indices allow most visible light to pass through it, enhancing photocurrent generation and device efficiency. Additionally, SnO₂ has higher electron mobility (200 to 250 cm² V⁻¹ S⁻¹) and its well-aligned conduction band with the perovskite conduction band facilitates efficient electron extraction and transportation, thus minimizing energy losses at the ETL-perovskite interface. Regarding stability, SnO₂ has better photostability and chemical stability than TiO₂ and ZnO. Its processing temperature below 150 °C expands the range of viable substrates for PSCs, including flexible and temperature-sensitive PET-based materials. Compared to fullerene derivatives, the superior thermal and chemical stability of SnO₂ as an inorganic material suggests the potential for improved long-term stability of PSCs. Furthermore, the adaptability of SnO₂ to diverse deposition methods, ranging from solution to vapor phase, enhances its flexibility in the fabrication process. It can be deposited as a precursor and converted into an oxide-thin film or as a pre-synthesized nanoparticle.
This versatility presents a significant advantage over fullerene-based ETLs, which mainly rely on vapor deposition methods and can introduce additional complexities in fabrication. The non-toxic and environmentally friendly nature of SnO₂ enhances its suitability as an ETL material for large-scale production and application in PSCs.

Figure 2.1. Progress in highest-certified PCE values for n–i–p PSCs employing SnO₂ as an ETL every year. (The bar diagram includes the number of publications per year calculated from the Scopus database). Open circles: certified PCE for n–i–p PSCs; open pentagons: reported PCE for SnO₂-based PSCs; solid pentagons: certified PCE for SnO₂-based PSCs.⁴⁷

2.2 Crystal Structure and Electronic Properties of SnO₂

Tin (IV) oxide is a transparent metal oxide characterized by its wide band gap (3.6 eV) and n-type nature. It uniquely features simultaneous conductivity and transparency among the group IV elements of the periodic table. This distinctive feature allows for a broad spectrum of applications, particularly in transparent conductive metal oxides (TCO) and as an electron transport layer material in perovskite photovoltaics. The direct band structure of SnO₂ reveals that the top of the valence band is primarily comprised of O(p)
states, while the bottom of the conduction band exhibits an anti-bonding character stemming from the Sn(4s) and O(p) states.\textsuperscript{63}

SnO\(_2\) can exist in several phases, including rutile-type (P4\(_{2}/\)mmm), CaCl\(_2\) type (Pnnm), α-PbO\(_2\) type (Pbcn), pyrite type (Pa\(\bar{3}\)), ZrO\(_2\) type orthorhombic phase I (Pbca), fluorite-type (Fm\(\bar{3}\)m), and cotunnite-type orthorhombic phase II (Pnam). Of these, the rutile-type tetragonal SnO\(_2\) is the most chemically and thermally stable crystalline structure of SnO\(_2\) at ambient pressure. Consequently, is the most extensively studied as an n-type semiconducting oxide. However, SnO\(_2\) crystals can exhibit various intrinsic point defects, such as oxygen vacancy (V\(_O\)), tin interstitial (Sn\(_i\)), tin antisite (Sn\(_O\)), tin vacancy (V\(_{Sn}\)), and oxygen interstitial (O\(_i\)) (Figure 2.2). These intrinsic defects, along with extrinsic dopants, primarily influence the material's electrical properties, optical properties, and energy levels.\textsuperscript{47}

![Figure 2.2](image.png)

Figure 2.2. Schematic illumination of various possible defects in SnO\(_2\) surface and crystals.\textsuperscript{47}

The multivalence nature of Sn leads to the dominance of Sn\(_i\) and V\(_O\) in the defect structure of SnO\(_2\), illustrating the inherent nonstoichiometry of this material. These defects have been demonstrated to create shallow donor levels, accounting for the n-type
conductivity observed in undoped SnO$_2$.\textsuperscript{64} This also clarifies how SnO$_2$ can maintain high carrier concentration with negligible impact on its transparency. The concept of transparent conductivity in SnO$_2$ is attributed to the presence of shallow donor levels near the conduction band formed by a substantial concentration of oxygen vacancies.\textsuperscript{63, 64}

2.3 Characteristics of SnO$_2$ as an Electron Transport Layer

The combination of several desirable characteristics makes SnO$_2$ an ideal ETL (Figure 2.3). These include its inexpensive synthesis and processibility, stability, optical properties, and electronic properties.

![Figure 2.3. Properties of SnO$_2$ as an ideal ETL for PSCs.](image)

2.3.1 Inexpensive Synthesis and Low Processing Temperature

The cost and availability of materials are critical for the large-scale production and commercialization of ETL materials for PSCs. Unlike organic ETL materials, SnO$_2$ is inexpensive and abundant, making it an attractive choice for large-scale production. Perovskite materials hold significant potential in rapidly fabricating flexible PSCs, especially on lightweight and flexible PET-based substrates, as the perovskite materials
offer the added advantage of low-temperature solution processibility. However, alongside perovskite materials, ETL and HTL that are processible at low temperatures are vital for the fabrication of flexible PSCs, particularly on substrates with low melting points, like PET. Unlike TiO$_2$, which requires high temperatures between 400 and 500 °C to achieve optimal crystallinity and structural integrity as ETLs, SnO$_2$ is distinctively advantageous.$^{62}$ SnO$_2$ can be processed at temperatures below 150°C, which aligns well with the heat-sensitive nature of substrates like PET.

2.3.2 Chemical and Photostability

The chemical and photostability remain fundamental when selecting ETL materials beyond processibility and cost. SnO$_2$ has superior chemical and photostability compared to ZnO and TiO$_2$. ZnO emerged as an alternative to TiO$_2$ for flexible PSCs on the low-melting substrate due to its enhanced optoelectronic properties and low-temperature processability.$^{65}$ However, the low-temperature processed ZnO contains a hydroxyl group, providing a basic nature to the ZnO. The basic nature of the ZnO leads to deprotonation of the perovskite, and it causes the decomposition of the perovskite into its constituents.$^{49, 50}$

The higher photocatalytic activity of TiO$_2$, especially under UV light, compromises the long-term stability of PSCs with TiO$_2$ as an ETL. In a PSC with TiO$_2$ as an ETL, UV illumination excites electrons from the valence band of TiO$_2$ into its conduction band. This process allows TiO$_2$ to extract electrons from I$^-$ in the perovskite forming I$_2$ with consequent perovskite degradation.$^{66, 67}$ Additionally, TiO$_2$ possesses numerous oxygen vacancies or Ti$^{3+}$ sites on its surface, which induce deep trap states.$^{68}$ Contrarily, SnO$_2$ is chemically inert, and the photocatalytic properties of SnO$_2$ are negligible compared to TiO$_2$ due to the wider band gap of SnO$_2$. 

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2.3.3 Optical Properties

The optical bandgap of a semiconductor plays a crucial role in determining the energy threshold for the absorption of incoming photons. The optical bandgap of SnO$_2$ is relatively wide, ranging from 3.60 to 4.5 eV, depending on the fabrication method. This wide bandgap characteristic allows SnO$_2$ to exhibit high transparency across the most visible light spectrum. Compared to other commonly used ETLs like TiO$_2$, ZnO, and C60 and its derivatives, SnO$_2$ stands out for its superior transparency to visible radiation. Due to the remarkably high transmittance of light through SnO$_2$ in the spectral region of 400nm to 800nm, SnO$_2$ minimizes parasitic absorption, ensuring efficient utilization of solar radiation by perovskite photoactive layers. This high transmittance $T$ of SnO$_2$ can be mathematically related to the absorption coefficient ($\alpha$) as shown in equation 2.1:

$$T = e^{-\alpha t}$$  \hspace{1cm} (2.1)

where $t$ represents the film thickness of the SnO$_2$ ETL, typically kept below 30 nm. With its minimal absorption coefficient ($\alpha$) for transmitted light, SnO2 ETL exhibits near-perfect transmittance, approaching unity. Moreover, SnO$_2$ ETLs possess remarkably low refractive indices in the visible spectrum. As a result, when used as TCOs such as ITO or FTO, they contribute to significantly lower overall refractive indices than other ETLs.

2.3.4 Electronic properties

Band alignment is critical when choosing the ETL material for perovskite photovoltaic application. The CB of the ETL should be slightly lower than that of the perovskite to enable the efficient extraction and transfer of photogenerated electrons from the perovskite photoactive layer to the cathode while simultaneously blocking the
movement of holes. The CB of SnO₂ is well aligned with the CB perovskites, whereas the VB of SnO₂ is deep enough to block the holes effectively. Compared to other ETL materials, SnO₂ exhibits smaller CB offsets when interfaced with perovskites, thereby reducing the risk of significant overpotential and $V_{oc}$ loss.$^{47}$

The maximum achievable open-circuit voltage ($V_{oc}$) for a specific device configuration can be determined using the quasi-Fermi level splitting (QFLS),$^{68}$ as shown in equation 2.2:

$$\text{QFLS (}\Delta \mu\text{)} = E_{F}^{\text{CB}} - E_{F}^{\text{VB}}$$  \hspace{1cm} (2.2)

Where $E_{F}^{\text{CB}}$ and $E_{F}^{\text{VB}}$ are the quasi-Fermi levels for the electron and holes, respectively.

Comparative analysis shows that QFLS values at the SnO₂/perovskite interface in an n-i-p device structure exceed those at the TiO₂/perovskite and C60/perovskite interfaces, as well as perovskite/PCBM interface in the p-i-n architecture.$^{70}$ It indicates a higher maximum $V_{oc}$ can be achieved with SnO₂ ETL interfaced with perovskite. Notably, the QFLS value at the SnO₂/perovskite interface closely approximates that of bare perovskite, indicating negligible non-radiative recombination at this interface.

One of the critical performance indicators in PSCs is the hysteresis index, which reflects the difference in performance between forward and reverse sweeping directions. Hysteresis is undesirable as it diminishes operational stability and results in less stabilized power output. Hysteresis in PSCs primarily arises from large conduction band offsets at the ETL/Perovskite interface and a significant mismatch between electron and hole extraction capabilities.$^{68,71}$ SnO₂ ETL addresses these issues effectively.
2.4 Deposition Methods of SnO$_2$ Thin Films

Till now, several methods have been explored for the fabrication of SnO$_2$ thin films, which can be broadly classified into solution process deposition and vapor deposition techniques. Solution process deposition methods are commonly employed due to their cost-effectiveness, ease of implementation, and versatility. The solution-processed SnO$_2$ ETL can be achieved through two different routes: 1) by thermolysis of tin salt solutions as precursors for SnO$_2$ and 2) by direct deposition of colloidal dispersions of pre-synthesized SnO$_2$ nanocrystals. Various deposition methods can achieve solution-processed deposition, including spin-coating, chemical bath deposition (CBD), spray pyrolysis, screen printing, blade-coating, and slot-die coating.

Spin coating is a technique suitable for small-area deposition in a lab, and most of the highly efficient devices are fabricated by spin coating (Figure 2.4a). Spin-coating is suitable for both inorganic ETL materials, such as SnO$_2$, and organic ETL materials, such as PCBM. In spin coating, it is difficult to achieve precise thickness control, and it has limited scalability for large-area fabrication. Another major limitation of spin coating is potential material waste due to the excess solution being spun off. Blade coating, also known as bar or knife coating, is a relatively simple and low-cost SnO$_2$ thin film fabrication method attractive for research and commercial applications (Figure 2.4b). Moreover, it can be integrated into a high-speed roll-to-roll process for the rapid deposition of ETLs. On the other hand, the slot-die technique is especially well-suited for large-scale roll-to-roll or sheet-to-sheet deposition of ETL nanomaterials, making it attractive for the commercial production of PSCs (Figure 2.4c). The process offers precise control over film thickness and uniformity by adjusting parameters such as slot-die gap, flow rate, and coating speed.
Additionally, it allows for efficient use of the precursor solution, minimizing waste and reducing material costs.

Figure 2.4. Various methods for the fabrication of SnO₂ ETL.⁶⁸

Chemical bath deposition (CBD) presents a promising method for the large-area deposition of SnO₂, enabling the direct fabrication of SnO₂ thin films on substrates (Figure 2.4d). Recently, the PCE for PSCs containing CBD-based SnO₂ ETL has been achieved at 25.8%.⁸² In this process, a substrate is submerged in a bath containing precursor chemicals, where a desired metal oxide film is deposited onto the substrate's surface through a chemical reaction. Variations in temperature or pH typically drive these reactions. Depositing thin films using CBD involves nucleation and particle growth, which are central to forming a solid phase from a solution.⁸³ When depositing metal oxide films, water contributes oxygen via OH⁻ ions, ensuring a continuous supply of hydroxyl. Factors such as pH, temperature, and concentration are essential in regulating the rate of CBD.⁸⁴
Specifically, for the deposition of SnO$_2$ through CBD, SnCl$_2$ or SnCl$_4$ is employed as the precursor. A solution of SnCl$_2$ or SnCl$_4$ is bath prepared in deionized water, utilizing urea as a binder and hydrochloric acid (HCl) as a stabilizer. The deposition temperature is maintained at approximately 70°C, typically controlled using an oven. CBD offers several advantages, including the production of dense, uniform films with high reproducibility using a relatively straightforward procedure. However, a limitation of this technique is the frequent waste of solution after each deposition.

Spray pyrolysis is a solution-processed deposition technique that can fabricate a SnO$_2$ thin film on a large area (Figure 2.4e). In this technique, the precursor solution is atomized into fine droplets and then sprayed onto a heated substrate. Upon contact with the substrate, the solvent in the droplets evaporates, initiating a chemical reaction that forms a thin film. For the deposition of a SnO$_2$ thin film using spray pyrolysis, one can utilize either a SnO$_2$ precursor solution or a pre-synthesized dispersion of SnO$_2$ nanoparticles.

Atomic layer Deposition (ALD) is a vapor-phase thin film deposition technique renowned for its precise control over film thickness, outstanding conformity, and uniformity. In the ALD-SnO$_2$ process, SnO$_2$ precursors are sequentially introduced onto the substrate within a reaction chamber. The ALD method utilizes a self-limiting reaction to control the growth rate of SnO$_2$ layers on the substrate and achieve atomic-level precision over film thickness. The SnO$_2$ film thickness can be modified by adjusting the number of ALD cycles. However, due to its slow pace and high costs, ALD may not be a viable option for large-area deposition of SnO$_2$ ETL on a commercial scale.
2.5 Brief History of SnO$_2$ ETLs for PSCs

As noted above, SnO$_2$ can be processed at low temperatures and demonstrates superior photostability, particularly against ultraviolet (UV) light, compared to TiO$_2$ and ZnO. This advanced photostability addresses the challenges of light-induced degradation, a significant issue associated with TiO$_2$ and ZnO-based PSCs (PSCs). Chemically, SnO$_2$ is stable in the presence of moisture and oxygen, and its hygroscopic nature is less pronounced than that of TiO$_2$ and ZnO, rendering it less susceptible to degradation in ambient environments. Additionally, as an inorganic material, SnO$_2$ exhibits enhanced thermal and chemical stability compared to fullerene derivatives.

In earlier research, W Ke and coworkers explored the potential of low-temperature, solution-processed SnO$_2$ as a high-efficiency ETL alternative to TiO$_2$ and ZnO for PSCs. They utilized SnCl$_2$$·$2H$_2$O solution in anhydrous ethanol as a precursor for spin-coating and annealed it at 180°C for 1 hour, achieving a champion efficiency of 17.21%.$^{72}$ Similarly, Juan Pablo Correa Baena and a colleague demonstrated an alternate method, focusing on low-temperature ALD to obtain a SnO$_2$ ETL suitable for planar PSCs. Their method resulted in nearly hysteresis-free PCEs above 18%, showcasing a record high voltage of up to 1.19V. $^{71}$

Seo and his coworker conducted a parallel study demonstrating the feasibility of using a low-temperature ALD method for SnO$_2$ ETL to develop efficient planar PSCs and tandem devices. By incorporating the ionic liquid methylammonium formate (MAF) as an additive in the perovskite precursor, they achieved a champion PCE above 19%.$^{89}$ Later, Anaraki and colleagues also explored low-temperature, solution-processed SnO$_2$ as an efficient ETL, focusing on high-performance planar PSCs. Their innovative approach
combined spin SC with CBD resulting in an impressive efficiency of 21%. This efficiency is comparable or superior to the results obtained with TiO$_2$-based mesoporous structures. Their methodology holds promise for scaling up low-temperature fabricated PSCs.

