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Fully Printable Single Layer Halide Perovskite/Peo Composite Thin Film LEDs

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FULLY PRINTABLE – SINGLE LAYER HALIDE PEROVSKITE/PEO COMPOSITE THIN FILM LEDS

By

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This thesis is dedicated to my family and friends. Thank you for all your support along the way.
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ABSTRACT

Traditional light emitting diodes (LEDs) involve a complicated device structure with multiple layers stacked over one another. Such a complex, multilayered architecture restricts the application of diverse fabrication techniques. Earth-abundant organometal halide perovskites (Pero) have been well astounded for their appealing optoelectronic properties, low cost and solution processability which make them ideal candidates for large size photovoltaic and LED applications. The objective of this thesis work is to fabricate Pero LED with uniform surface morphology, eliminating the multilayers with the help of Pero/Polyethylene oxide (PEO) composite thin film. Because of the simplicity in device architecture, this novel approach has the potential to surpass all the conceivable troubles involved in the fabrication of Pero LEDs. Preliminary results show a working device achieved by spin coating a thin film of Pero/PEO composite on ITO/glass serving as a bottom electrode and with In/Ga as the top electrode. Furthermore, fully printable and flexible Pero LEDs were developed from this approach which can be scaled to large commercial roll to roll manufacturing.
CHAPTER 1

INTRODUCTION

With the advent of crystalline silicon solar cells, several new concepts have emerged in the field of photovoltaics each surpassing the former. Majority of the research concentration focusses on the active material which led to the development of new era solar light absorbers, including polycrystalline or amorphous thin films, semiconductor nanoparticles, organic and metal complex dyes and organic semiconductors.[1]

In recent years, a new class of solar cells based on mixed organic- inorganic halide perovskites have emerged and progressed on a rapid scale considering to have a potential to transcend the leading photovoltaic technologies. Despite the fact that iodide based perovskite solar cells had a modest efficiency of 3.8% in 2009 [2], their efficiencies have reached at an extreme rapid rate to near 20% [3] by 2015 through materials processing techniques and device engineering efforts. Perovskite materials are advantageous regarding low cost, availability and low temperature processability. The unique properties of perovskites such as charge carrier lifetime, high absorption coefficient, electron/hole mobility, longer diffusion lengths, and smaller exciton binding energy make them promising materials for photovoltaics.[4] A broad range of fabrication approaches are employed for the growth of perovskite films such as spin coating, thermal evaporation, solution deposition process, spray coating, doctor blade fabrication technique and die coating.[5]–[9] where the coating techniques can be scaled to large roll to roll manufacturing process which demonstrates that the perovskite materials offer a high degree of commercialization. Such ideal properties and fabrication straightforwardness legitimizes the substantial interest appeared in the advancement of perovskite based photovoltaic innovation. Moreover, their
application is not only restricted to solar cells but are also being investigated for other optoelectronic applications such as LEDs and lasers.[10], [11]

1.1 Structure of Perovskites

The term ‘perovskite’ usually refers to any material which has the chemical formula of ABX₃, where A and B are cations, X is the anion and also A being larger than B. For hybrid halide perovskites of our present interest, the larger cation A constitutes the organic part which is generally methylammonium (CH₃NH₃⁺) or ethylammonium (CH₃CH₂NH₃⁺). Lead (Pb²⁺) has been mostly utilized as metal cation B, but reports show the utilization of tin (Sn²⁺) and also a mixture of Sn/Pb.[12], [13] The anion X is a halogen (I, Cl, Br), where iodine (I) is dominantly being used for photovoltaic applications. Along with hybrid perovskites, all inorganic CsSnI₃ and CsPbI₃ perovskites are also investigated.[13] By altering the composition of its constituents, a range of perovskites are possible that are utilized as metallic conductors, catalysts, superconductors, capacitors and also for piezoelectric, ferroelectric related applications.[14] In the ideal case, the

![Figure 1: Cubic perovskite crystal structure](image-url)
structure of perovskites is cubic at high-temperature phase. However, less symmetric orthorhombic and tetragonal structures are also possible due to octahedral tilting which is related to the size of the cations A and B.[15], [16]

The prime advantage of perovskite materials is that they have consolidated properties of both organic and inorganic materials within a single material. They include significant properties offered by organic materials such as luminescent properties, potential for conductivity; low-cost, low-temperature processability, which makes them accessible for large-scale and flexible applications along with the properties offered by their inorganic counterparts which include high carrier density and mobility, thermal stability, magnetic and ferromagnetic transitions.[17], [18] It is noteworthy that perovskite materials are ambipolar in nature implying that they are a well-balanced electron and hole transporters, which made them vital candidates, but not restricted to the development of photovoltaic technology[19]

1.2 Perovskites as Light Emitters

According to Shockley-Queisser detailed balance limit calculations, efficient light absorbing materials used in solar cell applications should also be good light emitters.[20] Most of the solar cells work in reciprocity i.e they have good external luminescence yield as much as they are efficient in absorbing photon energy.[20] Perovskite materials can emit light over the entire visible spectrum and are color tunable which goes to show that they offer flexibility in material design to fix the emission to desired color region. In light of this, perovskite materials that have turned out to be efficient light harvesters also have the potential to be used in lighting applications such as light emitting diodes (LEDs), lasers and optical sensors.[10], [21] Perovskite based LEDs were reported in early 1990s by using a layered perovskite compound where electroluminescence was observed at liquid nitrogen temperatures.[22] In recent years perovskite LEDs that show
luminescence at room temperature have been reported by several groups. Perovskite based quantum dots have also been reported and are developing rapidly.[23] [24]
CHAPTER 2

PROBLEM STATEMENT AND RESEARCH OBJECTIVES

2.1 Problem Statement

Lighting technologies have emerged as alternatives for sunlight. Over two centuries, incandescent and fluorescent lamps have been widely utilized for lighting applications. Owing to the fact that the energy requirements and climatic changes have been increasing over the time, development of eco-friendly and energy efficient technology is the need of the hour. In light of this, a new class of solid state lighting have been developed which utilizes semiconductor devices like light emitting diodes, organic light-emitting diodes (OLEDs) and light emitting polymers for clean and efficient lighting. Research groups throughout the world are investigating alternative materials for light emission to develop a sustainable and environmental friendly lighting technologies. LED technology has been widespread and are being utilized in several lighting applications including displays, home and decorative lighting. But they do bring with them several disadvantages such as high cost, heat generation and color deterioration. Currently, OLEDs have gained a great deal of prominence and are to a great extent being utilized as displays for mobile phones, TVs and other electronic devices. OLEDs are efficient, flexible, thin, transparent, have low power consumption and high brightness which make them superior over the conventional lighting technologies. However, their use for lighting applications is still at stake as they are expensive than the traditional lighting luminaries. High price factor coupled with limited performance makes OLEDs currently not viable for lighting applications.

Solid state lighting technologies including OLEDs employ a complex multilayer structure which hinders large scale roll-to-roll production and making the systems utilized for their manufacture imprecise. There is a hope for a sustainable and energy efficient technology that has
a potential to surpass the drawbacks currently present in this filed revolutionizing the world of solid state lighting. Perovskite materials with exceptional attributes pose as viable candidates for light emitting applications to overcome the drawbacks present in the lighting technology. The unprecedented development of the perovskite materials as light harvesters within a short span of time have stunned the photovoltaic community. This validates the hope for developing commercially available, efficient perovskite based lighting technology which can change the shape of the modern world lighting.