2.6 Strategies to Improve SnO$_2$ Performance

SnO$_2$ has emerged as a promising ETL for PSCs due to its favorable conduction band, high electron mobility, excellent transparency, and robust stability. Nevertheless, pristine SnO$_2$ presents certain challenges. It frequently contains defects and imperfections, including oxygen vacancies, uncoordinated Sn$^{4+}$ ions, hydroxyl groups, and oxides with different oxidation states, such as SnO and Sn$_2$O$_3$. These imperfections can significantly alter the structural, electronic, and optical properties of SnO$_2$. Specifically, such defects can modify the interaction at the SnO$_2$/perovskite interface, trap electrons, and impede the effective extraction and transport of charge. These complications can compromise device stability and reduce its efficiency. Therefore, tailoring SnO$_2$ ETLs is crucial to optimize the performance of SnO$_2$ ETLs and to improve the stability of PSCs.

2.6.1 Elemental Doping

Electron transport materials, such as n-type semiconductors, can substantially enhance their performance through doping. Doping of semiconducting metal oxides (MO$_x$) effectively modulates electrical properties such as carrier concentration and electron mobility and alters optical and structural properties. Till now, standard doping methodologies can be categorized as equivalent cation doping and nonequivalent cation doping.
In the case of equivalent cation doping, the incorporation of equivalent metal ions into the crystal lattice of the metal oxide semiconductor incurs offsetting of the crystal lattice, potentially altering the energy band structure. However, this does not enhance the carrier density as the dopants do not contribute additional electrons. Doping of SnO$_2$ with equivalent cations has been documented to improve defect densities, induce alterations in the energy band structure, improve carrier mobility, and diminish trap-state density by modulating the energy level, thus promoting superior energy band alignment with perovskite.\textsuperscript{68} Noh and coworkers demonstrated that Zr-doping on SnO$_2$ up-shifted the energy levels of SnO$_2$ nanoparticles and reduced the difference in the conduction band between perovskite and ETL. The better alignment of the conduction band of Zr-SnO$_2$ with perovskite would facilitate better electron extraction/transport capability for ETLs and increased built-in potential generation in the devices, contributing to improved PCEs for the resulting PSCs. Consequently, the champion device employing Zr-doped SnO$_2$ nanoparticles achieves a power conversion efficiency of 19.54\%, while the pristine SnO$_2$ nanoparticles yield 17.30\%.\textsuperscript{91}

Nonequivalent cation doping involves the incorporation of cations with valence states different from those of the host lattice ions. 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. P-type doping decreases the ETL conductivity by reducing the electron density in the CB, thereby suppressing charge recombination. Furthermore, replacing Sn$^{4+}$ and Ti$^{4+}$ with low-valence cations has been reported to reduce oxygen vacancies and induce an upward shift in the Fermi level, facilitating electron
transport and impeding charge recombination at the perovskite/ETL interface.\textsuperscript{92} The substitution of Sn\textsuperscript{4+} with Zn\textsuperscript{2+} in tetravalent SnO\textsubscript{2} results in an elevated conduction band edge (E\textsubscript{CB}), an expanded depletion region, and improved conductivity. The elevated E\textsubscript{CB} reduces energy loss and facilitates the extraction of photogenerated carriers, yielding a higher fill factor (FF) and short-circuit current density (J\textsubscript{SC}).\textsuperscript{92} After optimization of Zn-doping in SnO\textsubscript{2} ETLs, a device demonstrated a champion power conversion efficiency (PCE) of 17.78\%, with V\textsubscript{OC} of 1.098 V, J\textsubscript{SC} of 23.4 mA/cm\textsuperscript{2}, and FF of 69.2\%. By contrast, an undoped SnO\textsubscript{2} device achieved a champion efficiency of only 15.31\%. Park et al. reported an enhancement in conductivity and a downward shift in the conduction band of SnO\textsubscript{2} after Li doping, facilitating electron injection and transfer from the perovskite conduction band. The average PCE increased from 14.31\% to 16.64\% for a rigid substrate after Li doping.\textsuperscript{93} In another study, Yang and colleagues examined the effect of Y doping on the morphological, electrical, and optical properties of a SnO\textsubscript{2} nanosheet. They reported a more positive conduction band minimum (CBM) in Y-SnO\textsubscript{2} than in undoped SnO\textsubscript{2}. This Y doping optimizes the energy level matching between ETL and perovskite, enhances conductivity, and facilitates charge extraction and transport. After optimizing Yttrium concentration in Y-SnO\textsubscript{2}, the average PCE increased from (11.69 ± 0.40) \% to (15.60 ± 0.35) \%, with the champion device performance improving from 13.38\% to 17.29\% PCE.\textsuperscript{94}

The incorporation of higher valence cations such as Nb\textsuperscript{5+}, Sb\textsuperscript{5+}, and W\textsuperscript{6+} into the crystal lattice of tetravalent Sn\textsuperscript{4+} or Ti\textsuperscript{4+} results in n-type doping. This doping process enhances the electron density due to the contribution of extra electrons from dopants and causes a more positive shift in the CB. Such an increment in electron density and the consequent positive CB shift increases conductivity, facilitating the photogenerated
electron injection process.95-97 A noteworthy illustration of this has been provided by Ren and associates, who reported an enhancement in the performance of PSCs after Nb doping on the SnO₂ ETL. The enhanced performance of the Nb-doped SnO₂ ETL stemmed from the improved surface morphology, superior electron mobility, and enhanced electron extraction following Nb doping. Compared to a PSC with a pristine SnO₂ ETL, the PCE improved from 15.13% to 17.57% after utilizing an Nb-doped SnO₂ ETL.98 Moreover, Bai et al. revealed that incorporating Sb into a low-temperature solution-processed SnO₂ boosts the electron concentration and significantly enhances the film conductivity over an order of magnitude compared to pristine SnO₂. The extra free electrons partially fill the surface trap states and bring an upward shift in the Fermi level, which mitigates charge recombination and boosts perovskite device PCE from 15.7% to 17.2%.97 Recently, Mo et al. introduced nitrogen-doped SnO₂ (N-SnO₂) as an effective ETL material for PSCs. Their investigation elucidated that N doping triggers a downward shift in the CB minimum of N-SnO₂ compared to pristine SnO₂, offering superior band alignment with the perovskite. This optimal band alignment promotes electron mobility and facilitates electron transfer from perovskite to N-SnO₂, thereby reducing charge accumulation at the N-SnO₂/perovskite interface. As a result, the power conversion efficiency of devices incorporating an N-SnO₂ film increased from 20.55% to an impressive 23.41%.99

2.6.2 Surface Modification with Ionic Compounds

Several ionic compounds have been reported in the defect passivation of SnO₂, perovskite, and, in some instances, both simultaneously. Literature reports a range of ionic compounds, including alkaline earth metal salts such as KCl, KF, and RbF; ammonium
salts like NH₄Cl and NH₄F; and ionic liquids like 4-imidazole acetic acid hydrochloride (ImAcHCl).⁴⁷

Table 2.1. The optimized doping concentration of various elements reported for SnO₂.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Concentration</th>
<th>ETL</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Ref</th>
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<tr>
<td>Li</td>
<td>1.7 mol%</td>
<td>SnO₂</td>
<td>1.084</td>
<td>21.98</td>
<td>64.17</td>
<td>15.29</td>
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<tr>
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<td>SnO₂</td>
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<td>66</td>
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<td>Nb</td>
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<td>65.9</td>
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<td></td>
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<td>69.6</td>
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<td>Sb:SnO₂</td>
<td>1.06</td>
<td>22.6</td>
<td>72.0</td>
<td>17.2</td>
<td></td>
</tr>
</tbody>
</table>

These ionic compounds, comprised of cations and anions, are adept at passivating both negative and positive charge defects observed in SnO₂. These defects can include oxygen vacancies, uncoordinated Sn, and dangling bonds. Passivation is typically achieved through mechanisms like hydrogen bonding and electrostatic interactions.

Furthermore, when these ionic salts are present at the SnO₂/perovskite interface, they not only contribute to SnO₂ defect passivation but also support the nucleation, growth, and defect passivation of perovskite. The cations and anions of these ionic salts interact intimately with the perovskite precursor, which helps in the nucleation and subsequent
growth of perovskite crystals. Beyond the SnO₂ surface, the same cations and anions can also infiltrate the perovskite layer, passivating its defects through ion exchange or diffusion.

Considering the hybrid nature of organic-inorganic lead halide perovskite, which possesses both ionic and covalent character, it can interact with ionic compounds, including inorganic acids. These electrostatic interactions can integrate the ionic compounds with SnO₂ and perovskite layers. This integration of SnO₂ with perovskite through ionic compounds provides good passivation, allowing ionic salts to adjust the energy levels of SnO₂. The consequence is a better energy alignment between the ETL and the perovskite layer, which enhances electron transfer, limits recombination, and enhances performance.¹⁰⁰

For instance, when NH₄F is introduced at the interface between SnO₂ and perovskite, the ammonium ions (NH₄⁺) suppress surface hydroxyl groups. In contrast, the fluoride ions (F⁻) replace defect sites, such as bridging hydroxyls.¹⁰¹ This action helps to reduce energy losses and improve PSC efficiencies. In the case of KCl, the potassium ions (K⁺) occupy the lattice interstitial sites of the perovskite, addressing surface defects, while the chloride ions (Cl⁻) restrict the formation of deep trap defects at the SnO₂-perovskite interface.¹⁰² The ionic compound liquid 4-imidazole acetic acid hydrochloride (ImAcHCl) offers another compelling example. Interfaced between the SnO₂ and perovskite layers, its imidazole cations passivate negatively charged defects, such as Pb-I antisite substitutions in perovskite, and the Cl⁻ ions suppressed uncoordinated Pb²⁺ sites.¹⁰³
2.6.3 Surface Modification with Organic Compounds

Recent studies highlight the benefits of modifying the SnO$_2$ electron transport layer (ETL) with organic compounds possessing mixed charged functional groups, notably self-assembled monolayers (SAMs) and zwitterions. These compounds enhance the performance and stability of PSCs. By acting as a bridge between the SnO$_2$ ETL layer and the perovskite layer, SAMs and zwitterions serve to minimize interfacial defects and adjust interfacial energy levels, contributing to overall improved performance and stability.

In the case of SAMs, one terminal contains anchoring groups, which include sulfonic acid, phosphonic acid, carboxylic acid, and hydroxyl. This terminal is theorized to bond with the hydroxyl groups present on the SnO$_2$ surface. The other terminal of the SAM links with the perovskite, potentially filling the halide vacancies on the perovskite's bottom surface and removing the buried interface. As reported in the literature, the sulfonic acid group within p-aminobenzene sulfonic acid (ABSA) can coordinate with the uncoordinated Sn$^{4+}$ found on the SnO$_2$-ETL surface. Simultaneously, its electron-rich amino group donates electrons to uncoordinated Pb$^{2+}$ sites and passivates the Pb-I antisite substitution.

Another example is 3-iodopropyl trimethoxysilane, denoted as [Si(OCH$_3$)$_3$](CH$_2$I)$_3$] or I-SAM. This compound features an –Si(OCH$_3$)$_3$ anchor group, which engages in a silanization process with the OH groups of SnO$_2$ surfaces. This interaction substantially reduces the number of OH groups as new anchoring O–Si bonds are established. The –I terminal group of the molecule is supposed to form electrostatic bonds with the methylammonium lead halide thin film layered atop. An intriguing aspect of the SAM modification process lies in the varied electron densities at the organic
molecule's two terminals. This discrepancy can lead to the formation of dipoles at the interface. Consequently, these SAM-induced dipole moments introduce a downward band-bending at the SnO2/perovskite interface, optimizing electron transfer.\textsuperscript{106}

When introduced onto the SnO\textsubscript{2} surface, zwitterionic molecules interact chemically with SnO\textsubscript{2}, establishing a chemical bridge between perovskite and SnO\textsubscript{2}. Specifically, the negatively charged groups in the zwitterions, such as -COO\textsuperscript{-} and -SO\textsubscript{3}\textsuperscript{-}, create ester and chelate bonds by interacting with the SnO\textsubscript{2} surface.\textsuperscript{103} Furthermore, the zwitterionic molecules carry positively charged groups like NH\textsubscript{4}\textsuperscript{+}, which engage in electrostatic interactions with the halide anions. This interaction contributes to the passivation of Pb/I antisite defects within the perovskite lattice, resulting in improved thermal stability of the perovskite films. Additionally, much like SAMs, the zwitterionic compounds can induce the formation of an interfacial dipole, altering the work function of the SnO\textsubscript{2}. This modification helps in preventing reverse electron transfer, thereby inhibiting charge recombination.\textsuperscript{107} Overall, bifunctional organic compounds such as zwitterionic molecules and SAMs play a crucial role in enhancing the overall efficiency of PSCs by improving interfacial interactions and the thermal stability of perovskite films.

2.6.4 SnO\textsubscript{2}-Based Bilayer ETLs

The efficiency and stability of PSCs have been reported to improve through the integration of bilayer structures that combine SnO\textsubscript{2} with various metal oxides like TiO\textsubscript{2}, MgO, and ZnO, as well as organic ETLs materials such as fullerene like C60 and PCBM and their derivatives. This enhancement can be attributed to improvements in morphology and optimal energy band alignment.\textsuperscript{47}
Adding an additional metal oxide layer into the SnO$_2$ film can fill structural defects, such as cracks and pinholes, thereby optimizing the performance of the solar cells. Common configurations of this approach include ZnO/SnO$_2$, SnO$_2$/MgO, and SnO$_2$/TiO$_2$. For instance, adding a thin layer of MgO onto SnO$_2$ can reduce surface roughness, elevating the quality of perovskite thin film.$^{108}$ Furthermore, introducing a second metal oxide layer at the interface between SnO$_2$ ETL and perovskite creates a heterojunction with cascade energy levels. These structures with cascade energy levels, such as SnO$_2$/TiO$_2$ or SnO$_2$/ZnO, function as composite ETLs for PSCs. Adding a second TiO$_2$ layer on the SnO$_2$ layer, possessing a higher conduction band than SnO$_2$, can effectively prevent electrons in SnO$_2$ from recombining with photogenerated holes in the perovskite layer.$^{109}$ While SnO$_2$ stands out as a superior ETL material to many other metal oxides, the potential drawbacks of integrating SnO$_2$ with a secondary inorganic MO$_x$ layer should not be overlooked. For instance, TiO$_2$ can have issues related to UV stability. Similarly, due to the presence of residual hydroxyl groups and acetate ligands on its surface, the potential reactivity of ZnO might pose stability concerns.

In the p-i-n architecture of PSCs the SnO$_2$ ETL is commonly utilized as a secondary layer, positioned above the primary layer of organic ETL, forming a bilayer structure. Composite designs, such as C60/SnO$_2$ and PCBM/SnO$_2$, offer more cascaded energy alignments with perovskites than the pure C60 and PCBM ETLs. This results in decreased hysteresis and an overall enhancement in performance. Moreover, the SnO$_2$ layer on top serves as a protective barrier, safeguarding the underlying layers and contributing to the long-term stability of PSCs.$^{90}$
2.7 SnO$_2$ Nanoparticles

The low-temperature fabrication methodologies of SnO$_2$ have provided its aptness for developing flexible PSCs on low-melting substrates such as PET. Low-melting plastic-based substrates are capable of withstanding limited heat, and there is a growing necessity for the reduction of post-annealing temperatures. In this context, the as-synthesized SnO$_2$ colloidal precursor has been deemed a promising route to formulate the ETL for flexible PSCs.

The synthesis of SnO$_2$ nanoparticles is generally achieved through precipitation, hydrothermal, hot injection, and the inverse micelle-water injection methods.$^{110}$ Using nanoparticles circumvents the high-temperature sintering process, which would otherwise be integral in the transition from precursor to SnO$_2$ nanoparticles. Consequently, the utilization of pre-synthesized SnO$_2$ nanoparticles simplifies the process and holds the potential to shorten the total fabrication time. Additionally, pre-synthesized nanoparticles can be suspended in an array of solvents compatible with perovskite and directly coated onto the perovskite layer to serve as an upper CTL.

As an early pioneering work, Li and colleagues employed commercially available SnO$_2$ nanoparticles as the ETL and a scaffold layer in mesoscopic PSCs. This study notably demonstrated the competitive attributes of SnO$_2$ compared to TiO$_2$ and addressed the issue of charge recombination in mesoscopic SnO$_2$. By optimizing the thickness of the SnO$_2$ layer, they attained a PCE of 6.50%. Furthermore, they achieved a PCE of 10.18% following the passivation of SnO$_2$ with TiCl$_4$, illustrating the potential of SnO$_2$ nanoparticles in this application.$^{111}$
Table 2.2. PSCs fabricated with SnO$_2$-ETL by nanoparticle approach.