2.2 Research Objective

This research work aims to innovate a LED technology based on organometal halide perovskites. The typical characteristic of this technology are:

1. Single layer device architecture
2. Cost effective
3. Simple scalable fabrication technique
4. Applicable onto different substrates

As discussed earlier, perovskite materials have emerged as wonder materials gaining a lot of research interest throughout the world. As of late, several reports based on perovskite light emitters show that they have the potential to replace the dominant LED and OLED technology. Researchers hope that within few years it is possible to overcome the efficiency limitations pertaining to perovskite LEDs and make this a mainstream technology. Comparable to other LED technologies, the main drawback of perovskite based LEDs is the utilization of a multi-layer device architecture which significantly increases the cost and limits large scale manufacturing. This work focusses on replacing the multi-layer structure with a simple single light-emitting perovskite layer sandwiched
between two electrodes. This method would eventually eradicate the involvement of complex fabrication methods consequently reducing the cost and making mass production of perovskite LEDs possible. To fabricate a uniform light emitting layer with perovskite material alone would be requiring several complex surface modification treatments or device engineering efforts. As such, it would include unpredictability in the process and subsequently hinders cost effective mass production. In order to overcome such complexity and to produce a continuous and uniform light emitting layer, an ionic conducting polymer is planned to be incorporated into the perovskite material to form a uniform composite thin film.

The main objectives of this work are:

1. To innovate composite thin films utilizing halide perovskites and ionic conducting polymers to form single layer LEDs
2. To develop a fabrication technique to fully print the single layer perovskite LEDs that can be scaled to large roll to roll manufacturing
CHAPTER 3

LITERATURE REVIEW

The evolution of perovskite materials was extensively studied and numerous publications have been reported on their use as light harvesters. Large number of reports focus on various methods employed for perovskite material growth, deposition and device engineering techniques. However, in recent times perovskite materials are being investigated as light emitters due to the fact that they exhibit good photo and electroluminescence properties. Here, a small portion of such findings will be reviewed giving some insights into the progress of perovskites as LEDs.

Group led by M. Era were first to demonstrate Pero LEDs. They have fabricated an electroluminescent device by combining a layered perovskite compound \((\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4\) and an oxadiazole derivative (OXD7), which aided the electron transport. The perovskite layer was prepared by spin coating on indium-tin-oxide (ITO) anode. The electron transport layer and the top cathode MgAg, were sequentially vacuum deposited on the perovskite film. When a 24 V bias was applied, the device had an El intensity of about 10,000 cd m\(^{-2}\) at a current density of 2 A cm\(^{-2}\). The injected electrons from the OXD7 layer efficiently recombine with the confined holes in the perovskite layer thereby emitting light. But the El was observed only at liquid nitrogen temperature. As the temperature was increased from below 200 K to room temperature there was a significant drop in the EL.[22]

Toshiaki et.al reported heterostructure electroluminescent devices utilizing PbI based perovskite compound and an organic ammonium dielectric layer that were alternatively piled up. They have reported that such perovskite compounds which contained cyclohexenylethylamine or phenylybutylamine as an organic ammonium layers exhibited good exciton emission. Single crystals of PhE-PbI\(_4\) and CHE-PbI\(_4\) were prepared initially, and were then spin coated onto the
substrate by dissolving them in conventional solvents and the formation of the layered perovskite structure was validate through absorption spectra and X-ray diffraction measurements. The device architecture is as follows: ITO/Layered perovskite emissive layer/OXD7 electron transporting layer/MgAg, where the OXD7 and MgAg layers were vacuum-deposited on the spin coated layers. The layered device, had a luminance of 4000 cd m\(^{-2}\) with an external quantum efficiency (EQE) of 2.8\% at an applied voltage of 24 V at 110 K.[25]

To overcome the problem of electroluminescence occurring only at liquid nitrogen temperature, Konstantinos et.al developed organic-inorganic light emitting devices (OILED) by inserting a complex dye molecule (AEQT)PbCl\(_4\) into the layered perovskite structure. The dye molecule was carefully chosen to be able to fit in the perovskite structure. The dye incorporated perovskite film was deposited by using single source thermal ablation method reported elsewhere. To enhance the structure, the as prepared films were annealed at 115\°C for 5 min. Fig shows the multi-layered OILED device structure. To avoid shorting, a layer of silicon dioxide (SiO\(_2\)) was deposited using e-beam evaporation, followed by deposition of (AEQT)PbCl\(_4\) and subsequent vacuum deposition of electron transporting layer and the top electrode under inert environment.

Figure 2: Cross section of the OILED device [26]
The device performed at a low turn on voltage of 5.5 V which did not vary with the thickness of the film. It had a maximum efficiency of 0.1 lm/W at 8 V and 0.24 mA and a power conversion efficiency of 0.11% was reported.[26]

As of late, verging on over a decade the first organometal halide perovskite based light emitting diodes operating at room temperature were reported by Tan et.al. This group has incorporated the three-dimensional hybrid metal halide perovskites to achieve electroluminescence in the near infrared, green and red regions by altering the halide composition. The infrared (IR) device was fabricated by incorporating a thin layer of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ and green-light emitting device was achieved with CH$_3$NH$_3$PbBr$_3$, both sandwiched between electron transporting and hole injecting layers. The device architecture of the IR device is as follows:

![Device structure of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ and green PeLED][27]

ITO/TiO$_2$/CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$/F8/MoO$_3$/Ag. The device showed an infrared radiance of 13.2 Wsr-1m$^{-2}$ at a current density of 363 mAc$^{-2}$ with an EQE of 0.76% and a turn on voltage of 1.5 V. The green light emitting device had a device structure of: ITO/PEDOT:PSS/CH$_3$NH$_3$PbBr$_3$/F8/Ca/Ag. The luminance of this device was reported to be 364 cd m$^{-2}$ at a current density of 123 mAc$^{-2}$ with an EQE of 0.1% and a turn on voltage of 3.3 V. Red perovskite LEDs which share the same device architecture were also demonstrated by using a CH$_3$NH$_3$PbBr$_2$Imixed halide perovskite. Several fabrication methods including atomic layer
deposition for TiO2 layer, spin coating for the perovskite, PEDOT: PSS and F8 layers, vacuum thermal evaporation for MoO3, Ca and Ag layers involving a complex fabrication process. This report demonstrates that perovskite materials have the potential in lighting and display applications. [27]

The function of the F8 layer is to act as a spacer and prevent exciton quenching. But on the downside F8 was unstable in air and also causes color impurity in visible pero LEDs due to the formation of polyflourene. The fluorine-based, charge-blocking F8 layer was replaced with zinc.
oxide (ZnO) by a group led by Hoye. ZnO deposited by spray pyrolysis requires high temperature >350°C which is detrimental for it to be deposited onto perovskite material.

To overcome such limitations, spatial atmospheric atomic layer-deposition (SAALD) was employed for depositing the ZnO directly onto green light emitting methylammonium lead bromide perovskite at a relatively lower temperature of 60°C. By incorporating magnesium Mg into ZnO, the turn on voltage was reduced to 2 V and also the emission was pure and not contaminated by the electron injector. The perovskite LEDs reported had a structure as follows: ITO/PEDOT:PSS/CH$_3$NH$_3$PbBr$_3$/ZnO/Ca/Ag that showed electroluminescence at room temperature. The low temperature deposition employed reduced the pore size of the perovskite material, thus enhancing the performance.[28]

Kim et.al fabricated perovskite LEDs by using methylammonium lead bromide as the active light emitting layer with a self-organized buffer composed of PEDOT:PSS and a perfluorinated polymeric acid, tetrafluoroethylene-perfluoro-3,6-dioxa-4-methyl-7-octene-sulfonic acid copolymer (PFI), which acts as the hole injecting layer(HIL). The utilization of a high work function buffer-HIL was to overcome the high hole-injection barrier caused by the

![Figure 6: Structure and cross-sectional SEM images of CH$_3$NH$_3$PbBr$_3$ LED [4]](image-url)
conventional PEDOT: PSS polymer thereby reducing the luminescence quenching that occurs at HIL/emitting layer. This was achieved by the gradual increase in the work function from the bottom to top surface and also the enrichment of PFI on the top surface of the buffer-HIL. Multicolored devices were reported by substituting the bromide ions with chloride and iodide ions (CH$_3$NH$_3$PbCl$_x$Br$_y$I$_3$–x–y). This group was also the first to demonstrate flexible perovskite LEDs on a plastic substrate. The fabrication of the devices involved spin coating the buffer-HIL and perovskite layers followed by thermal deposition of the other layers in a high vacuum chamber. The device structure of the fabricated devices is as follows: ITO/Buffer-HIL/CH$_3$NH$_3$PbBr$_3$/TPBI/LiF/Al and PET/ITO/Buffer-HIL/CH$_3$NH$_3$PbBr$_3$/TPBI/LiF/Al for the flexible devices. The green light emitting device employing the buffer-HIL had a current efficiency of 0.577 cdA$^{-1}$, an EQE of 0.125% and a maximum luminance of 417 cdm$^{-2}$ which was a tremendous improvement over the devices that employed PEDOT: PSS as HIL.[4]

Li and coworkers fabricated perovskite LEDs by embedding perovskite nanocrystals in a thin matrix of dielectric polyimide precursor (PIP) forming a perovskite nanocrystal-PIP polymer
composite. The transparent and electrically insulating PIP helps in the formation of pin hole free thin film, which serves as a charge–blocking layer and also provides material stability. The perovskite nanocrystals were uniformly distributed in the thin-film matrix of PIP by in situ formation, which is achieved by blending perovskite precursor solution and commercially available aromatic polyimide precursor. The devices had an architecture as follows: ITO/PEDOT: PSS/Perovskite−PIP/F8/Ca/Ag and the device layers were deposited by spin coating and vacuum deposition techniques. Different weight ratios were employed while blending the perovskite and polymer solutions and it was observed that the size and area occupied by the perovskite crystals

**Figure 8: Structure of CH$_3$NH$_3$PbBr$_3$ PeLED and image of light emission [29]**

![Figure 8: Structure of CH$_3$NH$_3$PbBr$_3$ PeLED and image of light emission [29]](image)

**Figure 9: SEM images of (a) perovskite only, (b) 1/10 PIP/perovskite and (c) 1/2 PIP/perovskite on PEDOT: PSS coated silicon [29]**

![Figure 9: SEM images of (a) perovskite only, (b) 1/10 PIP/perovskite and (c) 1/2 PIP/perovskite on PEDOT: PSS coated silicon [29]](image)
decreased with increase in PIP-perovskite ratio. The best performing devices had a PIP-perovskite ratio between 1:2 and 1:1. The polymer also helped in clean color emission from the devices was also effectively preventing shorting between the F8 and PEDOT: PSS. The best performing devices had an EQE of 1.2%.[29]

Yu et.al demonstrated efficient optoelectronic devices through morphological control of the perovskite layer and surface treatment between the TiO$_2$ and perovskite layers. This treatment method was carried on conventional perovskite LEDs with planar structure. Ethanolamine (EA), an amine base solvent treatment on the TiO$_2$ layers increased the electron transport and also reduced defects on TiO$_2$. Toluene drop casting based CH$_3$NH$_3$PbBr$_3$ prepared from GBL+DMSO solvent, had better crystallinity and denser films were attained with very few pin holes whereas

Figure 10: SEM images and emission images from PeLEDs without EA treatment and with EA treatment respectively [30]
the one containing DMF showed incomplete surface coverage. However, it was reported that EL emissions of the devices were unstable and time-dependent EL as a function of morphology should further be investigated. The performance of EA treated LEDs with a device configuration of: ITO/c-TiO$_2$ /EA/CH$_3$NH$_3$PbBr$_3$/SPB-02T/MoO$_3$/Au increased remarkably when compared to those which were not treated by EA. The devices exhibited a maximum luminance of 544.65 cd m$^{-2}$, a luminous efficiency of 0.22cd A$^{-1}$ at 5.8 V and showed an EQE of 0.051%. The fabricated devices had a large area of 0.9 cm$^2$, showing the possibilities for perovskite LEDs to be employed for large panel light emitting devices.[30]

The first ever light-emitting electrochemical cells (LEC) based on perovskite nanoparticles were reported by Ayguler et.al. They have exploited the advantages of LECs such as ease of fabrication, low operating voltages, air stable layers, and a very simple device architecture to fabricate perovskite LECs. They have also reported that by replacing the organic cation group to formamidinium (FA), the tuning of photophysical features of this material is possible. The complex fabrication process involved the preparation of precursors, methylammonium bromide and formamidinium bromide following the procedures reported elsewhere. MAPbBr$_3$ nanoparticles and FAPbBr$_3$ nanoparticles were then synthesized from the as prepared precursors. The devices

Figure 11: Illustration of the device architecture employed [31]
were fabricated by printing PEDOT: PSS using a doctor blade. Then an electrolyte matrix containing LiCF$_3$SO$_3$ and TMPE was added to the perovskite nanoparticle suspension followed by thin film deposition of electrolyte matrix and perovskite nanoparticles using spray-pyrolysis with roughness less than 5%. The top electrode, aluminum was then thermally evaporated in an inert atmosphere. The addition of electrolyte helped in reducing injection voltage and also attain stable EL features. The device structure can be postulated as follows: ITO/PEDOT: PSS /FAPbBr$_3$ NP-electrolyte matrix /Al. The devices with MAPbBr$_3$ nanoparticles had a maximum luminance of 1.8 cd/m$^2$ and maximum efficiency value of 0.013 cdA$^{-1}$ while those incorporating FAPbBr$_3$ nanoparticles had a maximum luminance of 0.8cdm$^{-2}$ with maximum efficiency of 0.0005 cdA$^{-1}$. The devices showed a yellowish green luminance and the performance of the devices were not altered much even after storing them for two months in ambient conditions which can be attributed to the addition of the electrolyte matrix.[31]

Wang et.al reported an interfacial engineering technique to fabricate efficient near-infrared (NIR) and green light emitting perovskite LEDs. Multifunctional polyethyleneimine (PEI) was introduced between the emissive perovskite layer and electron transporting layer. The utilization
of the interfacial layer provided a hydrophilic surface for smooth pin-hole free perovskite thin films and also a low-work function cathode. High efficiency, CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$– based NIR and CH$_3$NH$_3$PbBr$_3$– based green light emitting perovskite LEDs were demonstrated using this technique. The multilayered device structure is composed of ITO/PEI-modified zinc oxide (ZnO)/CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$/poly (9,9 dioctyl-fluorene-co-N-(4-butylphenyl) diphenylamine) (TFB)/molybdenum oxide/ Au, where TFB served as the hole transporting layer. All the layers were solution processed by spin coating except for the top electrode layer (gold) for which thermal evaporation process was employed. The best performing NIR devices had an EQE of 3.5% at 2.2 V with a current density value of 160 ma cm$^{-2}$ and a high radiance of 28W sr$^{-1}$ m$^{-2}$ with a fair reproducibility. Such a performance can be attributed to the incorporation of PEI layer on top of the ZnO layer which helped in attaining crystalline, uniform pin-hole free perovskite thin films thereby reducing the shunting paths. The CH$_3$NH$_3$PbBr$_3$ based green light emitting devices had an EQE of 0.8% with a maximum luminance of 20000 cdm$^{-2}$ at a low voltage of 2.8 V. The inferior EQE of green devices when compared to NIR devices is due to the incomplete surface coverage of the CH$_3$NH$_3$PbBr$_3$ based LEDs on PEI treated ZnO layer.