<table>
<thead>
<tr>
<th>Device architecture</th>
<th>Deposition method</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>
</table>
| Regular (n-i-p) architecture
| ITO/Sb:SnO$_2$/ Perovskite/spiro-OMeTAD/Au | Spin Coating | 100 °C, 30 min | 22.60 | 1.06 | 72.00 | 17.20 | 97 |
| ITO/SnO$_2$/ Perovskite/spiro-OMeTAD/Au | Spin Coating | 80 °C, 15min | 19.70 | 1.13 | 79.00 | 17.70 | 112 |
| ITO/SnO$_2$/Perovskite/Spiro-OMeTAD/Au | Spin Coating | 150 °C, 30 min | 24.87 | 1.09 | 74.77 | 20.27 | 113 |
| ITO/SnO$_2$/Perovskite/Spiro-OMeTAD/Au | Spin Coating | 150 °C, 30 min | 25.20 | 1.18 | 78.40 | 23.32 | 113 |
| ITO/SnO$_2$/ perovskite/spiro-OMeTAD/MoO$_x$/Ag | Slot-die | air-knife, IPL | 23.70 | 0.91 | 52.00 | 11.24 | 114 |
| IOH/SnO$_2$/ perovskite / Spiro-OMeTAD/Au | Blade | 150 °C, 30 | 23.31 | 1.11 | 72.00 | 18.66 | 115 |
| ITO/Perovskite/ Spiro-OMeTAD/Au | Spray | 120 ± 10 °C | 22.20 | 1.17 | 76.10 | 19.80 | 80 |
| Inverted(p-i-n) architecture
| glass/ITO/NiO$_x$/ perovskite /ZnO/Al | Spin Coating | none | 21.00 | 1.01 | 76.00 | 16.10 | 116 |
| Glass-ITO/PTAA/PFN/ perovskite /SnO$_2$-A/Ag. | Blade | 100 °C, 10 min | 22.60 | 1.02 | 61.00 | 14.10 | 117 |
| PET/ITO/PTAA/PFN/ perovskite /Y:SnO$_2$-A/BCP/Ag | Blade | 100 °C, 2 min | 22.38 | 1.08 | 68.40 | 16.50 | 118 |
| PET/ITO/PTAA/PFN/ perovskite /Y:SnO$_2$-A/BCP/Ag | Blade | IPL | 23.70 | 1.09 | 65.70 | 16.90 | 119 |
Park et al. engineered highly dispersed ligand capped ultrafine SnO$_2$ quantum dots (QD) for flexible PSCs. The group deposited a non-aqueous dispersion of SnO$_2$ quantum dots on a flexible PEN-ITO substrate, followed by a short 15-minute annealing at 80 °C. In a separate research study, Song and colleagues employed commercially available colloidal SnO$_2$ nanoparticles, ranging in size from 22 to 43 nm, in a butanol dispersion to fabricate a low-temperature processible ETL. These studies contribute to the ongoing efforts to leverage SnO$_2$ nanoparticles for efficient, stable, and low-temperature processed PSCs. Later, Jiang and colleagues reported low-temperature processible commercial SnO$_2$ nanoparticles as an efficient ETL for planar PSCs. With commercial SnO$_2$ nanocrystals, they achieved a PCE of 19.9%. In a subsequent study, the same group managed to achieve a PCE of 21.6% in small-area planar PSCs, using low-temperature processed SnO$_2$ nanoparticles as the ETL. In a recent investigation, Qi Jiang and colleagues reported an impressive 23.32% certified PCE for mixed cation planar PSCs using low-temperature processed commercially available SnO$_2$ dispersion. These efforts underline the significance of the nanoparticle approach for the fabrication of lightweight and flexible PSCs and to reduce overall fabrication time.

2.8 Scalable Deposition of SnO$_2$ ETLs

PSCs hold significant potential for rapid fabrication and commercialization due to their fully solution-processible nature. However, scaling up ETL, HTL, and perovskite layers in PSCs is equally essential for commercializing PSCs. The rapid and large-scale deposition of the ETL on both rigid and flexible substrates is feasible using various techniques, including blade coating, slot-die coating, and gravure printing. The quality of the perovskite film in inverted PSC architecture largely depends on the quality of the ETLs
it is deposited upon. In particular, an ETL must have a high-quality film with complete surface coverage to ensure the fabrication of efficient and stable PSCs. However, achieving a scalable and uniform deposition of a solution processible ETL presents a significant challenge. So, it is essential to address the challenges regarding the scalability of ETL for advancing the practical application and mass production of PSCs.

Bu et al. demonstrated the possibility of scaling up SnO$_2$ ETL using slot-die for large-area fabrication of PSCs. After the interfacial passivation with potassium, they achieved a PCE of 20.50% for rigid PSCs and a PCE of 17.18% for flexible PSCs on a small area device with pre-synthesized SnO$_2$ as an ETL. They also reported a PCE of 15.22% for flexible PSCs based on slot-die-coated commercial SnO$_2$ and a PCE of 14.89% for lab synthesized SnO$_2$ NCs.$^{120}$ In another study, Dou et al. compared blade and slot-die coating with spin coating for room-temperature PSC fabrication. They achieved up to 19.6% PCE with blade-coated PSCs and 17.31% with slot-die coated PSCs using commercial SnO$_2$ nanoparticles as an ETL.$^{121}$ In blade-coated PSCs with commercial SnO$_2$ dispersion as an ETL, Peng et al. achieved a PCE of 17.0%. However, they adopted composition engineering and additive doping to achieve high efficiency.$^{122}$

Other approaches to high scale fabrication include Gravure printing and automated spray-coating (ASC). Gravure printing, an established printing technique, involves the transfer of ink from cavities patterned on a gravure cylinder to a web or substrate. This provides a cost-effective and high-throughput printing method that is compatible with roll-to-roll and enables industrial-scale production of PSCs on flexible substrates. Kim and colleagues demonstrated the fabrication of efficient PSCs on flexible substrates with low-temperature processible commercial SnO$_2$ nanoparticles as an ETL using gravure printing.
For their all-printed PSCs, they achieved a PCE up to 17.2%, with a $V_{oc}$ of 1.07 V, $J_{sc}$ of 20.7mA/cm$^2$, and a FF of 77.1%.\textsuperscript{123} Taheri et al. developed a simple and scalable ASC approach to prepare uniform and dense SnO$_2$ ETLs. They achieved a PCE of 15.3% on a flexible substrate in small-area devices and 12% on flexible modules in larger modules.\textsuperscript{124}

2.9 SnO$_2$ as an ETL for Inverted (p-i-n) PSCs

SnO$_2$ has been widely used as an ETL material in conventional (n-i-p) PSC structures. A thin film of SnO$_2$ can be directly deposited onto conductive substrates using various deposition methods. However, the application of solution-processed SnO$_2$ as an ETL in p-i-n structured PSCs is less explored. This gap is primarily due to solvent incompatibility between the SnO$_2$ dispersion medium and the perovskite absorber layer.\textsuperscript{116, 125, 126} The selection of solvents compatible with perovskite is limited, and those highly polar solvents, including water typically used for SnO$_2$ dispersions, are excluded. Moreover, converting precursor to SnO$_2$ on the perovskite surface requires prolonged high-temperature annealing, which risks degrading the perovskite layer underneath.

In most p-i-n devices with a MO$_x$ ETL, the MO$_x$ is deposited onto an organic ETL, resulting in bilayer structures such as PCBM/ZnO, C$_{60}$/SnO$_2$, and PCBM/SnO$_2$. This helps to circumvent the solvent incompatibility between the metal oxide and the perovskite. However, for direct MO$_x$ ETL deposition on the perovskite, the requirement arises for pre-synthesized MO$_x$ nanoparticles amenable to low-temperature processing and stable in a perovskite-compatible organic solvent. Recent literature offers some reports on replacing these organic ETLs with pre-synthesized ZnO and SnO$_2$ nanoparticles in inverted PSCs. For instance, You et al. studied the possibility of low-temperature processible pre-synthesized ZnO nanoparticles as an ETL in inverted (p-i-n) PSCs architecture.
The inverted PSCs, configured as Glass/ITO/NiO\textsubscript{x}/perovskite/ZnO/Al, demonstrated a notable PCE of 16.1%, retaining 90% of the original PCE following 60 days of storage in ambient air at room temperature. Contrastingly, control devices fabricated with organic transport layers experienced complete degradation within just five days.\textsuperscript{116}

The stability of pre-synthesized MO\textsubscript{x} nanoparticle dispersion in a desired solvent can be achieved via the coordination of ligands with MO\textsubscript{x} nanoparticles. However, the presence of bulky organic ligands introduces an electrical barrier within the film, mitigating the charge transfer capability of the ETL thereby diminishing the overall efficiency of the PSC. To overcome this, Chapagain et al. developed a strategy to directly deposit single-layer SnO\textsubscript{2} ETL onto perovskite films utilizing small ligands. This work will be described in detail in Chapter III of this dissertation. In short, SnO\textsubscript{2} nanoparticles were synthesized using a sol-gel technique followed by functionalization with acetic acid, resulting in acetate-functionalized tin oxide nanoparticles (SnO\textsubscript{2}-A). This functionalization enabled a stable colloidal dispersion of SnO\textsubscript{2}-A in anhydrous ethanol, which was then directly deposited onto a perovskite film. The inverted PSCs fabricated using colloidal dispersion of SnO\textsubscript{2}-A in anhydrous ethanol achieved a PCE of 14.1%.\textsuperscript{117} However, the efficiency was limited due to the high series resistance caused by the inferior crystallinity of the low-temperature processed SnO\textsubscript{2} nanoparticles compared to high-temperature processed. In the successive study, which is described in detail in Chapter IV, yttrium was doped into the SnO\textsubscript{2} crystal lattice during synthesis to address this limitation. With optimized yttrium concentration (2 mol%), the performance of the inverted flexible PSCs on PET-ITO with low-temperature processed SnO\textsubscript{2} ETL increased from 14.3% to 16.5%, demonstrating a notable enhancement in efficiency.\textsuperscript{118}
3.1 Materials

Unless noted otherwise, all materials were purchased from Sigma Aldrich without further purification. PbI$_2$ (99.99%, trace metals basis), PbBr$_2$ (>98%, low water content) and CsI (>99.0%) for perovskite precursor were purchased from TCI Chemical. Methylammonium iodide (MAI), formamidinium iodide (FAI), and methylammonium bromide (MABr) were purchased from Greatcell Solar. Diiodomethane (CH$_2$I$_2$, 99%) was purchased from Alfa Aesar. Anhydrous SnCl$_4$ (99%), Ammonia solution (28-30%) and NaOH pellets (97%), and Acetic acid glacial (≥99.7% ACS) were purchased from VWR, Ag pellets (99.999%) were purchased from Kurt J. Lesker Co.

3.2 Syntheses of SnO$_2$ and Y:SnO$_2$

The tin oxide (SnO$_2$) nanoparticle synthesis was carried out using a well-established sol-gel method.$^{127}$ This involved neutralizing an aqueous solution of tin(IV) chloride (SnCl$_4$) with sodium hydroxide (NaOH). Initially, a 1M solution of SnCl$_4$ was prepared by gradually adding anhydrous SnCl$_4$ to deionized (DI) water. Subsequently, a freshly made 5M solution of NaOH in DI water was slowly added to the vigorously stirred SnCl$_4$ solution until the pH reached 6.5. This process resulted in the formation of a white SnO$_2$ precipitate. This precipitate was then aged for 12 hours, collected by centrifugation, and repeatedly washed in a DI water and 1:1 DI water-ethanol mixture until the aqueous layer showed no traces of chloride.
The washed, hydrous SnO$_2$ particles were dried at room temperature for 24 hours. The presence of SnO$_2$ was verified using X-ray diffraction (XRD) analysis. Thermogravimetric analysis (TGA) revealed that the actual mass of SnO$_2$ in the hydrous SnO$_2$ was 70%.

Yttrium-doped SnO$_2$ (Y:SnO$_2$) nanoparticles were synthesized similarly. The yttrium doping was achieved in situ by incorporating yttrium precursor (Yttrium (III) chloride hydrate) into the tin oxide precursor during synthesis. To achieve 1, 2, and 3 mol.% yttrium doping in SnO$_2$, calculated amounts of yttrium (III) chloride hydrate were added to a 1M aqueous tin (IV) chloride solution.

3.3 Syntheses of Acetate Functionalized SnO$_2$-A and Y:SnO$_2$-A

The synthesis of acetate-functionalized tin oxide nanoparticles (SnO$_2$-A) followed a procedure detailed in the literature.$^{128}$ Hydrous-SnO$_2$ and glacial acetic acid were typically combined in a 1:1.25 mass/volume ratio. In a standard preparation, 4 grams of hydrous-SnO$_2$ were mixed with 5 milliliters of glacial acetic acid. This mixture was then heated to reflux for 1 hour in a sealed container. Initially, a milky white colloidal dispersion formed, which eventually turned colorless and transparent, indicating the formation of SnO$_2$-A. If the reaction mixture did not turn completely colorless and transparent, indicating the presence of undissolved hydrous-SnO$_2$, it could be separated through centrifugation. The concentration of SnO$_2$ in the solution was determined using TGA.

An aliquot of the concentrated SnO$_2$-A solution was dispersed in anhydrous ethanol to make ink with a 2% (mass/volume) SnO$_2$ concentration for practical application. This ink was suitable for direct deposition onto perovskite substrates using blade coating. For
analytical purposes, such as XRD and FT-IR analysis, the concentrated SnO$_2$-A solution was placed in an evaporating dish, and the solvent was allowed to evaporate overnight. The resulting solid product was further dried in a vacuum oven at 100 °C for 2 hours prior to analysis.

3.4 Preparation of HTL Inks

For PTAA inks, a portion of PTAA was dissolved in toluene to give a final concentration of 8 mg/mL concentration. For NiO$_x$, the pre-synthesized NiO$_x$ powder was dispersed in water to obtain a concentration of 20 mg/mL.

3.5 Perovskite Ink Formulations

The MAPbI$_3$ precursor solution of a concentration of 1.2M was prepared by dissolving 0.159 g of MAI, 0.461 g of PbI$_2$, and 5mg of MABr (as a dopant) in a mixture of DMF/DMSO/NMP with a volume ratio of 0.91:0.07:0.02.

The mixed cation perovskite solution was prepared by measuring 0.461 g PbI$_2$, 0.080 g MAI, 0.068 g FAI, 0.015 g MABr, and 0.003 g PEAI. These powders were then dissolved by addition, in sequential order, 400 μL 2-ME, 600 μL ACN, and 60 μL NMP.

A triple cation perovskite precursor solution, Cs$_{0.1}$(FA$_{0.83}$MA$_{0.17}$)$_{0.9}$Pb(I$_{0.85}$Br$_{0.15}$)$_3$, with a concentration of 1.1M, was prepared using a solvent system comprising DMF, THF, and NMP. We measured 0.312g of CsI, 0.0206 g of MABr, 0.0654 g of PbBr$_2$, 0.154g of FAI, and 0.471 g of PbI$_2$ in a glass container and ten mol% of MACl was added to the mixture to improve the crystal quality of the perovskite. Subsequently, 880 μL of DMF, 150 μL of THF, and 70 μL of NMP were introduced into the mixture. The mixture was then left to stir overnight inside a glove box.
An MA-Free perovskite (Cs$_{0.2}$FA$_{0.8}$PbI$_3$) precursor solution of concentration 1.1M was prepared using a DMF and NMP solvent system. The components included 0.0623 g of CsI, 0.165g of FAI, and 0.553 g of PbI$_2$ mixed in a container. To improve the crystal quality of the perovskite, ten mol% of MACl was added. Finally, 1030 µL of DMF and 70 µL of NMP were introduced into the mixture. The mixture was then left to stir overnight inside a glove box.