Figure 13: Images showing contact angles of water on bare ZnO film and PEI treated ZnO film [32]
Recently, Cho et.al demonstrated bromide based perovskite LEDs with a very high current efficiency. The performance of the devices was higher than that of all the previously reported perovskite devices. This group has incorporated stoichiometric modifications and nanograin engineering to limit the exciton quenching by reducing the exciton diffusion lengths and to enhance the luminescent properties. They have employed nanocrystal pinning and altered the proportion of MABr in order to enhance the MAPbBr$_3$ emissive layer. In order to prevent excess Pb atoms in the MAPbBr$_3$, the molar proportion of MaPbBr was increased so as to improve the luminance by reducing the non-radioactive decay rate. An additive form of chloroform was used

Figure 14: Schematics of NCP process during spin-coating to fabricate MAPbBr$_3$ nanograin films [33]

Figure 15: SEM images of MAPbBr$_3$ without NCP and with A-NCP; Photographs of normal and large area (2cm by 2cm pixel) PeLED [33]
for the nanocrystal pinning process to reduce the grain size. With the utilization of a self-organized conducting polymer in the multi-layered device structure, this group has demonstrated flexible devices and also the first large area LED of 2cm x 2cm. The best performing devices had a current efficiency of 42.9 cdA$^{-1}$ with an EQE of 8.53%.[33]

A group led by Sadhanala has reported a multi-layer perovskite LED by employing a conjugated polymer. Emission was observed from the interface of the perovskite-luminescent polymer and across the spectrum from near-infrared to visible regions. They have employed a mixed halide perovskite containing both chloride and iodide (CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$). They have demonstrated and compared devices utilizing Spiro-OMETAD and MEH-PPV polymer as hole injecting layers. The performance of the devices was enhanced by replacing a non- emissive semiconductor (Spiro-OMETAD) with a luminescent polymer (MEH-PPV).[34]

Qin et al. demonstrated a green light emitting bromide perovskite LED. High performing devices were fabricated by optimizing the thickness and improving the surface morphology of the light emitting layer. The device structure is as follows: ITO/ PEDOT: PSS /CH$_3$NH$_3$PbBr$_3$/1,3,5-
tri[(3-pyridyl)-phen-3-yl]benzene(TmPyPB)/LiF/Al, where TmPyPB and PEDOT:PSS serves as electron and hole transporting layers respectively. With an increase in the thickness of the perovskite emissive layer, the luminance increased thus improving the device performance. Upon increasing from 20nm, the luminance substantially increased and then decreased after 80 nm showing that the optimized thickness should be 80nm. The devices exhibited a power efficiency of 0.1lm W\(^{-1}\) and an EQE of 0.1%.\[35\]

Xiao et.al demonstrated an interesting dynamic poling phenomenon in perovskite materials. They have reported a switchable photovoltaic effect. This group has fabricated solar

\[\text{Figure 17: Luminance vs. the thickness of CH}_3\text{NH}_3\text{PbBr}_3\text{ layer and green electroluminescence of the CH}_3\text{NH}_3\text{PbBr}_3\text{ LED [35]}\]

\[\text{Figure 18: Schematics of ion drift in perovskite during positive and negative poling, respectively, showing that accumulated ions in the perovskite near the electrodes [36]}\]
cells with a vertical structure of ITO/ PEDOT: PSS /Perovskite/Au and also with lateral structure and demonstrated that most of the excitons dissociated into free holes and electrons inside the perovskite layer without any additional hole and electron transporting layers and the free charges were efficiently collected at the electrodes even at different diode directions. The negatively and positively charged vacancies present in the perovskite material resulted in p-type and n-type doping respectively. Upon the application of a bias, the accumulation of charges took place forming a p-i-n homojunction.[36]

Initially, it was believed that moisture has detrimental effects on methylammonium halide perovskite material in terms of damaging the crystallinity of the material. But of late, there were several reports demonstrating that the atmospheric humidity actually helped in improving the quality and efficiency of the perovskite films. Bass et.al in their work compared the properties and structures of the air exposed and non-air exposed methylammonium lead iodide and methylammonium lead bromide perovskites. It was observed that moisture triggered crystallization in these materials and also showed long luminescence lifetime when exposed or

Figure 19: Snapshots of the in situ recorded video, showing changed perovskite material close to the anode side during the poling [36]
prepared in air. But more study is required to clearly understand the principle behind this improvement.[37]

You et.al reported a moisture assisted growth process for solar cell fabrication where the precursor film was annealed in a humid environment. The SEM images show that the morphology of the films processed by exposing to air was superior to those that were either prepared in oxygen or nitrogen environment. Also as the amount of humidity increased the morphology of the film was enhanced relatively. Though beneficial, the amount of moisture should be taken care of as at relatively higher amounts (>80%), decomposition of the perovskite material takes place. The air exposed films also showed improvement in properties such as enhanced fill factor and longer photo luminescence lifetimes. Solar cells fabricated by this method had a maximum power conversion efficiency of 17.1%. [38]

The role of moisture in film formation and the performance of methylammonium lead halide perovskites was reported by Eperon and his group. They have demonstrated the effects of post and pre-treatments of moisture on CH$_3$H$_3$PbI$_3$ films. The exposure of moisture proved to be

Figure 20: SEM images of the perovskite film precursor films annealed under different conditions - in nitrogen, ambient air and in oxygen environment respectively [38]
advantageous in terms of improved film morphology along with photovoltaic properties such as higher open-circuit voltage, better and longer photoluminescence luminescence as compared to those processed in a dry atmosphere. The moisture helps in faster film formation and also in removing excess methylammoinum from the lattice by making it more soluble which eventually helped in removing defects from the film surface.[39]

### 3.1 Summary

Even though devices with good performance were reported in the literature, the main drawback of all the demonstrated devices is that they employ a multi-layer device architecture, analogous to OLEDs which involves complex fabrication techniques. Several surface engineering methods for different layers were employed to enhance the performance of the devices. This demonstrates that the idea of fabricating a single layer perovskite light emitting diode remains unexplored.

Table 1 outlines the performance of the perovskite LED devices reported. It is noteworthy that all the reported devices has utilized a multilayer device architecture which involves complex fabrication techniques and furthermore builds the cost. Such a mutli-layer structure additionally complicates the commercial manufacturing of such LEDs using roll to roll printing processes. Along these lines, the reported methods of fabrication are not feasible for real world application until further simplification of the device structure.
Table 1: Summary of reported perovskite based LEDs

<table>
<thead>
<tr>
<th>Report</th>
<th>Emission Layer</th>
<th>Maximum CE (cd A⁻¹)</th>
<th>Maximum EQE (%)</th>
<th>Device Architecture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tan et.al[27]</td>
<td>MAPbBr3</td>
<td>0.3</td>
<td>0.1</td>
<td>multi-layer</td>
</tr>
<tr>
<td>Kim et.al[4]</td>
<td>MAPbBr3</td>
<td>0.577</td>
<td>0.125</td>
<td>multi-layer</td>
</tr>
<tr>
<td>Hoye et.al[28]</td>
<td>MAPbBr3</td>
<td>~0.27</td>
<td>not reported</td>
<td>multi-layer</td>
</tr>
<tr>
<td>Kumawat et.al[40]</td>
<td>MAPbBr3, MAPbI3-xBr3</td>
<td>~1.8 x 10⁻², ~2.8 x 10⁻⁴</td>
<td>~6.5 x 10⁻³, ~1.1 x 10⁻³</td>
<td>multi-layer</td>
</tr>
<tr>
<td>Wang et.al[32]</td>
<td>MAPbBr3</td>
<td>Not reported</td>
<td>~0.8</td>
<td>multi-layer</td>
</tr>
<tr>
<td>Sadhanala et.al[34]</td>
<td>MAPbI3-xClx: MEH-PPV</td>
<td>Not reported</td>
<td>~0.005</td>
<td>multi-layer</td>
</tr>
<tr>
<td>Qin et.al[35]</td>
<td>MAPbBr3</td>
<td>Not reported</td>
<td>~0.1</td>
<td>multi-layer</td>
</tr>
<tr>
<td>Yu et.al[30]</td>
<td>MaPbBr3</td>
<td>0.22</td>
<td>0.051</td>
<td>multi-layer</td>
</tr>
<tr>
<td>Kumawat et.al[41]</td>
<td>MAPbBr₃₋ₓClₓ</td>
<td>~9 x 10⁻³ (green), 3.5 x 10⁻⁴ (blue)</td>
<td>~3 x 10⁻⁴ (blue)</td>
<td>multi-layer</td>
</tr>
<tr>
<td>Cho et.al[33]</td>
<td>MAPbBr3</td>
<td>42.9</td>
<td>8.53</td>
<td>multi-layer</td>
</tr>
</tbody>
</table>
CHAPTER 4

SINGLE LAYER PEROVSKITE LED

All the reported perovskite based LEDs utilizes a multi-layer device architecture with several layers stacked onto each other. Most of the perovskite based LED devices include a thin hole injection layer (HIL) adjacent to the anode which aides efficient hole injection into the active layer. An active light emitting layer of perovskite and an electron injecting layer (EIL) is placed next to the cathode to facilitate the injection of electrons. Apart from hole injection and electron injection layers, several different layers are incorporated into the device architecture as well. The layers employed would help in efficient charge transportation by lowering the energy barriers and increasing the electroluminescence efficiency. However, the role and importance of HIL and EIL layers in Pero LEDs has not yet been systematically studied. Each layer might require different fabrication technique thus making the process complex. Also, increase in the complexity of fabrication, increases the cost. Due to this, one simple technique cannot be employed for the fabrication of the several layers involved. This hinders the commercialization of such LEDs where

Figure 21: Traditional multilayer device structure vs proposed single layer LED structure
simplicity in fabrication and cost are the driving factors. As described in the literature review the self-poling phenomenon reported by Xiao et al indicated that the Pero material could be polarized under external electrical field to form a p-i-n homojunction. In this regard, efficient LEDs may be achieved simply by using a single-layer Pero thin film sandwiched between two opposite electrodes without using any HIL or EIL. This eradicates the complexity involved in device fabrication and paves the way for fabricating the perovskite LEDs using commercially available roll-to-roll printing techniques.

4.1 Perovskite/Peo Composite Thin Films

As mentioned earlier the self-poling phenomenon observed in the perovskite materials forms the motivation to innovate a method of fabricating LED devices with a single light emitting layer. To obtain an efficient LED, one of the most important factor is the surface morphology of the emitting layer. Several processing and deposition methods and solvent engineering techniques have been proposed to attain uniform perovskite thin films.\textsuperscript{[42]}–\textsuperscript{[48]} In this work, composite thin films containing ionic conducting polymer, polyethylene oxide and perovskite are utilized to achieve a uniform pin-hole free film of the emitting layer. The use of PEO as an ionic conductor is prominent in fabrication of polymer electrolytes for lithium batteries.\textsuperscript{[49]} High molecular weight PEO has the ability to dissolve a wide range of salts which makes it an efficient host polymer aiding the ion transportation.\textsuperscript{[50]} The rubbery like properties of the PEO at room temperature helps in attaining uniform and smooth films while preserving the ionic conductivity within the perovskite/polymer composite thin film. To validate the performance of PEO other polymers such as polyvinylidene fluoride (PVDF) and polystyrene (PS) are used in place of PEO in the composite. Methylammonium lead halides and their mixed halide forms have been intensively investigated for solar cell and LED applications. In this work, methylammonium lead bromide (\textit{CH}_3\textit{NH}_3\textit{PbBr}_3)
is utilized in the composite as perovskite alongside PEO. CH$_3$NH$_3$PbBr$_3$ is chosen as it has more air stability at room temperature than methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$). This is due to the fact that at room temperature, CH$_3$NH$_3$PbBr$_3$ has a more stable cubic phase than CH$_3$NH$_3$PbI$_3$, which has a tetragonal phase.[51] It was also reported that CH$_3$NH$_3$PbBr$_3$ was more resistant to humidity than CH$_3$NH$_3$PbI$_3$ which decomposed over 55% relative humidity.[4]

4.2 Fabrication Process

The composite thin films containing perovskite and PEO were solution processed by using a one-step spin coating method. Green light emitting LEDs can be achieved with methylammonium lead bromide perovskites. For the perovskite precursors, methylammonium bromide (MABr) and lead bromide (PbBr) were mixed and dissolved in anhydrous dimethylformamide (DMF) solvent. PbBr and MABr were taken in a molar ratio of 1:1.5. It is noteworthy that excess MABr is advantageous in terms of limiting the presence of metallic lead atoms in the perovskite which causes a significant drop in the efficiency of the LED devices. This efficiency drop can be attributed to the fact that lead atoms increase the non-radiative decay rate while decreasing the radiative decay rate.[33] [52], [53]

The following illustration demonstrates the fabrication process.

*Figure 22: Schematic illustration of single layer perovskite LED fabrication process*
The detailed description of the fabrication process is described below:

1. For perovskite precursor solution, MABr and PbBr are weighed according to the desired molar ratio (1.5:1) and added into a glass vial.

2. Anhydrous DMF is added into the mixture to give a concentration of $\sim 500\text{mg mL}^{-1}$ and the solution is stirred at 70$^\circ$C for 30 minutes.

3. PEO with average molecular weight of $\sim 600,000$ is dissolved in anhydrous DMF with concentration of $16\text{mg mL}^{-1}$ and is stirred at 70$^\circ$C for 30 minutes.

4. The perovskite/PEO composite solution is prepared by mixing the two solutions in desired concentration. Here, the concentration refers to the relative weight ratio of PEO to the total weight of the perovskite precursor.

5. The composite solution is stirred without heating for 30 minutes.

6. Indium tin oxide (ITO) /glass substrates were cleaned with soap water and subsequently sonicated in acetone, isopropyl alcohol and distilled water for 15 minutes each and were dried with nitrogen.

7. The cleaned substrates were treated with oxygen plasma at 100 W for 5 minutes.

8. 30ul of the perovskite/PEO composite solution was dropped onto the substrates and was spun-coat at 2000rpm for 1 minute and annealed at 80$^\circ$C for 3 minutes.

9. The solution preparation, fabrication process were carried out inside a nitrogen filled glove box with oxygen and moisture levels maintained at $\sim 1\text{ppm}$.

10. ITO on glass acts as the bottom electrode for the LED device and for the top electrode indium-gallium eutectic is used.
4.3 Composite Thin Film Characterization

4.3.1 Scanning Electron Microscopy (SEM)

The surface morphology of the perovskite/Peo composite thin films was characterized by using scanning electron microscope (SEM). The SEM images of the composite thin films with different PEO concentrations are shown in the figure below.