3.6 Fabrication of perovskite solar cells (PSCs)

ITO-PET substrate was cut into 3 x 6 in. pieces, and they were blown with an air gun and wiped using IPA. Those cleaned PET substrates were treated with UV-Ozone for 15 minutes immediately before the sequential deposition of PTAA, PFN, Perovskite, and SnO$_2$ dispersion by blade coating inside a dry box. A 35 µL of the PTAA solution was used for blade coating with a blade gap of 100 µm at a coating speed of 10 mm/s, followed by heating at 100 °C for 10 min and then cooling down to room temperature. Next, 30 µL of a 0.4 mg/mL PFN solution in methanol was blade-coated on the PTAA layer at a coating speed of 10 mm/s with a blade gap of 100 µm. About 35 µL of the perovskite precursor solution such as MAPI, MC, TC, or MA-free perovskites was deposited by blade coating with a blade gap of 150 µm and at a coating speed of 10 mm/s. Immediately after the deposition of perovskite precursor solution, the wet film was pre-dried using an N$_2$ air knife, followed by hotplate annealing. Different perovskites were optimized to anneal at different temperature such as MAPI and MC for 140 °C for 2 minutes, TC for 10 min at 120 °C, and MA-free perovskites for 10 minutes at 130 °C. Finally, 30 µL of SnO$_2$-A or Y:SnO$_2$-A in anhydrous ethanol was deposited on the perovskite with a blade gap height of 100 µm and at a coating speed of 10 mm/s, followed by annealing at 100 °C for 2 to 3
min. An active area of 0.1 cm² was completed by depositing 5nm of BCP and 100 nm of silver employing thermal evaporation.

3.7 Device performance: J-V Measurements

The J-V curves were measured using Autolab PGSTAT128-N potentiostat coupled with a class A superstrate simulator equipped with a Newport LCS-100 lamp and AM 1.5G filter. A minimum of 10 cells were measured to calculate average performance statistics. Before measurement, the lamp irradiance was calibrated to 1 sun using KG-5 filter certified by National Renewable Energy Laboratory. The J-V parameters include the short-circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), and PCE were calculated from linear sweep voltammetry (LSV). During the LSV scan, the current is measured as the potential is varied linearly at predetermined step sizes. The J-V parameters are summarized in Figure 3.1.

The open-circuit voltage ($V_{oc}$) is the potential difference across a solar cell when no current flows through it. It can be described as shown in equation 3.1:

$$V_{oc} = \frac{n k T}{q} \ln \left(\frac{J_L}{J_0} + 1\right)$$  \hspace{1cm} 3.1

in which $k$ is the Boltzmann’s constant, $T$ is the temperature, $q$ is the electronic charge, $J_L$ is the light-generated current density, and $J_0$ is the dark saturation current density. The short-circuit current density ($J_{sc}$) signifies the maximum current across the solar cell when no potential difference exists. The product of open circuit voltage and circuit current density gives power density in a solar cell. The maximum power point $P_{max}$ is the solar cell’s maximum operating power and is used to calculate FF in a solar cell. The FF in a
solar cell is the ratio of $P_{max} (J_{max} V_{max})$ to the product of $J_{sc}$ and $V_{oc}$ and is a measure of the squareness of the J vs. V profile, equation 3.2.

$$FF = \frac{V_m \times J_m}{V_{oc} \times J_{sc}}$$  \hspace{1cm} 3.2

The values $J_m$ and $V_m$ are the current and voltage generated at the maximum power point, and $J_{sc}$ and $V_{oc}$ are the short circuit current density and open circuit voltage, respectively. The power conversion efficiency ($\eta$) of the solar cell is then related to the fill factor, equation 3.3.

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}}$$  \hspace{1cm} 3.3

where $\eta$ is the efficiency, $J_{sc}$ is the short circuit current density, $V_{oc}$ is the open circuit voltage, FF is the fill factor, and $P_{in}$ is the incident light power density. The Standard Test Condition (STC) for solar cells is the Air Mass (AM) 1.5 spectrum with an incident power density of 1000 W/m$^2$ and a temperature of 25 °C. The AM 1.5 spectrum corresponds to the sun being at an angle of elevation of 42°.
Figure 3.1. Schematic representation of a $J-V$ Curve for a solar cell, highlighting the relevant parameters of $J_{sc}$, $V_{oc}$, $J_{max}$, $V_{max}$ FF, and PCE.

3.8 Physical Methods

X-ray photoelectron spectroscopy (XPS) analysis was carried out using VG Thermo-Scientific MultiLab 3000 ultra-high vacuum surface analysis system using an Al Kα source of 1486.6 eV excitation energy. The SEM images were taken using FEI Nova NanoSEM 600 with an accelerating voltage of 1.5 kV and a working distance of 5-6 mm and Thermo-Fisher Scientific Apreo C LoVac FESEM with an accelerating voltage of 1.5 kV and a working distance of 5-10 mm. The cross-section SEM images were obtained using a JEOL 7000 field-emission scanning electron microscope. Energy Dispersive X-ray Spectrometry (EDS) spectra were obtained by TESCAN Vega3 SEM with an EDS detector. Powder XRD patterns were acquired using a Bruker D8 Discover X-ray diffractometer with Cu Kα radiation (1.54Å, 40 KV). Infrared spectra were collected using
a Thermo Nicolet Avatar 360 FT-IR spectrometer with Smart iTR. PL analysis was conducted using a Renishaw in Via Raman microscope with a CCD detector and a 632 nm He–Ne laser source. UV-Vis analyses were carried out by Agilent 8453 diode array spectrophotometer and PerkinElmer Lambda 950 equipped with Integrating Spheres. The $J$-$V$ curves were measured using Autolab PGSTAT128-N potentiostat coupled with a class A superstrate simulator equipped with a Newport LCS-100 lamp and AM 1.5G filter. EIS analysis was carried out using Autolab PGSTAT128-N potentiostat coupled with a class A superstrate simulator equipped with a Newport LCS-100 lamp and AM 1.5G filter. The impedance data were measured under one sun illumination (AM1.5G, 100 mW/cm$^2$) at an open circuit potential.
CHAPTER 4 – DIRECT DEPOSITION OF NONAQUEOUS SNO₂ DISPERSION BY BLADE COATING ON PEROVSKITES FOR THE SCALABLE FABRICATION OF P–I–N PEROVSKITE SOLAR CELLS

4.1 Introduction

Among commonly used inorganic electron transport materials (ETMs), titanium dioxide (TiO₂), zinc oxide (ZnO), and tin dioxide (SnO₂) are most commonly employed based on their superior properties as described in Chapter 1. For applications on flexible substrates, like polyethylene terephthalate (PET) and polyethylene naphthalate (PEN), the low melting point and heat-sensitivity of the substrate are driving the demand for materials with low post-annealing temperatures.¹³⁰ For this reason, the high-temperature processing of TiO₂ renders it unsuitable for use with flexible substrates. As alternatives, SnO₂ and ZnO have gained popularity due to their compatibility with low-temperature processing techniques, which makes them ideal for PET-based flexible Perovskite Solar Cells (PSCs).⁴⁷ Nonetheless, ZnO suffers from poor photostability under UV irradiation, whereas SnO₂ offers better stability.⁵⁰ While SnO₂ has been proven efficient as an Electron Transport Layer (ETL) in conventional n-i-p structures, its direct deposition on the perovskite layer in p-i-n architectures remains underexplored. Limited research exists on the direct deposition of single-layer metal oxide (MOₓ) ETLs onto perovskite in p-i-n structures, mainly due to solvent incompatibility between the MOₓ and the underlying perovskite layer. In the limited number of examples of p-i-n PSC architectures with a MOₓ
ETL, an organic ETL is first layered on the perovskite, allowing the formation of bilayer structures like PCBM/ZnO, C60/SnO₂, and PCBM/SnO₂.⁵¹,⁵²

More typically, fullerene and its derivatives, including C60, C70, PC61BM, and PC71BM, are predominantly used as organic ETL materials in inverted perovskite solar cells.¹³¹ These fullerene-based materials are favored for their low-temperature processing capabilities and high performance. They can be applied to the perovskite layer through either physical vapor deposition (PVD) or solution deposition methods that use perovskite-inert solvents. However, the high production costs and questionable long-term stability of these fullerene derivatives present significant barriers to widespread commercial adoption.¹³²,¹³³ Consequently, future research should focus on cost-effective and stable ETL alternatives.

One promising avenue is the use of pre-synthesized nanoparticles dispersed in perovskite-compatible solvents. Recent studies suggest that substituting organic ETLs with pre-synthesized ZnO nanoparticles can be effective.¹¹⁰ For instance, a study by You et al. demonstrated the use of solution-processed p-type nickel oxide (NiOₓ) and n-type ZnO nanoparticles as hole and electron transport layers in inverted PSCs.¹³⁴ These devices maintained 90% of their original power conversion efficiency (PCE) of 16.1% even after 60 days of storage at room temperature, unlike control devices with organic transport layers, which degraded within just five days.

Based on these successes, we wanted to develop a similar strategy for applying SnO₂ nanoparticles in p-i-n structures without using a bilayer. SnO₂ nanocrystals can be synthesized using precipitation, hydrothermal, hot injection, and inverse micelle-water injection.¹¹²,¹³⁵-¹³⁷ These pre-synthesized nanocrystals can potentially be suspended in
perovskite-compatible solvents and directly deposited onto perovskite without high-temperature sintering, thereby simplifying the fabrication process and reducing overall fabrication time. Nevertheless, the stable dispersion of these MOx nanoparticles in desired solvents remains a challenge. This often requires the coordination of bulky organic ligands, which may impede the ETL's charge transfer capability, thus lowering the overall efficiency of the PSC.125, 138, 139

To overcome these challenges, we developed a strategy using small, chelating ligands for the dispersion pre-synthesized SnO2 nanoparticles into perovskite compatible solvents for direct deposition onto the perovskite layer in a p-i-n device structure. The results described in this chapter are included in the publication Direct Deposition of Nonaqueous SnO2 Dispersion by Blade Coating on Perovskites for the Scalable Fabrication of p–i–n Perovskite Solar Cells by Chapagain et al.117 We utilized the sol-gel method to synthesize SnO2 nanoparticles and then functionalized them with acetic acid to create tin oxide acetate (SnO2-A). This functionalization results in a stable colloidal dispersion of SnO2-A in anhydrous ethanol, suitable for direct application to the perovskite film. We selected acetate as the ligand because of its short chain length and small size, minimizing its impact on the SnO2 and the electrical properties of the film. Devices fabricated through this method achieved an average power conversion efficiency (PCE) of 12.27%, peaking at 14.1%. Furthermore, these devices retained 95.8% of their initial average PCE after 40 days, following the ISOS-D-1 protocols for shelf-life assessment. These results are promising and suggest the potential for scaling up PSCs using cost-effective, inorganic ETLs.
4.2 Results and Discussion

4.2.1 Characterization of SnO$_2$ and SnO$_2$-A

We prepared a perovskite-compatible SnO$_2$ ink by functionalizing SnO$_2$ nanoparticles to improve their dispersibility in non-aqueous solvents, as shown in Figure 4.1a-c. Initially, hydrous SnO$_2$ was synthesized from stannic chloride and sodium hydroxide, following established procedures in the literature. These hydrous SnO$_2$ nanoparticles were then subjected to a ligand exchange reaction with acetic acid, resulting in SnO$_2$ functionalized with acetate (SnO$_2$-A).

X-ray diffraction (XRD) patterns of both hydrous SnO$_2$ and SnO$_2$-A displayed peaks at 26°, 34°, 52°, and 65°, which correspond to the (110), (101), (211), and (112) planes of the rutile crystal structure of SnO$_2$ (Figure 4.1d). The similarity between the XRD patterns confirms that the ligand exchange process is a surface modification without altering the underlying crystal structure. Fourier transform infrared (FT-IR) spectroscopy further verified the coordination of acetate ligands to the metal oxide surface. Possible binding modes of the carboxylate ligand include monodentate, bidentate, or bridging. The FT-IR spectra revealed common features between hydrous SnO$_2$ and SnO$_2$-A (Figure 4.1e), particularly a peak at 650 cm$^{-1}$ associated with Sn-O stretching. The spectrum for hydrous SnO$_2$ displayed a broad band at 3300 cm$^{-1}$ and a sharp band at 1640 cm$^{-1}$, linked to O-H stretching and bending from adsorbed water on the hydrous SnO$_2$ surface. In contrast, SnO$_2$-A showed a significant reduction in the O-H stretching band, indicating that the hydroxyl groups on the hydrous SnO$_2$ surface have been replaced. This is further corroborated by the presence of bands at 1715 cm$^{-1}$ and 1380 cm$^{-1}$ in the SnO$_2$-A spectrum,
which are associated with C=O stretching and acetate scissoring vibrations, respectively. This confirms the successful coordination of acetate ligands in SnO$_2$-A.

Figure 4.1. Schematic illustration of the synthesis of hydrous-SnO$_2$, functionalization of hydrous-SnO$_2$ with acetic acid to yield SnO$_2$-A, and preparation of a stable colloidal dispersion in anhydrous ethanol; d-e) XRD diffraction patterns and FTIR spectra of hydrous-SnO$_2$ and SnO$_2$-A.

4.2.2 Non-aqueous Dispersion of SnO$_2$-A

In contrast to hydrous SnO$_2$, the SnO$_2$-A nanoparticles are readily dispersed in protic organic solvents such as ethanol and isopropanol. The enhanced dispersibility of the SnO$_2$-A particles in protic organic solvents is attributed to the formation of a hydrogen bonding network between the surface-bonded acetate, excess acetic acid, and ethanol.\textsuperscript{128} Although longer chain carboxylates would more effectively prevent agglomeration of the SnO$_2$ nanoparticles and enable the formation of a stable colloidal dispersion of SnO$_2$ in
perovskite-compatible non-polar organic solvents, the residual longer chain ligand in the ETL would hamper the charge transfer process and reduce the overall efficiency of the PSCs. As such, we selected to functionalize SnO$_2$ with a short-chain carboxylic acid even though this limits our selection of solvents for the ink formulation to anhydrous ethanol. The choice of blade coating further complicates this balance between colloidal stability and solvent compatibility as the deposition technique, where solvent evaporation can be slower than in spin coating techniques. Hence, the perovskite layer may be exposed to solvent for a longer period.

4.2.3 Perovskite Compatibility of SnO$_2$-A Dispersion

To study the perovskite compatibility, a dispersion of SnO$_2$-A in anhydrous ethanol was deposited directly on the top of the perovskite absorber layer of CH$_3$NH$_3$PbI$_3$ via blade coating. The XRD patterns of perovskite before and after deposition of SnO$_2$ on the perovskite are shown in Figure 4.2a. Before deposition, the perovskite XRD pattern shows a prominent peak at 14.1° as expected for CH$_3$NH$_3$PbI$_3$. The XRD pattern is unchanged after the deposition of the SnO$_2$, indicating the perovskite layer remains intact. No additional peak at 12.7° indicating moisture-assisted degradation resulting in PbI$_2$ formation was observed. The XRD patterns confirm that a SnO$_2$-A dispersion in anhydrous ethanol can be directly dispensed on the perovskite and deposited without any detectable degradation of the surface. It should be noted that no interfacial layer was deposited before the deposition of the SnO$_2$ colloidal dispersion, and yet there is no apparent damage to the perovskite layer.
4.2.4 Efficient Charge Extraction

The dynamics of the charge carrier activity of the solution phase deposited SnO$_2$ layer on perovskite were studied employing photoluminescence (PL) and time resolved P.L. (TRPL) spectroscopy. The steady-state PL spectra of the perovskite and perovskite/SnO$_2$ on a glass substrate are shown in Figure 4.2b. The photoluminescence of the perovskite is strongly quenched in the presence of SnO$_2$-A, indicating a significant drop in the charge carrier density, consistent with efficient charge transfer from the perovskite layer to the ETL. The TRPL measurements of the perovskite before and after deposition of SnO$_2$-A on the perovskite support the result of PL analysis. In Figure 4.2c, the TRPL spectra, taken from the glass side, of the glass/perovskite and glass/perovskite/SnO$_2$-A samples show a significant decrease in the photoluminescence lifetime after deposition of the SnO$_2$-A. This decrease in photoluminescence lifetime confirms the effective charge extraction by the ETL from the perovskite absorber layer. This efficient charge carrier transfer is accomplished without an added interfacial layer between the perovskite and SnO$_2$. 

Figure 4.2. (a) XRD patterns, (b) photoluminescence spectra, and (c) time-resolved photoluminescence data for CH$_3$NH$_3$PbI$_3$ perovskite films before and after deposition of SnO$_2$-A.
4.3 Solar Cell Fabrication

Based on the encouraging XRD, PL, and TRPL results, PSCs were fabricated with a p-i-n architecture employing SnO$_2$-A as the ETL. A series of planar PSCs were fabricated on indium tin oxide (ITO) coated glass with a polytriarylamine (PTAA) hole transport layer (HTL) and a poly[(9,9-bis(3’-(N, N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) interfacial layer. The overall device architecture is ITO/PTAA/PFN/CH$_3$NH$_3$PbI$_3$/SnO$_2$-A/Ag. PTAA was chosen for the baseline device since it is often used in literature as a hole transport layer. The SnO$_2$-A layer was annealed for 10 min at 100°C to remove solvents, and finally, silver was thermally evaporated as a top contact layer. The annealing process was optimal at 100°C and 10 min. Device performance at other annealing temperatures is described below. Additionally, it was noticed that the perovskite undergoes degradation at a higher temperature, which limits the annealing of SnO$_2$-A deposited on the perovskite. The optical images of the perovskite film, deposition of SnO$_2$-A over perovskite film, and the full device stack are shown in Figure 4.3.

![Figure 4.3. Optical images during fabrication of the SnO$_2$-A PSC. A) Fully converted perovskite film; B) Blade coated SnO$_2$-A film on top of perovskite; C) Full device stack after deposition of thermally evaporated silver on top of SnO$_2.$](image)
A schematic representation of device architecture is shown in Figure 4.4a, highlighting the solution-phase blade coating of SnO$_2$-A as the ETL on the top of the perovskite. The PTAA, PFN, and MAPbI$_3$ layers were deposited using blade coating at ambient conditions.$^{144}$ The deposition of SnO$_2$-A on the fully converted perovskite yields a uniform layer with a reflective surface. Further, the top surface SEM shows that the perovskite is fully converted and compact, with no pinholes prior to (Figure 4.4b) and after (Figure 4.4c) SnO$_2$ deposition. Figure 4.4d shows a cross-sectional scanning electron microscopy (SEM) image of the proposed p-i-n device structure. Each of the individual layers can be clearly identified. Notably, the perovskite layer has no visible physical deformation due to the deposition of the SnO$_2$-A ink directly on the perovskite. The optimized thickness of the SnO$_2$ ETL was measured to be 36.7 ± 3.4 nm. This is significant since the deposition of a solution phase SnO$_2$ layer by blade coating did not impart any pinholes or other deformation of the perovskite films.
Figure 4.4. (a) Schematic illustration of the blade coating of SnO$_2$-A on the perovskite and (b) Top surface SEM images of perovskite film (c) SnO$_2$ layer on the perovskite film and (d) Cross-sectional SEM image of the full device.

4.3.1 Solar Cell Performance

The J-V characteristics of the 0.25 cm$^2$ fabricated cells were measured under one sun condition (AM 1.5G, 100 mW/cm$^2$), and their corresponding photovoltaic parameters, including PCE, fill factor (FF), short-circuit current density ($J_{sc}$), and open-circuit voltage ($V_{oc}$) were recorded. The champion device exhibited a PCE of 14.1% with a $J_{sc}$ of 22.61 mA/cm$^2$, a $V_{oc}$ of 1.023 V, and an F.F. of 61% (Figure 4.5a). As a comparison, a 0.25 cm$^2$ standard device with the device architecture ITO/PTAA/PFN/CH$_3$NH$_3$PbI$_3$/C$_{60}$/BCP/Ag (BCP = bathocuproine) was fabricated and evaluated under the same conditions. The
standard n-i-p device using the same absorber yielded a PCE of 15.11% with a $J_{sc}$ of 18.88 mA/cm$^2$, a $V_{oc}$ of 1.024, and an FF of 76.76% (Figure 4.5b). A large area SnO$_2$-A device with an area of 1 cm$^2$ device yielded a 9.47% PCE and demonstrated a small hysteresis effect (Figure 4.5c).

Figure 4.5. (a) J-V curve of the champion device, (b) J-V curve of the controlled device, and (c) J-V hysteresis of a 1 cm$^2$ SnO$_2$ device.

SnO$_2$ and C60 devices demonstrated remarkably similar $V_{oc}$ values, indicating that SnO$_2$-A is effective for charge collection. However, the SnO$_2$ device had a lower FF than the control device, which may suggest charge recombination at the interface or a higher ETL thickness. The high series resistance of the SnO$_2$ device is the leading cause for obtaining a lower fill factor. The SnO$_2$-based device showed a higher series resistance of 11.39 $\Omega$ cm$^2$ compared to the controlled device of 5.55 $\Omega$ cm$^2$. The current density of the champion SnO$_2$ and controlled devices are 22.61 mA/cm$^2$ and 18.88 mA/cm$^2$ respectively. Interestingly, the $J_{sc}$ value is higher for the SnO$_2$-A device. The improved current density of the SnO$_2$-based device is due to the defect passivation of the perovskite at the SnO$_2$/perovskite interface by the acetic acid present in the SnO$_2$ dispersion. Device performance at different annealing temperatures and times can be found in Figure 4.6.
Figure 4.6. Effect of SnO$_2$-A annealing conditions on J-V characteristics. Comparison of the average $V_{oc}$, $J_{sc}$, FF, and PCE for PSC with various annealing conditions for the SnO$_2$-A ETL. Conditions include no heating (no heat) and thermal annealing at 100 °C for 2 minutes, 140 °C for 2 minutes, and 100 °C for 10 minutes.

To analyze the cause of high series resistance on the J-V curve of the SnO$_2$ device, we increased the thickness of the SnO$_2$ layer by increasing the concentration of SnO$_2$ dispersion from 2% to 4%. The J-V curve of the device having a thicker SnO$_2$ layer shows severe deviation due to very high series resistance (Figure 4.7). The average series resistance value of the SnO$_2$ device containing 4%.
Figure 4.7. J-V curve for 4% SnO₂ device a) without BCP b) with BCP at the interface between SnO₂ ETL and top contact Ag.

SnO₂ was calculated to be 21.63 Ω cm² from the J-V curve. The average series resistance had reduced significantly from 21.63 Ω to 6.65Ω when we deposited a 6 nm BCP buffer layer at the interface between SnO₂ ETL and top metal contact Ag (Figure 4.7). The thin BCP buffer layer reduces interfacial charge recombination between SnO₂ ETL and top contact Ag by maintaining proper ohmic contact.⁵¹,¹⁴⁶,¹⁴⁷ This observation suggests the need for either an interfacial layer or further optimization of tin oxide to improve efficiency by decreasing the charge carrier recombination at the interface.

4.3.2 Device Stability

To understand the stability of the fabricated device, sample devices were stored in a nitrogen flow box after initial J-V measurements were recorded. The devices were stored without encapsulation, and the J-V characteristics were re-evaluated after 40 days. This testing procedure complies with the ISOS protocol ISOS-D-11.¹⁴⁸ Figure 4.8 shows the device performance statistics of the stability test. After 40 days, 95.8% of the average initial efficiency was retained. The loss of efficiency is mainly due to a decrease in $J_{sc}$, which decreased by 15.59% on average. Interestingly, after storage, the average $V_{oc}$ and FF values
increased by 4.85% and 8.42%, respectively. No clear mechanism explains the increase in $V_{oc}$ and FF over time. Possible factors include age-induced recrystallization of the perovskite, strain reduction of the perovskite thin film, or disappearance of the trap state.\textsuperscript{149}

Figure 4.8. Stability study $J$-$V$ characteristics of unencapsulated p-i-n devices before (1) and after (2) storage for 40 days in a nitrogen flow box.

4.4 Conclusions

In summary, the solution phase deposition of a non-aqueous dispersion of SnO$_2$ nanoparticles directly onto a CH$_3$NH$_3$PbI$_3$ perovskite by a blade coating technique was demonstrated on a p-i-n device architecture. The acetate functionalized nanoparticles, SnO$_2$-A, were synthesized using a traditional aqueous reaction pathway that allowed for the formulation of a stable dispersion in anhydrous ethanol. There was no observation of a PbI$_2$ peak in the XRD spectrum after the deposition of the ink on CH$_3$NH$_3$PbI$_3$, indicating
no observable damage to the perovskite thin film. The photoluminescence results demonstrated that the electrons are transported from the perovskite layer, and the cross-sectional SEM shows a smooth interface between the CH$_3$NH$_3$PbI$_3$ and SnO$_2$ films. The champion PSCs exhibited a PCE of 14.1% with an active area of 0.25 cm$^2$ and maintained 95.8% of this after 40 days. The work establishes a technique to deposit a metal oxide nanoparticle dispersion directly on a perovskite thin film, which has implications for moving the technology towards high throughput manufacturing, such as roll-to-roll fabrication of perovskite modules. It is evident from these results that further work is needed to establish the optimal ink chemistry, including doping, interfacial treatments, surfactants, and sintering aids. It is also necessary to study the post-deposition processing to reduce the time required to anneal the thin film fully.
5.1 Introduction

In the previous chapter, we discussed strategies to address the challenges of depositing fully solution processed SnO$_2$ directly onto the perovskite absorber layer without degrading it. Our approach centered on synthesizing and functionalizing SnO$_2$ nanoparticles, enabling a stable dispersion in perovskite-compatible solvents. Utilizing this innovative material, we successfully achieved large-area solution-phase deposition of SnO$_2$ nanoparticles directly onto perovskite thin films, reaching a peak efficiency of 14%. However, a high series resistance of 11.39 $\Omega$ cm$^2$ hindered the device's performance. This limitation primarily stemmed from the inferior electrical and optical properties associated with low-temperature annealing of these solution-processed nanoparticles, in contrast to the properties of SnO$_2$ annealed at higher temperatures.$^{85, 97}$

This chapter focuses on improving the performance of ETL materials, particularly SnO$_2$, through elemental doping. Prior research has shown that doping strategies can effectively alter various properties of semiconducting metal oxides (MO$_x$), such as carrier concentration, electron mobility, and optical and structural characteristics.$^{151}$

Specifically, several groups have demonstrated enhanced performance of SnO$_2$ ETLs through doping with aliovalent cations like Y$^{3+}$, Nb$^{5+}$, Li$^+$, Mg$^{2+}$, and Sb$^{3+}$.$^{93, 94, 97}$
In this work, we introduce yttrium-doped SnO$_2$ nanoparticles (Y:SnO$_2$) to improve the electronic properties of SnO$_2$. The results described in this chapter are included in the publication *High Performing Inverted Flexible Perovskite Solar Cells via Solution Phase Deposition of Yttrium Doped SnO$_2$ Directly on Perovskite* by Chapagain et al.$^{118}$ This doped material satisfies the low-temperature annealing conditions necessary for fabricating flexible Perovskite Solar Cells (PSCs) on PET substrates. Yttrium doping has improved charge extraction and transport, resulting in champion PCEs ranging from 14.4% to 16.5% for SnO$_2$ and Y:SnO$_2$ devices, respectively, when prepared on flexible PET substrates. The report aims to discuss the development and potential applications of this yttrium-doped SnO$_2$ material, which can be blade-coated directly onto perovskite layers.

5.2 Results and Discussion

5.2.1 Synthesis and Characterization of Y:SnO$_2$

Yttrium-doped tin(IV) oxide (Y:SnO$_2$) nanoparticles (NPs) were synthesized by slightly modifying the sol-gel process reported for pristine tin(IV) oxide (SnO$_2$) particles.$^{117}$ During the synthesis, yttrium chloride was incorporated into anhydrous SnCl$_4$ in specific ratios to achieve doping concentrations of 1, 2, and 3 mol% Y. These concentrations are denoted as 1% Y:SnO$_2$, 2% Y:SnO$_2$, and 3% Y:SnO$_2$. To improve their dispersibility in perovskite-compatible organic solvents, the Y:SnO$_2$ nanoparticles were functionalized with acetate, resulting in Y:SnO$_2$-A.$^{117,128}$ This acetate functionalization transforms the Y:SnO$_2$ from an amorphous white powder to a clear, colorless solution of functionalized tin oxide (Y:SnO$_2$-A) in glacial acetic acid. Characterization data is specifically provided for the 2% Y:SnO$_2$ and 2% Y:SnO$_2$-A formulations, although findings for the 1% and 3% doped materials were consistent.
X-ray diffraction (XRD) analyses were performed to assess the crystal structures of the synthesized nanoparticles. The XRD pattern for 2% Y:SnO$_2$ showed no structural changes or separate phase formations compared to undoped SnO$_2$ (Figure 3.1a). The characteristic XRD peaks observed at angles 26.4, 33.75, 51.86, and 64.37° are attributed to the (110), (101), (211), and (301) planes of the tetragonal rutile crystal structure common to both SnO$_2$ and Y:SnO$_2$. Furthermore, the presence of Y, Sn, and O in the Y:SnO$_2$ particles was confirmed by energy dispersive X-ray spectrometry (EDS) as shown for 2% Y:SnO$_2$ in Figure 3.1b. The EDS analysis for 2% Y:SnO$_2$, as shown in Figure 3.1b, indicated a uniform distribution of yttrium throughout the material (Figure 5.1c-e).

Figure 5.1. Characterization of Y:SnO$_2$. (a) XRD patterns of pristine SnO$_2$ and 2% Y:SnO$_2$, (b) EDS spectra of 2% Y:SnO$_2$ and elemental mapping of c) tin, d) oxygen, and e) yttrium in 2% Y:SnO$_2$.

The elemental composition of SnO$_2$-A and Y:SnO$_2$-A films was evaluated by X-ray photoelectron spectroscopy (XPS) on the glass-ITO substrate. The survey spectra of SnO$_2$ and 2% Y:SnO$_2$-A indicate the presence of C1s, O1s, and Sn3d peaks along with
other associated peaks (Figure 5.2a). The high-resolution core level spectra of Sn3d for Y:SnO$_2$ contain doublet peaks at 487.4 eV and 495.8 eV, corresponding to Sn3d$_{5/2}$ and Sn3d$_{3/2}$ (Figure 5.2b). The doublet separation of Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$ of 8.4 eV is consistent with Sn$^{4+}$ of SnO$_2$. There is no significant difference in the line shape of Sn 3d$_{5/2}$ of the SnO$_2$ and Y:SnO$_2$ thin film deposited on the glass-ITO substrate (Figure 3.2c), which supports observations by XRD that yttrium doping does not change the SnO$_2$ crystal structure. Yttrium doping introduces yttrium 3d peaks in the spectrum of Y:SnO$_2$-A at 158.8 eV that are absent in SnO$_2$-A (Figure 5.2d).

Figure 5.2. XPS characterization of Y:SnO$_2$. (a) The survey spectrum of Y:SnO$_2$-A, which indicates the presence of C1s, O1s, and Sn 3d peaks along with other associated peaks, (b) high-resolution XPS spectra of Sn3d for 2% Y:SnO$_2$, (c) XPS spectra of Sn 3d in SnO$_2$ and Y:SnO$_2$ after normalization of height. There is no significant difference in Sn 3d$_{5/2}$ line shapes and (d) comparison of XPS spectra Y3d for SnO$_2$ and 2% Y:SnO$_2$. 
The functionalization of Y:SnO$_2$ with acetate to yield Y:SnO$_2$-A was confirmed by FT-IR spectroscopy (Figure 5.3a). The spectra of Y:SnO$_2$ and Y:SnO$_2$-A show a common feature at 650 cm$^{-1}$ associated with Sn-O stretching.$^{159,160}$ The spectrum of Y:SnO$_2$ shows a broad band at 3300 cm$^{-1}$ and a sharp band at 1640 cm$^{-1}$ associated with OH stretching and bending of adsorbed water at the surface. The intensity of these bands is significantly reduced in Y:SnO$_2$-A as expected for ligand exchange of hydroxyl groups on the surface with acetate. The addition of bands at 1715 and 1380 cm$^{-1}$ associated with CO stretching and scissoring vibrations of acetate after functionalization provides direct evidence for acetate coordination in the spectrum of Y:SnO$_2$-A. Additionally, The X-ray diffraction pattern of Y:SnO$_2$ and Y:SnO$_2$-A shows no structural changes or separate phase formations after functionalization (Figure 5.3b).

Figure 5.3. (a) FTIR spectra and (b) XRD patterns of Y:SnO$_2$ and Y:SnO$_2$-A.

5.2.2 Solar Cell Fabrication and Characterization

The overall process of preparing dispersions of Y:SnO$_2$-A inks for solution deposition on perovskite is shown in Figure 5.4a. As described above, the addition of Y:SnO$_2$ powder to acetic acid yields functionalized Y:SnO$_2$-A NPs as a 40% (w/v) solution
upon heating. In contrast to unfunctionalized Y:SnO2 powder, Y:SnO2-A NPs are readily dispersed in protic organic solvents such as ethanol, isopropanol, and butanol, which is attributed to the formation of a hydrogen-bonding network between the surface-bonded acetate, excess acetic acid, and alcohol.\textsuperscript{128} Inks for deposition on perovskites were prepared by diluting the Y:SnO2-A with anhydrous ethanol to obtain a 1.5% final concentration of Y:SnO2 in the diluted solution.