![Figure 23: Top view SEM images of perovskite composite films with different concentration of PEO [54]](image-url)
The trend in the morphology of the composite films can be seen in the above SEM images. It can be noted that with perovskite only film without any addition of PEO, large crystals with 3-5 \( \mu \text{m} \) range are formed. Such crystals connected with each other forming large sized islands with only 50\% of overall surface coverage on the substrate. Such morphology is never suitable for the LED devices as the discontinuous layer cannot completely isolate the top and bottom electrodes thereby leading to short-circuited devices. In order to overcome the non-uniformity of the film, PEO was incorporated into the bromide perovskite. As seen from the figure 23, there is a significant change in the surface morphology of the film with addition of PEO. Addition of 5\% PEO into the

Figure 24: Top and cross-sectional SEM images of perovskite composite films with different concentration of PEO [54]
perovskite solution made a large improvement in the surface coverage (>80%) with a decrease in crystal size to about 1 μm. This demonstrates that the incorporation of PEO into the perovskite had actually helped in the improvement of the surface morphology. As the concentration of PEO was increased to 15% and 25%, the crystal size was further reduced to ~100 nm range with surface coverage more than 95%. At 50% PEO, there is further enhancement in the surface of the composite thin film. No noticeable crystals can be observed in the SEM showing that the crystals were well embedded within the composite. At 75% PEO concentration, a very smooth continuous film with no pin-holes can observed. There is no significant height variations in the film which goes to show that the film became much smoother than the composite film with 50% PEO. With further increase in the concentration of PEO to 100%, micrometer sized particles can be observed on the surface. This is the excess PEO which precipitates out when the threshold is reached. Figure 23 gives the cross-section view of the composite thin films. The cross-section SEM images validate the top view observations. With no PEO, a discontinuous film with large separation between the perovskite crystals can be observed. The size of the perovskite crystals is also prominent at this stage. At 100% PEO concentration, the crystal size drastically reduced with fine dispersion within the composite leading to a continuous film. The composite films had a thickness of about 240 nm.

### 4.3.2 Xrd Analysis

The composite thin films were further investigated using X-ray diffraction (XRD) for gaining more insights into the crystallinity of the films. A θ-2θ scans were performed on the perovskite composite films with varying PEO concentration. The sharp peak at ~25° corresponds to Mylar sheet which was utilized to protect the films from degradation during the XRD measurements. The peaks related to bromide perovskite were indexed by referring to reported literature.[54]–[56] The intensities of the diffraction peaks decreased with increase in the PEO
concentration due to the fact that the amount of the perovskite decreases in the composite. The peak at 19° corresponds to PEO and it becomes more significant with increase in the concentration.

### 4.3.3 Photoluminescence and Absorption Spectra

Photoluminescence (PL) spectra and absorption spectra were collected to understand the optical properties of the composite thin films. Bromide perovskite has a direct band gap of 2.3 eV.
and as such a sharp transition which corresponds to bromide perovskite could be seen at around 530 nm. The intensity of the PL peak is highest at 532 nm. The intensity of the PL spectra decreased with increase in PEO composition, however the shape and position of the peaks remained the same.

All the characterization measurements show that the bromide perovskite was well crystallized within the composite maintaining the structural and optical properties.

4.4 IVL Characterization

The performance of the LED devices are evaluated by current density-voltage and luminance-voltage characteristics. The turn on voltage, maximum brightness and the current efficiency of the devices can be obtained from IVL measurements. All the measurements were carried out by using a calibrated silicon photodiode and a Keithley 2400 source meter. The inset in figure () shows an actual working device with 75% PEO concentration. It can be noted that the emission was uniform which attributes to the uniform and continuous film surface as observed in the SEM images. The bottom electrode, ITO acts as the anode and the top electrode, In-Ga serves as the cathode. The working area of the device is approximately 3mm. For the IVL measurements, devices with 50%, 75% and 100% PEO concentration were considered. The turn on voltage, defined at 1 cdm$^{-2}$ luminance for the 50%, 75% and 100% PEO concentration devices were found out to be 2.8V, 2.9V and 3.1V respectively. Such values for the turn on voltage were on par with the values in the reported literature which employed a multi-layer device architecture.[4], [27], [28], [35], [57], [58]. The devices were effective in charge injection and transportation without the utilization of any additional EIL or HIL as demonstrated by the low turn on voltage. Devices with 75% PEO showed better luminance intensity when compared to those containing 50% and 100% PEO. The 75% PEO devices had a maximum luminance intensity of 4064 cdm$^{-2}$ at 5.5 V
bias while for the devices with 50% and 100% PEO, the values were at 133 cd m\(^{-2}\) and 113 cd m\(^{-2}\) respectively.

This goes to show that an optimal amount of PEO (75%) to form a uniform film is desirable to obtain devices with good performance. Incorporating additional amount of PEO after the formation of continuous film would only precipitate out the excess PEO thereby limiting the device performance. The current efficiency of the 50%, 75% and 100% PEO devices were 0.24 cd A\(^{-1}\), 0.38 cd A\(^{-1}\) and 0.74 cd A\(^{-1}\) respectively.

The external quantum efficiency, which is the ratio of number photons emitted from the device to the number of excitons passing through the device was calculated by assuming a
Lambertian emission profile. The external quantum efficiencies were calculated using the formulae as below:

The total number of photons:

$$n_{\text{photon}} = \frac{\pi SB}{k_m hc} \int \frac{I(\lambda)d\lambda}{\Phi(\lambda)I(\lambda)} d\lambda$$

Where $S$: emission area of device; $B$: luminance; $k_m$: photo-power equivalent (680 lm/w); $\Phi_\lambda$: visible function.

The external quantum efficiency:

$$n_q = \frac{B}{J} \frac{\pi q_0}{K_m hc} \int \frac{I(\lambda)d\lambda}{\lambda \Phi(\lambda)I(\lambda)} d\lambda$$

Where $J$: current density; $q_0$: charge

The devices with 50%, 75% and 100% PEO had a maximum external efficiencies of 0.053%, 0.083% and 0.165% respectively.

![Figure 28: Perovskite/PEO LED device under constant current operation mode [54]](image-url)
To test the stability, a constant current was applied onto the device with 75% PEO concentration. The device was stable until 4 minutes after which the luminance intensity dropped below 100 cm m-2. The working of the PEO/perovskite composite LED can be postulated to the ability of the perovskites to form p-i-n homojunction. Xiao et al. reported that under an external electrical field, the migration of the charge carriers, the electrons and holes takes place which accumulate at the electrodes. This “poling” phenomenon might be the driving mechanism for the light emission in the PEO/perovskite LEDs. The ionic conductivity of the PEO polymer helped in the movement of the ions generated within the composite and also enhanced the surface morphology to a great extent. As a control experiment, LEDs were fabricated without the incorporation of PEO. It is worth noting that the success rate of such devices was very low, at least 95% of the fabricated devices failed. Figure 29 shows the IVL characteristics of perovskite only LED device. The device had a maximum luminance of 642cd m-2 with a modest efficiency value of ~0.09 cd A⁻¹. The inset in the figure shows the image of an actual working perovskite only device. The emission is not uniform because of the non-uniform surface morphology as seen in the SEM analysis. This demonstrates that addition of PEO improved the characteristics and yield

\[\text{Figure 29: Current density, luminance and efficiency vs voltage of a single layer pure perovskite without any PEO. Inset shows photo of a working device [54]}\]
of the devices. As a control experiment, PEO was replaced by PVDF, a poor ionic conductor and PS an ionic insulator and the concentration of polymer was maintained at 100% within the composite. The luminance-voltage characteristics of the as prepared composite devices are shown

![Graph](image)

*Figure 30: Luminance and current density vs voltage characteristics of perovskite/PVDF and perovskite/PS composite thin films respectively [54]*

in figure 29. The composite devices made with PVDF had a turn-on voltage of 19 V and reached a luminance of 4 cd m\(^{-2}\) at 25 V. The devices with PS did not show any luminance even at 25 V due to the restriction of ionic migration. When compared to PEO devices, the devices with PVDF and PS also have very low current density values.

To summarize, the incorporation of PEO into the perovskite helped in obtaining a pin-hole free uniform film. The composite thin films deposited through simple one step spin coating process were sandwiched between top and bottom electrodes to obtain single-layer LEDs. The ability of fabricating LEDs with a single light emitting layer without the use of any other charge conducting layers opens up a groundbreaking opportunity to manufacture perovskite LEDs on a large commercial scale.
CHAPTER 5

PRINTED PEOVSKITE LED

Printing technologies have emerged as an alternative to conventional fabrication techniques paving the way to produce new era low-cost wearable, flexible opto-electronic devices. [59]–[62] Among various printing techniques, screen printing, roll-to-roll printing and inkjet printing processes have been widely used to commercially fabricate electronics on a large scale. Most commonly used substrates like glass and silicon are brittle and cannot be employed in such printing processes. To overcome the limitations of the commercially available rigid substrates, conventional printing techniques were further extended onto polymer substrates.[63] The solution processability of the aforementioned perovskite/PEO composite thin films have the potential to dominate the commercial market of LEDs as they can be fabricated on a variety of substrates by utilizing the diverse printing technologies currently available. The ultra-simple device structure gives an unprecedented opportunity to fabricate the perovskite composite LEDs utilizing a commercially accessible printing technology. This gives the motivation to develop printed LED devices by exploiting the perovskite/PEO composite films. Screen printing method was chosen to print the perovskite/PEO composite films. To limit the experimental variation, the substrate was chosen as ITO/glass which serves as the bottom electrode. Once the coating process was optimized, a printed bottom electrode would eventually replace the ITO/glass substrate. Silver nanowires possess excellent electrical, thermal and optical properties coupled with the ability to be coated onto various flexible substrates by roll-to-roll manufacturing techniques making them ideal candidates for the top electrode[64]. Several reports demonstrated the use of silver nanowires for optoelectronics such as organic solar cells, OLEDs and polymer light emitting diodes. [65]–[67] In this regard, highly conductive silver nanowires was utilized as the top electrode.[68]
5.1 Fabrication Process

The simplicity, and the ability to process at a low temperature makes the perovskite composite LEDs eminent which can be utilized to fabricate devices on a cost-effective, large commercial scale. One of the principle challenges that have been encountered during the screen printing process was that the devices, when tested were always electrically shorted after the application of top silver nanowire electrodes. This was due to the fact that the perovskite/PEO composite film was too thin and caused electrical shortage between the top silver nanowires and bottom ITO. Also, the lower molecular weight PEO utilized for spin coating process, may not withstand the dense network of silver nanowires. In order to overcome the electrical shortage, PEO with a higher molecular weight of 5,000,000 g/mole was used as precursor for the composite solution. With the increase in the molecular weight of PEO, the chemical properties remains the same. However the physical properties such as viscosity changed with change in the molecular weight. This change in the viscosity was used for obtaining a thicker composite film that would isolate the printed silver nanowires from bottom electrode. The schematic illustration of the fabrication process is given below:

*Figure 31: Schematic illustration of the perovskite composite thin film printing process [68]*
The detailed description of the fabrication process is described below:

1. The perovskite precursor solution was prepared by a similar method used for the fabrication of single layer LED devices through one step solution processing.

2. PEO with average molecular weight of \(~5,000,000\) g/mole is dissolved in anhydrous DMF with concentration of 10 mg mL\(^{-1}\) and is stirred at 70°C for 30 minutes.

3. The composite solution of PEO and bromide perovskite had a weight ratio of 0.75:1 in DMF.

4. 40 ul of the composite solution was dropped onto pre-cleaned and oxygen plasma treated ITO/glass substrate.

5. The solution was then smeared with the help of a doctor blade to form the composite thin film.

6. The substrates were then annealed at 80°C for 3 minutes.

7. Solvent resistant kapton tape was patterned into desired shape using laser cutting machine and is spread uniformly onto the composite film.

8. The area of the active device was usually 3mm by 3mm but other patterns are also demonstrated in the later sections.

9. Silver nanowires were dispersed in isopropyl alcohol to give a concentration of 50 mg mL\(^{-1}\). The suspension was then dropped onto the kapton mask. The electrode area is defined by the pattern of the kapton mask.

10. The devices were then annealed at 80°C for 1 minute before testing. The device fabrication was carried out in ambient environment while the application of silver nanowires and the device testing was done inside nitrogen filled glove box.
The figures below show the photos of the printed LED devices revealing the top view and rear view of the printed LED devices with uniform composite film and printed silver nanowire electrode.

![Top view and rear view of the printed LED devices](image)

*Figure 32: Top view and rear view of the printed LED devices with printed top AgNW electrode [68]*

### 5.2 Printed Perovskite/Peo Composite Film Characterization

#### 5.2.1 Surface Morphology Characterization

Several reports have demonstrated the role of moisture in the crystallization of methylammonium lead bromide perovskite. It has been reported that above 50% relative humidity, the surface morphology of the perovskite films were greatly affected with a very poor surface coverage.[39], [69] The concept of incorporating polymer into pure perovskite to form composite films has helped to overcome the detrimental effect of high humidity on the perovskite layer. The printing of the devices was carried out in ambient environment with temperature at ~25°C and 70-85% relative humidity. For the morphological characterization, optical microscope images and scanning electron microscope images of the PEO/perovskite composite films were obtained at different weight ratios of 0.5:1, 0.75:1 and 1:1. As seen from the optical microscope images the film with 0.5:1 weight ratio of PEO to perovskite had only 60% surface coverage with 20-30 µm sized dendritic perovskite crystals. With increase in the weight ratio, the surface coverage increased further with the shape of the perovskite crystals transforming into more cuboid shape.
The film with 0.75:1 weight ratio had a surface coverage of 90% with a fine grain size of around 5 µm. Thus, the composition with a weight ratio of 0.75:1 was used for the printing process. The SEM images showing the top and cross sectional view of the 0.75:1 film on silicon further validates the superior quality of the film which is continuous and pin hole free and prevented the electrical shortage between the bottom electrode and the dense silver nanowire top electrode layer after the printing process.

Figure 33: Optical microscopic images of the printed composite films with different weight ratios of PEO/perovskite [68]

Figure 34: Cross-sectional and top view SEM images of 0.75:1 PEO/perovskite composite film [68]
5.2.2 XRD Analysis

The crystallinity of the printed composite film was verified by x-ray diffraction. A θ-2θ scans were performed on the printed PEO/perovskite composite film with a weight ratio of 0.75:1. The x-ray peaks conform to the characteristic peaks of the bromide perovskite affirming the presence of bromide perovskite crystals within the polymer matrix.

5.2.3 Photoluminescence and Absorption Spectra

To get insights into the optical properties of the printed composite films, photoluminescence (PL) spectra and absorption spectra were obtained. Bromide perovskite has a direct band gap of 2.3 eV which goes in accordance with the peak of the PL spectrum and the sharp transition in the absorption spectrum, both occurring at a wavelength of 545 nm. The printed composite film with 0.75:1 ratio had the intensity of the PL peak highest at 545 nm. The PL and the absorption spectra are presented in the figure below.
5.3 Moisture Effect on Printed Perovskite Composite Film

A time dependent study was carried out on the perovskite/PEO composite films printed in ambient atmosphere. Photoluminescence (PL) spectroscopy measurements were obtained to investigate the stability of the printed composite films. The PL intensity of the composite films in

![Photoluminescence and absorption spectra of 0.75:1 weight ratio PEO/perovskite composite film](image)

Figure 36: Photoluminescence and absorption spectra of 0.75:1 weight ratio PEO/perovskite composite film [68]

![PL spectra evolution and peak intensity evolution with exposure to ambient environment for the composite film](image)

Figure 37: PL spectra evolution and peak intensity evolution with exposure to ambient environment for the composite film [68]
ambient environment increased with time. The PL spectra were obtained immediately after film was printed and after exposing to ambient air with 70-85% relative humidity and at 25° C for a certain period of time. As seen in figure 37, the Pl peak intensity at 545 nm increased at a substantial scale and after 32 hours, the intensity increased by 612% compared to the as-prepared films. The intensity of the films reached maximum and further exposing the film to ambient environment above 32 hours did not alter the intensity much or almost remained unchanged. The trend in Pl intensities of perovskite/PEO composite films prepared and exposed in ambient air versus the films prepared and kept inside a nitrogen filled glove box with oxygen and moisture maintained at < 1ppm can be compared in the figure below. The film inside the glove box had only a slight increase in the Pl intensity when compared to those prepared and exposed to humid ambient air. Exposure of the films to air did not alter the crystallinity of the perovskite crystals in the

![Figure 38: Photos of the composite film under 365 nm UV lamp irradiation inside glove box (top) vs in ambient air (bottom) [68]](image-url)
composite. The optical images and the XRD patterns of the film before and after exposure to air shows that the structure and crystallinity were not affected by the exposure. Reports demonstrate that the morphology and crystallinity of the iodide based perovskites were greatly affected upon exposure to moisture.[39], [70] However, the PL intensity of the printed PEO/perovskite composite films increased with exposure to humidity without deterioration of the composition and morphology of the perovskite crystals which makes this approach novel for printing processes in ambient environment.