![Figure 5.4. Preparation and deposition of Y:SnO2-A inks. (a) Functionalization of tin oxide and dilution of functionalized tin oxide in anhydrous ethanol, (b) Schematic of the blade coating demonstrating direction deposition of Y:SnO2-A dispersion on the perovskite layer.](image)

The diluted Y:SnO2-A ink was depositsed directly on the top of the MAPbI3 perovskite layer via blade coating, as shown in Figure 5.4b. The ink concentration was optimized to be 1.5% (w/v) of SnO2 for a larger area of blade coating on the flexible PET substrate. A dry air knife was used to rapidly remove excess solvent after deposition, and samples were annealed for 2 to 3 minutes at 100°C on a hotplate inside a box filled with
dry air. The effect of Y:SnO$_2$-A deposition on the integrity of the perovskite layer was evaluated by scanning electron microscopy (SEM), X-ray diffraction (XRD), and UV-visible spectroscopy. Figures 5.5a-b show top surface SEM images of the perovskite films before and after Y:SnO$_2$-A deposition. The perovskite film before Y:SnO$_2$-A deposition (Figure 5.5a) shows well-developed perovskite domains without observable pinholes. After Y:SnO$_2$-A deposition, the perovskite structure is partially obscured, consistent with a uniform layer of Y:SnO$_2$-A (Figure 5.5b).

![Figure 5.5a](image1)
![Figure 5.5b](image2)

Figure 5.5. Characterization of Y:SnO$_2$ films on perovskite. (a) top-surface SEM micrographs of the perovskite film, (b) Y:SnO$_2$-A layer on the perovskite film, (c) XRD diffraction patterns of perovskite before and after Y:SnO$_2$-A deposition, and (d) UV-Vis spectra of perovskite films before and after Y:SnO$_2$-A deposition.

The XRD patterns of the perovskite before and after deposition of Y:SnO$_2$-A (Figure 5.5c) further demonstrate the integrity of the perovskite layer is intact following deposition. Before deposition, a prominent peak is observed at $14.1^\circ$ as expected for CH$_3$NH$_3$PbI$_3$. The diffraction pattern is unchanged following the Y:SnO$_2$-A ink deposition.
on the perovskite surface. If deposition had induced degradation to PbI$_2$, a peak at 12.7° would be expected. The UV-visible spectra of the perovskite before and after Y:SnO$_2$-A deposition (Figure 5.5d) are also comparable, indicating no significant change in the optical absorption of the perovskite film and no change in the band edge of the absorption spectra. However, the slight increase in absorption below 450 nm in the absorption spectra of SnO$_2$ and Y:SnO$_2$ samples is associated with the absorption by SnO$_2$. Overall, the SEM, XRD, and UV-visible data confirm that Y:SnO$_2$-A ethanol inks can be deposited on perovskite without changing perovskite crystallinity and grain size.

Next, steady-state photoluminescence (PL) measurements were performed to evaluate the effect of yttrium doping on the charge carrier dynamics between the perovskite active layer and the ETL (Figure 5.6). The perovskite film on the PET substrate exhibited the highest PL intensity, whereas the perovskite films with SnO$_2$-A and Y:SnO$_2$-A demonstrated significant PL quenching. It is observed that Y:SnO$_2$-A ETL shows a higher PL quenching as compared to pristine SnO$_2$-A, which indicates that the charge transfer is more efficient in the perovskite/Y:SnO$_2$-A interface than that of the perovskite/SnO$_2$-A interface.$^{153}$
5.2.3 Solar Cell Performance

To analyze the effect of yttrium doping on the photovoltaic performance of the PSCs, a series of planar PSCs were fabricated on a flexible PET/ITO-based substrate (f-PSCs) employing SnO$_2$-A or Y:SnO$_2$-A as the ETL. The overall device structures were PET/ITO/PTAA/PFN/CH$_3$NH$_3$PbI$_3$/SnO$_2$-A/BCP/Ag and PET/ITO/PTAA/PFN/CH$_3$NH$_3$PbI$_3$/Y:SnO$_2$-A/BCP/Ag, where a polytriarylamine (PTAA) is used as a hole transport layer (HTL) and a poly[(9,9-bis(3’-(N, N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) as an interfacial layer. PTAA, PFN, perovskite, and SnO$_2$ layers were deposited by one-step blade coating, whereas BCP and silver were deposited by thermal evaporation. Before silver deposition, underlying layers were removed using GBL etching, and a series of f-PSCs with an active area of 0.1 cm$^2$ were fabricated. 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 mismatch factor. Device performance statistics of the f-PSCs as a function of Y doping concentrations in the Y:SnO$_2$ ETL yttrium are presented in Figure 5.7.

![Device performance statistics as a function of yttrium doping concentration in the Y:SnO$_2$ ETL. The photovoltaic parameters are (a) $V_{oc}$, (b) $J_{sc}$, (c) FF, and (d) PCE.](image)

Figure 5.7. Device performance statistics as a function of yttrium doping concentration in the Y:SnO$_2$ ETL. The photovoltaic parameters are (a) $V_{oc}$, (b) $J_{sc}$, (c) FF, and (d) PCE.

The PCEs increased with increasing yttrium concentrations until an optimum performance was achieved with 2 mol. % of yttrium in Y:SnO$_2$. The photovoltaic performance statistics of the f-PSCs with SnO$_2$ and Y:SnO$_2$ ETLs are summarized in Table 5.1. The increase in PCE is attributed to increases in open-circuit voltage ($V_{oc}$), fill factor (FF), and short-circuit current density ($J_{sc}$), as shown in Table 5.1. As shown in Table 5.2, the same trends are observed in the J-V parameters of the champion devices.
Table 5.1. Summary of the average photovoltaic performance statistics of 0.1 cm² f-PSCs with yttrium-doped SnO₂ ETLs.

<table>
<thead>
<tr>
<th>Y doping (mol. %)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_s$ (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.01 ± 0.03</td>
<td>22.18 ± 0.80</td>
<td>57.8 ± 2.5</td>
<td>13.0 ± 0.8</td>
<td>10.8 ± 2.8</td>
</tr>
<tr>
<td>1</td>
<td>1.02 ± 0.02</td>
<td>22.83 ± 0.77</td>
<td>60.8 ± 5.0</td>
<td>14.2 ± 1.1</td>
<td>8.1 ± 1.7</td>
</tr>
<tr>
<td>2</td>
<td>1.07 ± 0.01</td>
<td>22.62 ± 0.68</td>
<td>64.2 ± 3.2</td>
<td>15.6 ± 1.0</td>
<td>5.2 ± 0.8</td>
</tr>
<tr>
<td>3</td>
<td>1.00 ± 0.02</td>
<td>22.38 ± 0.67</td>
<td>64.7 ± 4.5</td>
<td>14.5 ± 1.1</td>
<td>7.2 ± 1.3</td>
</tr>
</tbody>
</table>

The increase in $V_{oc}$ and $J_{sc}$ indicates an enhancement in conductivity after yttrium doping. We calculated the conductivity of pristine SnO₂ and 2%Y:SnO₂ thin film on the Glass-ITO substrate from the I-V curve (Figure 5.8a) using the relation $\sigma = \frac{d}{AR}$ Where $\sigma$ is the conductivity, $d$ is the thickness of SnO₂ and Y:SnO₂ layers (75 nm), $A$ is the area under measurement (0.1cm²), and $R$ is the resistance calculated from Ohms law, i.e., $V = IR$. The conductivity ($\sigma$) of the SnO₂ and Y:SnO₂ thin films were calculated to be $13.27 \times 10^{-6}$ S cm⁻¹ and $25.95 \times 10^{-6}$ S cm⁻¹ respectively.

Table 5.2. Champion device photovoltaic performances of 0.1 cm² f-PSCs with yttrium-doped SnO₂ ETLs.

<table>
<thead>
<tr>
<th>Y doping (mol. %)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_s$ (Ω cm²)</th>
<th>$R_{sh}$ (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.01</td>
<td>22.40</td>
<td>63.3</td>
<td>14.3</td>
<td>6.2</td>
<td>498</td>
</tr>
<tr>
<td>1</td>
<td>1.05</td>
<td>22.96</td>
<td>67.2</td>
<td>16.2</td>
<td>5.3</td>
<td>730</td>
</tr>
<tr>
<td>2</td>
<td>1.08</td>
<td>24.34</td>
<td>68.8</td>
<td>18.2</td>
<td>4.2</td>
<td>1587</td>
</tr>
<tr>
<td>3</td>
<td>1.02</td>
<td>22.70</td>
<td>70.4</td>
<td>16.3</td>
<td>5.7</td>
<td>1389</td>
</tr>
</tbody>
</table>
Thus, the increase in the electrical conductivity of Y:SnO$_2$ after yttrium doping improves the charge extraction, which may have led to improved $V_{oc}$. This is supported by electrochemical impedance spectroscopy (EIS) measurements (Figure 5.8b). Additionally, yttrium doping led to decreased series resistance ($R_s$) and increased shunt resistance ($R_{sh}$), which improved the FF parameters.$^{94,98}$ These effects are optimized values in 2% Y:SnO$_2$ PSCs.

Figure 5.8. (a) From the I-V curve, the conductivity measurement of pristine SnO$_2$ and 2%Y:SnO$_2$ thin film on the Glass-ITO substrate.$^{92}$ (b) Nyquist plots of the f-PSCs with SnO$_2$ and Y:SnO$_2$ as ETLs measured under illumination at OCP, including equivalent circuits for the cells.

An image of blade-coated f-PSCs is presented in Figure 5.9a. Notably, the PCE of the champion f-PSC with 2% Y:SnO$_2$-A is ~2% higher than the PCE of the champion f-PSC with pristine SnO$_2$-A. The device with 2% Y:SnO$_2$-A exhibited a champion PCE of % 16.55 with a $J_{sc}$ of 22.38 mA/cm$^2$, a $V_{oc}$ of 1.08 V, and an FF of 68.36% (Figure 5.9b). Figure 5.9c highlights minimal hysteresis between forward and reverse scans of the f-PSCs with 2% Y:SnO$_2$ as an ETL.
5.3 Conclusions

In summary, we have developed functionalized yttrium-doped tin (IV) oxide nanoparticles that allow for direct deposition of fully solution-processed Y:SnO\textsubscript{2} ETLs on perovskite by a scalable blade coating method. The non-aqueous dispersion of Y:SnO\textsubscript{2}-A did not induce any observable damage to the perovskite during deposition, as evident by XRD and UV-Vis. At the optimum yttrium concentration of 2 mol. %, the inverted f-PSCS with Y:SnO\textsubscript{2} as an ETL exhibits improved performance due to increased \(V_{oc}\) and FF compared to pristine SnO\textsubscript{2}-A devices. Using this approach, the champion device achieved 16.55\% PCE, unprecedented for f-PSCS on ITO-PET substrate employing SnO\textsubscript{2} as an ETL. The fully solution-processed Y:SnO\textsubscript{2}-A is a promising ETL. This material possesses minimal cost, scalability, and manufacturing advantages over traditional organic ETLs that could improve the competitiveness of commercial perovskite solar modules.
CHAPTER 6 – HIGHLY PEROVSKITE COMPATIBLE LIGAND STABILIZED SNO₂ DISPERION FOR INVERTED PEROVSKITE SOLAR CELLS

6.1 Introduction

In planar PSCs, the most efficient devices commonly employ a regular (n-i-p) architecture in which low-temperature processed tin (IV) SnO₂ serves as the electron transport layer (ETL) with 2,2’,7,7’-tetrakis[N,N-bis(p-methoxyphenyl)amino]-9,9’-spirobifluorene (spiro-OMeTAD) as the hole transport layer (HTL). Since the charge carrier mobility of pristine spiro-OMeTAD is inherently low, it is often doped with hygroscopic and deliquescent dopants such as bis(trifluoromethane)sulfonamide lithium salt (LiTFSI), 4-tertbutylpyridine (tBP), and/or cobalt(III) complexes. These dopants enhance charge mobility but also tend to increase hysteresis and reduce the overall PSC stability. Therefore, finding a balance between high efficiency and good operational reliability in the standard doped HTL of the n-i-p structure remains a challenge.

An alternate approach is to use an inverted (p-i-n) architecture with fullerenes and their derivatives, such as C₆₀, C₇₀, PC₆₁BM, and PC₇₁BM, as a top layer ETL without doping. These ETLs exhibit superior electron mobility, low temperature processability, and higher intrinsic stability as they do not require doping. The use of undoped HTLS and intrinsically stable ETLs has been associated with improved stability and reduced hysteresis in inverted PSCs.
Additionally, fullerenes and their derivatives are reported to passivate defects and suppress non-radiative recombination in perovskite films, thanks to their electron-rich heteroatoms or heterocycles.\textsuperscript{165} Consequently, inverted PSCs with fullerenes as ETL materials have reached power conversion efficiencies exceeding 25\% in single-junction planar structures on glass substrate and 23\% on flexible substrate making inverted PSCs a promising option for practical applications.\textsuperscript{54, 166, 167}

Despite their advantages, the broader adoption of fullerene based ETLs in commercial applications faces significant challenges, particularly due to their high production costs and limited device stability.\textsuperscript{132, 133, 164} Fullerene and its derivatives tend to self-aggregate, making these thin films prone to cracking and fracture, ultimately leading to device failure.\textsuperscript{168-170} Additionally, their small molecular size and low solution viscosity might not provide complete surface coverage for optimized film thicknesses as an ETL.\textsuperscript{168} Such incomplete coverage can lead to direct contact between the electrode and the perovskite layer, accelerating device degradation.\textsuperscript{163} Furthermore, fullerene derivatives are susceptible to reaction with air and moisture, which further contributes to the degradation process.\textsuperscript{163}

To overcome this challenge, future research needs to prioritize the development of cost-effective alternatives to fullerenes, which will be vital in advancing the commercial viability of perovskite solar technology. Solution-processed tin oxide (SnO\textsubscript{2}) has shown significant promise as an inexpensive and efficient ETL in the regular PSC architecture.\textsuperscript{47, 68} Its potential as an alternative ETL to fullerenes and their derivatives in inverted PSCs is particularly noteworthy due to its low-temperature solution processibility and superior optoelectronic properties.\textsuperscript{68} Additionally, SnO\textsubscript{2} is several orders of magnitude less
expensive than C<sub>60</sub> (price comparison in SI). However, the broader application of solution processed SnO<sub>2</sub> in inverted PSCs has been limited, mainly because of the solvent incompatibility between the SnO<sub>2</sub> dispersion medium and the perovskite absorber layer. In our prior research, we have successfully demonstrated the viability of using solution-processible, ligand-stabilized SnO<sub>2</sub> nanoparticles as an ETL in an inverted PSC architectures with MAPbI<sub>3</sub> and MA<sub>0.6</sub>FA<sub>0.4</sub>Pb(I<sub>0.95</sub>Br<sub>0.05</sub>)<sub>3</sub>.<sup>117, 118</sup> From those studies; it was found that devices with 2 mol% yttrium-doped SnO<sub>2</sub> (Y:SnO<sub>2</sub>) have enhanced performance compared to devices with pristine SnO<sub>2</sub>.<sup>118</sup>

In this work, we report an expanded solvent scope for the deposition of pre-synthesized Y:SnO<sub>2</sub> nanoparticles directly on perovskite to include several lower alcohols and select polar aprotic solvents. The results demonstrate the compatibility of this approach with four different lead halide perovskite layers: 1) MAPbI<sub>3</sub> (MAPI); 2) MA<sub>0.6</sub>FA<sub>0.4</sub>Pb(I<sub>0.95</sub>Br<sub>0.05</sub>)<sub>3</sub> (mixed cation, MC); 3) Cs<sub>0.2</sub>FA<sub>0.8</sub>PbI<sub>3</sub> (MA-free); and 4) Cs<sub>0.1</sub>(FA<sub>0.83</sub>MA<sub>0.17</sub>)<sub>0.9</sub>Pb(I<sub>0.85</sub>Br<sub>0.15</sub>)<sub>3</sub> (triple cation, TC) were studied. MAPI has been a popular choice due to its early adoption in PSC development. However, its energy band gap (<i>E<sub>g</sub></i>) of 1.57 eV exceeds the ideal 1.4 eV according to the Shockley–Queisser limit, which limits its performance.<sup>24, 88</sup> FAPbI<sub>3</sub>, with a band gap closer to the ideal at 1.47 eV, offers potentially better performance and greater thermal stability than MAPI. However, achieving photoactive phase stability in pure FAPbI<sub>3</sub> remains a challenge.<sup>24, 171</sup> In mixed-cation (MC) perovskites, the partial replacement of MA present at the A-site with FA has improved thermal stability and performance compared to MAPbI<sub>3</sub>.<sup>172</sup> Furthermore, the incorporation of the inorganic cation Cs in MA-free perovskites, specifically (Cs/FA)PbI<sub>3</sub>, has been proposed to increase thermal and moisture stability.<sup>173</sup> Triple-cation (TC) mixed
halide perovskites are another popular choice due to their improved efficiency and stability. In these perovskites, the simultaneous substitution of both A-site cations and X-site anions has shown superior thermal and moisture stability, further enhancing overall solar cell performance.\textsuperscript{174} Furthermore, substituting iodide with bromide expands the band gap, making it suitable as a top cell in tandem devices.

A stable dispersion of pre-synthesized Y:SnO\textsubscript{2} nanoparticles was accomplished by functionalization with acetate ligands. The Y:SnO\textsubscript{2}-A nanoparticle dispersions were then directly deposited via blade coating onto four different lead halide perovskite layers, and a series of inverted flexible PSCs (f-PSC) on ITO-coated PET substrate were fabricated. The performance of these f-PSCs achieved champion power conversion efficiencies (PCEs) of 16.90\%, 18.68\%, 17.71\%, and 20.41\%, and average PCEs of 15.27\%, 16.63\%, 16.13\%, and 19.02\% for MAPI, MC, TC, and MA-free devices respectively. The unencapsulated TC devices retained 90\% of their initial average PCE after 600 hours under continuous light illumination in an atmosphere-controlled box at 10\% humidity and a temperature of 35 ± 5°C.

6.2 Formulation of Perovskite Compatible SnO\textsubscript{2} Dispersions

6.2.1 Establishing the solvent scope of SnO\textsubscript{2} dispersions

The synthesis of the Y:SnO\textsubscript{2} nanoparticles and the acetate functionalization were performed as described in Chapter 3 or previously published work.\textsuperscript{118} Figure 6.1 provides an overview of the ink preparation and subsequent blade coating processes. The previously optimized yttrium concentration in SnO\textsubscript{2} of 2.0 mol % was used in the current study. The
concentrated Y:SnO$_2$-A was diluted to the desired concentration of 1.6% w/v of Y:SnO$_2$ for direct deposition on the perovskite via the blade coating technique.

Figure 6.1. Schematics of the deposition of nonaqueous SnO$_2$ dispersion directly on the perovskite.

Using an air knife with low air pressure (2 to 3 psi) during SnO$_2$-A deposition was found to be beneficial to promptly remove the bulk of the ethanol. This was followed by a short annealing period of 2 minutes at 100°C to remove any remaining residual solvent. The previous work demonstrated that Y:SnO$_2$-A yields stable dispersions in anhydrous ethanol. Ethanol, a polar solvent, is ideal for maintaining a stable dispersion of the metal oxide and is also volatile, allowing for minimized exposure to the perovskite layer.
Inks for the direct deposition of HTLs or ETLs onto the perovskite thin films are limited by the perovskite compatibility of the solvent. However, it would be advantageous for scalable manufacturing to expand the selection of compatible solvents. The deposition of $C_{60}$ directly onto a perovskite layer using blade coating has been achieved with non-polar solvents like chlorobenzene, but such lower polarity solvents may affect the stability of metal oxide inks. Polar aprotic solvents are more suitable for metal oxides, but these are typically less volatile than alcohols and may require more energy to remove, potentially damaging the perovskite film. Thus, there is a balance between ink stability and evaporation, impacting the economics of high-volume manufacturing and perovskite compatibility and affecting device performance. This work considers the impact of the solvent on Y:SnO$_2$-A ink stability and perovskite compatibility.

The Y:SnO$_2$-A concentrate was diluted to 1.6% w/v of Y:SnO$_2$ in various solvents, categorized into three groups: non-polar, polar aprotic, and protic. The inks were visually monitored for up to 6 hours and graded as stable dispersions (no visible changes) or unstable inks (precipitation or gelling), as summarized in Table 1.
Table 6.1. Stability of Y:SnO$_2$-A dispersions in different solvents.

<table>
<thead>
<tr>
<th>Solvent Type</th>
<th>Solvents</th>
<th>Stability$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Polar</td>
<td>Toluene</td>
<td>unstable</td>
</tr>
<tr>
<td></td>
<td>Chlorobenzene</td>
<td>unstable</td>
</tr>
<tr>
<td></td>
<td>Benzene</td>
<td>unstable</td>
</tr>
<tr>
<td></td>
<td>Hexane</td>
<td>unstable</td>
</tr>
<tr>
<td>Apotic polar</td>
<td>Acetone</td>
<td>unstable</td>
</tr>
<tr>
<td></td>
<td>Acetonitrile</td>
<td>unstable</td>
</tr>
<tr>
<td></td>
<td>Dimethylformamide (DMF)</td>
<td>unstable</td>
</tr>
<tr>
<td></td>
<td>Tetrahydrofuran (THF)</td>
<td>unstable</td>
</tr>
<tr>
<td></td>
<td>Methyl ethyl ketone (MEK)</td>
<td>unstable</td>
</tr>
<tr>
<td></td>
<td>Gamma-butyrolactone (GBL)</td>
<td>stable</td>
</tr>
<tr>
<td></td>
<td>Dimethyl sulfoxide (DMSO)</td>
<td>stable</td>
</tr>
<tr>
<td></td>
<td>Diethyl ether</td>
<td>unstable</td>
</tr>
<tr>
<td>Protic polar</td>
<td>2 methoxy ethanol (2-ME)</td>
<td>stable</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>stable</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>stable</td>
</tr>
<tr>
<td></td>
<td>Propanol</td>
<td>stable</td>
</tr>
<tr>
<td></td>
<td>2-Propanol (Isopropanol)</td>
<td>unstable</td>
</tr>
<tr>
<td></td>
<td>1-Butanol</td>
<td>stable</td>
</tr>
<tr>
<td></td>
<td>2-Butanol</td>
<td>unstable</td>
</tr>
</tbody>
</table>

$^a$Inks were visually monitored for up to 6 hours and graded as stable (no visible changes) or unstable (precipitation or gelling).

The Y:SnO$_2$-A dispersions have limited stability in most perovskite-compatible solvents, with lower alcohols being the notable exceptions. Digital images of Y:SnO$_2$-A dispersions in the lower alcohols methanol, ethanol, propanol, 2-propanol (isopropanol),
and butanol are presented in Figure 6.2. The dispersions displayed good stability except for isopropanol, which became cloudy within one hour.

![Digital images Y:SnO$_2$-A dispersions lower alcohols (methanol, ethanol, propanol, 2-propanol, and butanol) at three different time points.](image)

Figure 6.2. Digital images Y:SnO$_2$-A dispersions lower alcohols (methanol, ethanol, propanol, 2-propanol, and butanol) at three different time points.

The perovskite compatibilities of the stable lower alcohol Y:SnO$_2$-A dispersions were evaluated by blade-coating them directly onto MAPbI$_3$ perovskite, simulating Y:SnO$_2$-A coating conditions. Evaluation of the X-ray diffraction (XRD) patterns (Figure 6.3) shows that the perovskite peak at 14.2° remained unchanged for all alcohol dispersions except for methanol, in which case a small peak at 12.7° associated with lead iodide was observed.
Figure 6.3. XRD patterns of MAPbI$_3$ before and after blade coating with lower alcohols. X-ray diffraction data were collected on a A) MAPbI$_3$ film before and after blade coating with B) methanol, C) ethanol, D) propanol, E) isopropanol, or F) butanol. During deposition, an air knife with a low air pressure of 3 psi was applied to promptly remove the alcohol, followed by 2 minutes of annealing at 100 °C. The peak at 12.7° in panel B is assigned to the degradation product PbI$_2$.

The UV-Vis spectra (Figure 6.4) of the perovskite coated with ethanol to butanol dispersions exhibited remarkable similarity to the control (MAPbI$_3$), indicating perovskite stability. However, methanol adversely affects the perovskite as evidenced by a reduced UV-Vis absorption onset of MAPbI$_3$ around 790 nm. The results clearly show that Y:SnO$_2$-A can be dispersed into several lower alcohols yielding an expanded library of available solvents for the deposition of Y:SnO$_2$ directly on perovskite. Additionally, the stability of the Y:SnO$_2$-A dispersions in the aprotic polar solvents GBL and DMSO suggest that solvent combinations could also be employed to improve ink stability and deposition. For the remainder of this work, anhydrous ethanol was used due to its good ink stability and faster evaporation rate.
Figure 6.4. UV-Vis absorption spectra of MAPbI₃ film after blade coating of methanol, ethanol, propanol, 2-propanol, and butanol directly onto MAPbI₃.

6.3 Establishing compatibility of SnO₂ dispersions with diverse perovskites

6.3.1 Perovskite Ink Formulation for Blade Coating

Four different lead halide perovskite compositions (MAPI, MC, TC, and MA-free) covering a range of perovskite formulation, as described in the introduction, were investigated for their compatibility with Y:SnO₂-A dispersions. MAPI serves as a control since it is a standard, easy to fabricate perovskite. The mixed cation (MC, TC, MA-free) and mixed halide (MC, TC) perovskite materials are of particular interest as they are well-suited for fabricating efficient multijunction solar cells due to their highly tunable band gap.¹⁷⁶

The ink formulation and blade coating parameters for MAPI and MC perovskites were derived from our previously published work.¹¹⁸,¹¹⁹ The TC and MA-free perovskite precursor inks were briefly optimized for blade coating under ambient conditions on the flexible PET-based substrate. Figure 6.5a shows the annealing optimization of TC, which demonstrates that TC was fully converted to the perovskite at a temperature of 120 °C for...
10 minutes without any intermediate phase. Figure 6.5b shows the blade-coated perovskite film before annealing but after air knife treatment and Figure 6.5c shows the triple cation film during annealing.

Figure 6.5. (a) XRD pattern of the TC perovskite at different annealing temperatures; (b) the intermediate phase of TC perovskite before annealing and after air knife treatment; and (c) the conversion process of the intermediate stage to perovskite during annealing.

The optimal annealing temperature for MA-free perovskite differs from TC perovskite. As shown in Figure 6.6a, the optimum annealing condition for MA-free perovskite is 130 °C for 10 minutes. Figure 6.6b presents the fully converted MA-free perovskite film after annealing at 130°C for 10 min. It is noted that at annealing conditions of 120 °C for 10 minutes, 130 °C for 5 minutes, and 140 °C for 5 minutes, there is still the presence of NMP adducts. This indicates that these conditions are either insufficient in temperature or duration for complete conversion, leading to the residual presence of adducts.
Figure 6.6. (a) XRD pattern of MA-free perovskite at different annealing temperatures; (b) fully converted MA-Free perovskite on flexible PET-ITO substrate.

6.3.2 Diverse Perovskite Compatibility

To investigate the compatibility of the Y:SnO$_2$-A dispersion as an ETL in PSCs with varied perovskite compositions, Y:SnO$_2$-A dispersions in anhydrous ethanol were directly deposited onto MAPI, MC, TC, and MA-free perovskite surfaces using blade coating. The integrity of the perovskite layers post-SnO$_2$ deposition was assessed by XRD and UV-visible spectroscopy. Previously published works demonstrate the compatibility of fully solution-processed Y:SnO$_2$-A as an ETL in inverted PSCs with MAPI and MC perovskites.\textsuperscript{117-119} The XRD patterns of MAPI, MC, MA-free, and TC perovskites before and after the deposition of Y:SnO$_2$-A dispersions are presented in Figure 6.7. Notably, the XRD patterns of all four perovskites with different compositions displayed a distinct peak around 14.2°, which aligns with expectations for a perovskite. This pattern remained consistent even after Y:SnO$_2$-A deposition, suggesting that the integrity of the perovskite layer is preserved. Importantly, no additional peak was found at 12.7°, a marker typically indicative of moisture-assisted degradation leading to the formation of PbI$_2$. These
consistent XRD patterns affirm that the Y:SnO$_2$-A dispersion in anhydrous ethanol can be directly applied to halide perovskites with diverse compositions without causing noticeable surface degradation.

Figure 6.7. XRD patterns of perovskite films before and after deposition of Y:SnO$_2$-A. X-ray diffraction patterns before and after the deposition of a Y:SnO$_2$-A layer via blade coating on A) MAPbI$_3$ (MAPI), B) MA$_{0.6}$FA$_{0.4}$Pb(I$_{0.95}$Br$_{0.05}$)$_3$ (MC), C) Cs$_{0.2}$FA$_{0.8}$PbI$_3$ (MA-free), and D) Cs$_{0.1}$(FA$_{0.83}$MA$_{0.17}$)$_{0.9}$Pb(I$_{0.85}$Br$_{0.15}$)$_3$ (TC).

The UV-visible spectra of MAPI, MC, MA-free, and TC perovskites before and after Y:SnO$_2$-A deposition, as shown in Figure 6.8, reveal remarkable consistency. This consistency in the UV-visible spectra before and after Y:SnO$_2$-A deposition confirms that there are no significant changes in the optical absorption of the perovskite film. It emphasizes the preservation of the band edge of the absorption spectra and attests to the stability and integrity of those perovskites.\textsuperscript{177, 178} Taken together, the XRD and UV-Vis
analyses confirm that the adopted methodology ensures the perovskite layer remains pristine, underscoring its reliability for practical applications with commonly used halide perovskites, in addition to its applicability for MAPI and MC perovskites reported in earlier works.

Figure 6.8. UV-vis spectra of perovskite films before and after deposition of Y:SnO$_2$-A. UV-visible spectra before and after the deposition of a Y:SnO$_2$-A layer via blade coating on A) MAPbI$_3$ (MAPI), B) MA$_{0.6}$FA$_{0.4}$Pb(I$_{0.95}$Br$_{0.05}$)$_3$ (MC), C) Cs$_{0.2}$FA$_{0.8}$PbI$_3$ (MA-free), and D) Cs$_{0.1}$(FA$_{0.83}$MA$_{0.17}$)$_{0.9}$Pb(I$_{0.85}$Br$_{0.15}$)$_3$ (TC).

We investigated photoluminescence quenching to assess electron transfer dynamics from a perovskite layer to a solution-phase deposited Y:SnO$_2$ layer. Figure 6.9 presents the PL emission spectra of MAPI, MC, MA-free, and TC perovskite films interfaced with the solution-phase deposited Y:SnO$_2$-A layer. Notably, the photoluminescence intensities of these perovskites are markedly quenched upon introducing the Y:SnO$_2$-A layer, implying a significant decrease in the charge carrier density within these perovskites. This reduction
in carrier density aligns well with the theoretical expectation of efficient charge extraction by the solution-phase deposited Y:SnO₂-A from the underlying perovskite layer.

![Figure 6.9](image)

Figure 6.9. Steady-state PL spectra. Steady-state PL spectra of A) MAPI, B) MC, C) MA-free, and D) TC perovskites before and after the deposition of Y:SnO₂-A dispersions. Where PET/perovskite (black) and PET/perovskite/SnO₂ (red).

6.3.3 Device Performance

The performance of a fully solution-processed Y:SnO₂-A thin film paired with various perovskite compositions such as MAPI, MC, MA-free, and TC was evaluated using an inverted device architecture (p-i-n). The overall device structures comprised: (a) PET/ITO/PTAA/PFN/MAPI/Y:SnO₂-A/BCP/Ag, (b) PET/ITO/PTAA/PFN/MC/ Y:SnO₂-A/BCP/Ag, (c) PET/ITO/PTAA/PFN/MA-free/Y:SnO₂-A/BCP/Ag and, (d) PET/ITO/PTAA/PFN/TC/Y:SnO₂-A/BCP/Ag. In these configurations, polytriarylamine
(PTAA) served as the hole transport layer (HTL), and poly[(9,9-bis(3′-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) acted as an interfacial layer. A 3 nm thick bathocuproine (BCP) buffer layer was deposited between Y:SnO$_2$ layer and Ag. PTAA, PFN, perovskite, and SnO$_2$ layers were deposited by one-step blade coating, whereas BCP and silver were deposited by thermal evaporation. We employed dry air knife quenching to promptly convert the perovskite precursor to an intermediate phase by eliminating excess solvent. Prior to the deposition of silver, any underlying layers were cleared away with GBL etching. Subsequently, a series of f-PSCs, each consisting of at least 10 pixels and having an active area of 0.1 cm$^2$, were fabricated.