Figure 39: Optical microscopic images and XRD patterns of the printed film immediately after printing and after 20 hour exposure in air [68]
5.4 IVL Characterization

To test the performance of the printed devices, current-voltage-luminance data was obtained. The composite films with 0.75:1 PEO/perovskite weight ratio were printed onto ITO/glass substrates. The printed films were exposed to air for 32 hours before the application of silver nanowires (AgNW) which served as the top electrode. For a comparative analysis, devices were made inside the glove box and tested for their performance. The current density-voltage, luminance-voltage and current efficiency-voltage characteristics of the LED devices both printed

![Figure 40: I-V-L characteristics of the devices printed in air and nitrogen. Comparison of maximum luminance and EQEs of this work and reported perovskite LEDs [68]](image-url)
in air and glove box are presented in the figure below. The devices printed in air showed better performance than those printed in nitrogen filled glove box. This can be attributed to the reduction in surface defects thereby enhancing efficient hole/electron injection between the emissive perovskite layer and the electrodes. The device printed in air exhibited a maximum luminance of 21,014 cd m$^{-2}$, a low turn on voltage of 2.6 V, a maximum current efficiency of 4.91 cd A$^{-1}$ and an EQE of 1.1% with a 256% enhancement in EQE and a 484% enhancement in luminance compared to the device printed in glove box which had a maximum luminance of 3,446 cd m$^{-2}$, a turn on voltage of 3.1 V, a maximum current efficiency of 1.42 cd A$^{-1}$ and an EQE of 0.3%. The IVL data validates the increase in PL intensity after the air exposure of the printed films. The high luminance coupled with high EQE exceeded the performance of the reported perovskite LED literature employing multilayer strategy and complex fabrication processes. The photos of the printed devices with 3 mm by 3 mm and 1.5 cm by 1.5 cm device area presented in the picture below show uniform illumination. Devices with “FSU” pattern were fabricated by patterning the mask which further shows the versatility of the printing process.

Figure 41: Photos of working devices and “FSU” patterned LED [68]
CHAPTER 6

FULLY PRINTED AND FLEXIBLE PEROVSKITE LED

Fully printable electronic devices eliminate the complexity in fabrication along with the need for expensive vacuum equipment and promotes scalable manufacturing thereby reducing costs. Additionally, fully printed technology has advantages in terms of system integration at the manufacturing stage. The first ever concept of composite perovskite reported in this work has the potential to be extended onto making fully printable and flexible perovskite LEDs. Moving further, the brittle ITO/glass substrate utilized in the printing process was replaced by a flexible polyacrylate polymer substrate. Single-walled carbon nanotubes (SWNT) were embedded inside the polymer substrate which served as the transparent bottom electrode. The choice of SWNT as the transparent electrode is due to the fact that they possess high length to diameter aspect ratio, low sheet resistance and high transmittance making them a reliable alternative to conventional transparent electrodes.[71] The device structure of the fully printed and flexible perovskite LED is illustrated below:

Figure 42: Device configuration of fully printed and flexible perovskite LED
6.1 Fabrication Process

The detailed description of the fabrication process is described below:

1. PDMS solution was spread onto a glass substrate and was cured at 90°C for 5 mins.
2. The single walled carbon nanotube conductive ink was printed onto the cured PDMS using a Meyer rod and was annealed at 100°C for 10 minutes.
3. Photocurable monomers bisphenol-A-ethoxylate diacrylate and photo initiator 2-2-dimethoxy-2-phenyl acetophenone were mixed in 100:2 weight ratio and were applied onto the CNTs/PDMS.
4. The monomers cured to form solid polyacrylate film when exposed to UV irradiation for 2 minutes. By this process the CNTs get attached to the polymer which was later peeled off and served as the substrate for the fully printable and flexible device.
5. The PEO/perovskite composite solution was then printed onto the CNT/polymer substrate and left in the ambient air for 32 hours.
6. Silver nanowires were later printed onto the perovskite composite film.

*Figure 43: Fabrication process of fully printed and flexible perovskite LED*
6.2 Performance Characterization of Fully Printed and Flexible Perovskite LEDs

The performance of the flexible perovskite LEDs were characterized by the current-voltage, current-luminance and current efficiency-voltage data. The turn on voltage of the flexible device stands at 2.6 V. The flexible device had a maximum luminance of 360 cd m\(^{-2}\) at 6.1 V with a maximum current efficiency of 0.6 cd A\(^{-1}\) and an EQE of 0.14%. The IVL data for the flexible device is presented in the figure below. The decrease in the performance of the flexible devices as compared to the printed perovskite LEDs on ITO/glass can be attributed to the higher sheet resistance of the CNT network. However they offer flexibility which is advantageous during roll-to-roll printing. The flexible device was robust, and showed no degradation in performance after the device was bent to ~ 5 mm radius of convex curvature. The performance was nearly constant even after a few bending cycles.

*Figure 44: Luminance voltage, current density -voltage and efficiency-voltage date for flexible perovskite LED device. Photos of working devices [68]*
CHAPTER 7

CONCLUSION

Perovskite materials are believed to have the potential to dominate the optoelectronic industry within few years transcending the available technologies. Their astounding performance coupled with abundance and low cost makes them promising contenders for silicon based electronics. Research communities throughout the world are focusing on exploiting this material for other optoelectronic applications and as such these materials pose as promising alterative in lighting, sensing and other fields. In this work the first ever single layer perovskite composite based LEDs are reported, thanks to the polymer matrix which enhanced the morphology of the films without affecting the electrical properties of the perovskite material. This simple device structure gives an unprecedented opportunity to fabricate LEDs at an ultra-low cost. Despite the modest structure, the performance of the fabricated devices is on par with the reported literature till date which employed a complex multi-layer device architecture involving complex fabrication systems. This simple concept opened the doors for the fully printable and flexible devices which can be fabricated using conventional printing techniques on a substantial scale. The stability and performance of the perovskite composite LEDs in humid air goes to show that this innovation has an additional advantage of not requiring any controlled environment during fabrication which is greatly beneficial in commercial manufacturing. The reported work can potentially reform lighting technology providing affordable and efficient lighting luminaries.
REFERENCES


BIOGRAPHICAL SKETCH

Sri Ganesh Rohit Bade was born July 19, 1991 in Andhra Pradesh, India. He is currently in his 2nd year of study in the Industrial and Manufacturing Engineering Program at Florida State University. In August 2015, he will graduate with a Master of Industrial and Manufacturing Engineering degree, with a focus on developing new era optoelectronics towards efficient and affordable lighting technology. Mr. Bade received his Bachelor of Technology in Mechanical Engineering from Vellore Institute of Technology in 2013. He has served as a Research Assistant at the High Performance Materials Institute at Florida State University. His current research focusses on developing efficient and affordable perovskite based LEDs. He has published two journal papers (one at Advanced Materials, another at ACS Nano) based on such work. He is an active member of Florida State Chapter of the Society for the Advancement of Material and Processing Engineering (SAMPE) and Institute of Industrial Engineers (IIE).