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 mismatch factor. The average and champion $J$-$V$ performance statistics of f-PSCs utilizing MAPI, MC, MA-free, and TC perovskites are presented in Figure 6.10 and summarized in Table 6.2 The average $V_{oc}$, $J_{sc}$, FF, and PCE values for devices employing TC perovskite as the photoactive layer are $1.15 \pm 0.016$ V, $22.91 \pm 0.71$ mA/cm$^2$, $72.17 \pm 2.92\%$, and $19.02 \pm 0.72\%$ respectively. For f-PSCs utilizing MAPI, MC, and MA-free perovskite as photoactive layers, the champion and average PCE are recorded as 16.9\% and $15.27 \pm 1.13\%$, 18.68\% and 16.63 $\pm 1.18\%$, 17.71\% and $16.13 \pm 0.87\%$ respectively.
Figure 6.10. Comparison of device performance statistics for inverted f-PSCs with different perovskite absorbers. Box plots of A) open-circuit voltage ($V_{OC}$), B) short circuit current density ($J_{SC}$), C) fill factor (FF), and D) power conversion efficiency (PCE) for ITO-PET/PTAA/PFN/perovskite/Y:SnO$_2$-A/BCP/Ag devices with MAPbI$_3$ (MAPI), MA$_{0.6}$FA$_{0.4}$Pb(1$_{0.95}$Br$_{0.05}$)$_3$ (MC), Cs$_{0.2}$FA$_{0.8}$PbI$_3$ (MA-free), or Cs$_{0.1}$(FA$_{0.83}$MA$_{0.17}$)$_{0.9}$Pb(I$_{0.85}$Br$_{0.15}$)$_3$ (TC) as the perovskite absorber.

The champion $J$-$V$ curves, a schematic of the device, and an image of the flexible device are presented in Figure 6.11a-c. Notably, the highest-performing PSCs, featuring TC as the perovskite, demonstrated a PCE of 20.41%, accompanied by a remarkably high $V_{OC}$ of 1.17 V, $J_{SC}$ of 23.56 mA/cm$^2$, and FF of 74.13%. The improved performance of the TC PSCs is attributed to superior phase purity and enhanced moisture and thermal stability over MAPI, MC, and MA-free devices.$^{24, 174, 179}$
Table 6.2. Summary of the average photovoltaic performance statistics for inverted f-PSCs with different perovskite absorbers.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Perovskite</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPI</td>
<td>1.078 ± 0.023</td>
<td>22.65 ± 0.60</td>
<td>62.48 ± 0.036</td>
<td>15.27 ± 1.13</td>
</tr>
<tr>
<td></td>
<td>1.096</td>
<td>22.87</td>
<td>67.45</td>
<td>16.9</td>
</tr>
<tr>
<td>MC</td>
<td>1.074 ± 0.017</td>
<td>23.42 ± 0.40</td>
<td>66.10 ± 0.040</td>
<td>16.63 ± 1.18</td>
</tr>
<tr>
<td></td>
<td>1.095</td>
<td>23.73</td>
<td>71.89</td>
<td>18.68</td>
</tr>
<tr>
<td>MA-free</td>
<td>1.056 ± 0.022</td>
<td>22.85 ± 0.42</td>
<td>66.8 ± 0.034</td>
<td>16.13 ± 0.87</td>
</tr>
<tr>
<td></td>
<td>1.088</td>
<td>23.21</td>
<td>70.13</td>
<td>17.71</td>
</tr>
<tr>
<td>TC</td>
<td>1.150 ± 0.016</td>
<td>22.91 ± 0.71</td>
<td>72.17 ± 2.92</td>
<td>19.02 ± 0.72</td>
</tr>
<tr>
<td></td>
<td>1.168</td>
<td>23.56</td>
<td>74.13</td>
<td>20.41</td>
</tr>
</tbody>
</table>

$V_{OC}$ is the open-circuit voltage, $J_{SC}$ is the short circuit current density, FF is the fill factor, and PCE is the power conversion efficiency. \textsuperscript{a}Device architecture is ITO-PET/PTAA/PFN/perovskite/Y:SnO$_2$-A/BCP/Ag where the perovskite is MAPbI$_3$ (MAPI), MA$_{0.6}$FA$_{0.4}$Pb(I$_{0.95}$Br$_{0.05}$)$_3$ (MC), Cs$_{0.2}$FA$_{0.8}$PbI$_3$ (MA-free), or Cs$_{0.1}$(FA$_{0.83}$MA$_{0.17}$)$_{0.9}$Pb(I$_{0.85}$Br$_{0.15}$)$_3$ (TC).

The observed performance limitations predominantly stem from the low conductivity and high sheet resistance of the PET-ITO substrate, rated at 50 Ω/cm$^2$. This will increase the contact resistance which is evident from the angle of the $J$-$V$ curve crossing the voltage axis, indicating a high series resistance of 4.74 Ω as calculated from the $J$-$V$ curve of the champion device. The operational stability of the f-PSC devices was evaluated under continuous light illumination inside a humidity-controlled box filled with nitrogen.

Owing to the superior performance of the TC devices, they were chosen for stability testing. The unencapsulated devices maintained approximately 90\% of their initial average PCE even after 600 hours, as shown in Figure 6.11d.
Figure 6.11. Champion device performance, architecture, and stability. A) Champion light and dark J-V curves for ITO-PET/PTAA/PFN/perovskite/Y:SnO$_2$-A/BCP/Ag devices with perovskite = MAPbI$_3$ (MAPI), MA$_{0.6}$FA$_{0.4}$Pb(I$_{0.95}$Br$_{0.05}$)$_3$ (MC), Cs$_{0.2}$FA$_{0.8}$PbI$_3$ (MA-free), or Cs$_{0.1}$(FA$_{0.83}$MA$_{0.17}$)$_{0.9}$Pb(I$_{0.85}$Br$_{0.15}$)$_3$ (TC), B) schematic of device architecture, C) photograph of flexible device, and D) operational stability of ITO-PET/PTAA/PFN/perovskite/Y:SnO$_2$-A/BCP/Ag under continuous light illumination.

6.4 Conclusions

In this work we have explored the solvent compatibility of pre-synthesized Y:SnO$_2$ nanoparticles for direct deposition on four different lead halide perovskite layers, MAPI, MC, TC, and MA-free. Most notably, f-PSCs featuring TC perovskite as the photoactive layer achieved a peak efficiency of 20.41%, accompanied by a $V_{OC}$ of 1.17 V, $J_{SC}$ of 23.56 mA/cm$^2$, and FF of 74.13%. When employing MAPI, MC, and MA-free perovskites as the photoactive layers, the champion efficiencies reached 16.9%, 18.68%, and 17.71%, with
average PCEs of 15.27 ± 1.13%, 16.63 ± 1.18%, and 16.13 ± 0.87% respectively. These results are particularly noteworthy considering the fabrication method of blade-coating on PET-ITO substrates.

The results expand our previous work with SnO₂ dispersions in anhydrous ethanol, demonstrating the compatibility of perovskite with several other lower alcohols. The use of co-solvent systems, combining lower alcohols with other protic and aprotic solvents, suggests a potential for a larger solvent space. This result broadens the solvent options for SnO₂-based ETL inks in p-i-n PSCs and opens possibilities for tandem devices that are dominated by C₆₀.

The compatibility of pre-synthesized Y:SnO₂ nanoparticles with mixed cation (MC, TC, MA-free) and mixed halide perovskites is particularly compelling due to their suitability for efficient multijunction solar cells, stemming from their highly tunable band gap ranging from 1.20 eV to 2.3 eV through compositional engineering.¹⁷⁶

It highlights the significance the compatibility of fully solution-processed Y:SnO₂ electron transport layers (ETLs) with mixed halide compositions for cost-effective and stable Si/perovskite, perovskite/CIGS and perovskite/perovskite tandem solar cells.
SnO$_2$ materials have become a promising electron transport layer (ETL) alternative to TiO$_2$ and ZnO in perovskite solar cells (PSCs), achieving power conversion efficiencies (PCEs) exceeding 25% in single-junction planar structures. As a wide bandgap n-type semiconductor, SnO$_2$ exhibits excellent optoelectronic properties, making it a superior ETL material for PSCs. It has been extensively utilized in conventional (n−i−p) PSC structures, where a thin SnO$_2$ film can be directly deposited onto conductive substrates using appropriate deposition methods.

The use of solution-processed SnO$_2$ as an ETL in p-i-n structured PSCs is less explored, primarily due to solvent incompatibility between the SnO$_2$ dispersion medium and the perovskite absorber layer. The selection of perovskite-compatible solvents is limited, excluding highly polar solvents like water typically used for SnO$_2$ dispersions. Additionally, converting the precursor to SnO$_2$ on the perovskite surface requires prolonged high-temperature annealing, which risks degrading the underlying perovskite layer.

In most p-i-n devices with a metal oxide (MO$_x$) ETL, the MO$_x$ is deposited onto an organic ETL, resulting in bilayer structures such as PCBM/ZnO, C60/SnO$_2$, and PCBM/SnO$_2$. This approach addresses the solvent incompatibility between the metal oxide and the perovskite. However, for direct MO$_x$ ETL deposition on the perovskite, pre-
synthesized MOₙ nanoparticles suitable for low-temperature processing and stable in a perovskite-compatible organic solvent are necessary.

This work describes the solution-phase deposition of a nonaqueous dispersion of SnO₂ nanoparticles directly onto a CH₃NH₃PbI₃ (MAPI) perovskite using a blade-coating technique in a p-i-n device architecture. The acetate-functionalized nanoparticles, SnO₂-A, were synthesized via a traditional aqueous reaction pathway, enabling the formulation of a stable dispersion in anhydrous ethanol. After depositing the ink on MAPI, the XRD patterns showed no observable damage to the perovskite thin film. The PL results confirmed electron transport from the perovskite layer, and the cross-sectional SEM revealed a smooth interface between the MAPI and SnO₂ films. The champion PSCs exhibited a PCE of 14.1% with an active area of 0.25 cm² and maintained 95.8% of this after 40 days.

Building on this, functionalized yttrium-doped tin (IV) oxide nanoparticles were developed that allow for direct deposition of fully solution-processed Y:SnO₂ ETLs on perovskite by a scalable blade coating method. At the optimum yttrium concentration of 2 mol %, the inverted (p-i-n) f-PSCS with Y:SnO₂ as an ETL exhibited improved performance, exceeding the champion PCE above 16.5% in a flexible plastic substrate. The improvement in PCE comes from increased V_{OC} and FF compared to pristine SnO₂-A devices. The improved device performance results from an enhancement of the charge extraction.

This work further investigated the compatibility of ligand-stabilized Y:SnO₂-A dispersion as an ETL with diverse perovskite composition in inverted f-PSCs. Remarkably, ligand-stabilized Y:SnO₂-A dispersion demonstrated good compatibility with various
perovskite compositions, including MAPI, MC, MA-free, and TC. Most notably, f-PSCs featuring TC perovskite as the photoactive layer achieved a peak efficiency of 20.41%, accompanied by a $V_{OC}$ of 1.17 V, $J_{SC}$ of 23.56 mA/cm$^2$, and FF of 74.13%. When employing MAPI, MC, and MA-free perovskites as the photoactive layers, the champion efficiencies reached 16.9%, 18.68%, and 17.71%, with average PCEs of 15.27 ± 1.13%, 16.63 ± 1.18%, and 16.13 ± 0.87% respectively.

These results are particularly noteworthy considering the fabrication method of blade-coating on PET-ITO substrates. This work establishes a technique to deposit a metal oxide nanoparticle dispersion directly on a perovskite thin film which has implications toward moving the technology toward high-throughput manufacturing such as roll-to-roll fabrication of perovskite modules. It is evident from these results that further work is needed to establish the optimal ink chemistry including doping, interfacial treatments, surfactants, and sintering aids. It is also necessary to study the post-deposition processing to reduce the time required to fully anneal the thin film.

The fully solution-processed Y:SnO$_2$-A is a promising ETL. This material possesses minimal cost, scalability, and manufacturing advantages over traditional organic ETLs that could improve the competitiveness of commercial perovskite solar modules. Given its cost-effectiveness and fully solution-processed nature, ligand-stabilized SnO$_2$ dispersion can be an attractive choice for silicon-perovskite tandem devices and a range of other optoelectronic applications. This work provides for the broader adoption of ligand stabilized SnO$_2$ nanoparticles as a promising ETL in inverted PSCs.
REFERENCES

1. BP *bp Statistical Review of World Energy* 2022; 2022.
7. Reinders, A. H.; Van Sark, W., 1.34-Product integrated photovoltaics. **2012**.


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EDUCATION

Ph.D. in Chemistry 2018-2024
University of Louisville, KY, USA
Mentors: Prof. Craig A. Grapperhaus and Dr. Thad Druffel
Research area:
- Synthesis, characterization, and functionalization of semiconducting tin (IV) oxide nanoparticles for photovoltaic applications
- Methods development to formulate nonaqueous dispersion of tin (IV) oxide nanoparticles to scale up electron transport layer in inverted perovskite solar cells
- Perovskite ink formulation for the large-area fabrication of perovskite solar cells under ambient condition
- Large-area fabrication of flexible perovskite solar cells on the PET-based substrate via blade and slot-die coating

MS in Chemistry 2016-2018
Middle Tennessee State University, TN, USA
Mentor: Dr. Charles C. Chusuei
Research area:
- Detection of uric acid using hydrothermal ZnO/MWCNT-COOH nanocomposite by electrochemical methods
- GC/MS analysis of indoor particulate matters and volatile organic compounds

Tri-Chandra Multiple College, Tribhuvan University, Kathmandu, Nepal
Mentor: Prof. Amar Prasad Yadav
Research area:
- Studied electrochemical behavior of Zn-Ni galvanized alloy employing potentiodynamic polarization at room temperature

WORK EXPERIENCES

SoFab Inks, LLC,  
Louisville, KY  
Co-Founder  
- Co-founded a startup specializing in manufacturing chemical inks for perovskite solar cell fabrication  
- Focused on fully solution process tin (IV) oxide ETL materials for inverted perovskite solar cells  
  **Responsibilities:**  
  - Method development  
  - Quality control  
  - Performance analysis

Internship at the National Renewable Energy Laboratory (NREL)  
Aug 2020- Dec 2020  
**Accomplishments:**  
- Successful deposition of fully solution processed SnO$_2$ on the top of the perovskite  
- Large-area fabrication of perovskite solar cells  
- Characterization and performance analysis of perovskite solar cells

Graduate Teaching Assistant  
University of Louisville, Department of Chemistry  
2018-Present

Graduate Teaching Assistant  
Middle Tennessee State University, Department of Chemistry  
2016-2018

AWARDS  
- American-Made Perovskite Startup Prize; US Department of Energy (as a group)  
  Aug 2022  
- Doctoral Dissertation Completion Award, College of Arts & Science UofL  
  Fall 2023

PATENTS AND PUBLICATIONS

**Patent:**  

**Publications:**  

**TECHNICAL SKILLS**

**Glove box system:**
▪ Train new users, exchange nitrogen dewars, catalyst regenerations, refill pump oil, replace air filters, and reinstall butyl gloves.

**Organic and inorganic Synthesis:**
▪ Synthesis of organic compounds and a wide range of Inorganic metal oxides, including tin and nickel oxides

**Thin-film fabrication:**
▪ Blade coating, slot-die coating, spin coating, and physical vapor deposition

**Intense pulse light:**
▪ Energy optimization for radiative annealing of perovskite precursors and metal oxides

**Material characterization:**
▪ Solar simulator: lamp replacement, calibration data acquisition, and analysis
▪ Powder X-ray Diffraction: Data acquisition and analysis
▪ AC Impedance Spectroscopy: Data acquisition, analysis, and fitting
▪ X-ray Photoelectron Spectroscopy: Data acquisition, analysis, and fitting
▪ Nuclear Magnetic Resonance Spectroscopy
▪ Scanning Electron Microscopy
▪ Raman Spectroscopy and Photo Luminescence Spectroscopy
- Gas Chromatography, High-Performance Liquid Chromatography, Mass Spectrometry, Infrared Spectroscopy, and UV-vis spectroscopy

**WORKSHOP**

- Attended 10th DOE/NREL Hands-On PV Experience (HOPE) workshop (virtual) July 6-15, 2021
- Attended "LaunchIt" - Production Innovation Bootcamp, University of Louisville Sept 15 to Nov 3, 2022

**CONFERENCE PRESENTATIONS**


References:
1. Prof. Craig A. Grapperhaus, Ph.D. supervisor, Chemistry Department, University of Louisville
2. Prof. Robert M. Buchanan, Ph.D. supervisor, Chemistry Department, University of Louisville
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