Engineering of Hole Transport and Perovskite Absorber Layers to Achieve High Efficiency and Stable Perovskite Solar Cells

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ENGINEERING OF HOLE TRANSPORT AND PEROVSKITE ABSORBER LAYERS TO ACHIEVE HIGH EFFICIENCY AND STABLE PEROVSKITE SOLAR CELLS

BY

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ENGINEERING OF HOLE TRANSPORT AND PEROVSKITE ABSORBER LAYERS TO ACHIEVE HIGH EFFICIENCY AND STABLE PEROVSKITE SOLAR CELLS

This dissertation is approved as a creditable and independent investigation by a candidate for the Doctor of Philosophy in Electrical Engineering degree and is acceptable for meeting the dissertation requirements for this degree. Acceptance of this dissertation does not imply that the conclusions reached by the candidates are necessarily the conclusions of the major department.

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Table 4.24 Fitted charge transport lifetime and carrier life time of PSCs based on PEDOT:PSS and the different PANI films as HTMs 137
Perovskite solar cells (PSCs) offer tremendous potential for simple and low-cost solution-based fabrication with high power conversion efficiency, making it a promising renewable energy source alternative to the most common non-renewable energy sources as fossil fuels. The most widely used perovskite for solar cell applications is methylammonium lead triiodide (CH$_3$NH$_3$PbI$_3$). The two structures for PSC are the regular nip device typically fabricated using Spiro-OMeTAD as a hole transport material (HTM), and the inverted pin device fabricated using PEDOT:PSS as a HTM. They have achieved over 20% power conversion efficiency. However, devices are not reproducible or stable and HTMs are expensive, thus hindering its commercialization. It is important to find out ways to achieve high quality, defect-free solution, processed perovskite film, simple and scalable synthesis of cheap hole transport material, and efficient charge extraction from perovskite absorbers, to enable high efficiency and stability of perovskite photovoltaics.

The goal of this dissertation was to obtain cheap PSCs with high performance via engineering hole transport and perovskite absorber layers by doping of perovskite precursor solution using additives, substituting conventional high cost spiro-OMeTAD by the facile synthesized thiophene-based materials, synergistic combination of PEDOT:PSS with graphene oxide (GO) and polyaniline (PANI), targeting stable perovskite solar cells with high efficiency, and substituting conventional high cost PEDOT:PSS by facile synthesis of polyaniline electrochemically. These goals were achieved by investigating doping of perovskite precursor solution for nip PSCs by adding optimized amounts of
TBAI₃, LiI, LiTFSI, and BMImI as additives and preparing nanocomposites of PEDOT:PSS, GO, and PANI. Thin films of the doped perovskite, HTM nanocomposites, and thiophene based materials were prepared. PANI thin films were synthesized electrochemically.

Structural, optical and morphological characterizations were performed for the prepared thin films, followed by fabrication of n-i-p and p-i-n PSCs using these thin films. Doping of PbI₂ with a heteroatom containing molecule (1) increased its solubility in DMF and enhanced its reaction with methylamine iodide, leading to a perovskite film with higher crystallinity, (2) decreased perovskite film roughness resulting in better charge transport in the film and across the interface at the perovskite/charge transport layer, and (3) enhanced injection of electrons into the conduction band of TiO₂ via adsorption of the heteroatom on the TiO₂ surface, resulting in an enhancement in Jsc and a positive shift in the Fermi level (Eₔ) of TiO₂ thus increasing Voc. These enhancements in PV parameters as a result of doping greatly enhanced PSC efficiency. Furthermore, the heteroatom of dopant improved PSC stability as it binds to the carbon radical once any C–H bond is broken by heat or light through donating an electron, thus blocking its propagation into more free radicals and improving its stability.

Dithieno[3,2-b:2',3'-d]pyrrole (DTP) derivatives are one of the most important organic photovoltaic materials due to better π-conjugation across the fused thiophene rings. H16 and H18 have been obtained through a facile synthetic route by cross linking triarylamine-based donor groups with the 4-(4-methoxyphenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (MPDTP) and N-(4-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)phenyl)-4-methoxy-N-(4-methoxyphenyl)aniline (TPDTP) units, respectively. The H16 HTM outperforms the H18 in terms of conductivity, mobility, and hole transport at interface and this could be attributed to the high quality of film exerted by the MPDTP core in H16. The optimized device based on H16 exhibits a high power conversion efficiency (PCE) of 18.16%, which is comparable to those obtained with the state-of-the-art HTM spiro-OMeTAD (18.27%). Furthermore, long-term aging test shows that the
H16 based device has good stability after two months of aging in controlled (20%) humidity in the dark. Importantly, the synthetic cost of H16 is roughly 1/5 of that of spiro-OMeTAD. The present finding highlights the potential of DTP based HTMs for efficient PSCs.

A synergistic engineering between GO, PANI, and PEDOT:PSS introduced additional energy levels between perovskite and PEDOT:PSS and increased the conductivity of PEDOT:PSS. Doping PEDOT:PSS with PANI improved PCE from 11.02% to 16.29%, while doping GO with PANI improved PCE from 6.24% to 14.35%, and a composite of these three materials achieved PCE of 18.12%. The hydrophobic PANI has very poor adhesion to substrate, which is the reason for its low conductivity. The gaps between the GO micro-flakes trap charge carriers resulting in very poor conductivity. PANI/PEDOT:PSS/GO (1:1:1) film achieved the highest Jsc as PANI nanoparticles fill those gaps among GO microparticles, and GO improves adhesion of PANI, while PEDOT:PSS increases the film compactness. PANI and GO increased the work function of PEDOT:PSS, thus increasing the open circuit voltage of the device fabricated from the nanocomposite as HTM. V_{OC} increased to 1.05 V for the PANI/PEDOT:PSS/GO nanocomposite-based PSC from the pristine PEDOT:PSS (V_{OC} = 0.95 V) and PANI/PEDOT:PSS (V_{OC} = 0.99 V) - based PSCs. The reported use of PANI in perovskite solar cells involves chemical synthesis methods that are prone to contamination with impurities as it requires several materials for polymerization and adhesion improvement with substrate, contributing to the low device efficiencies. This project will mitigate this issue by the use of electrochemical method that is low cost, less time consuming and capable of producing transparent thin films of PANI with high purity and excellent adhesion to substrates without any additives. Thus, this method enables simple and scalable synthesis of PANI as HTM alternative to PEDOT:PSS, enabling an important step towards commercialization of the pin PSC with the roll-to-roll manufacturing. Results showed that efficiency of PANI-PSC is 16.94% compared to 15.11% for the PEDOT:PSS-PSC. The PANI-PSC achieved better Jsc with lower hysteresis but with lower V_{OC} and FF compared to
PEDOT:PSS-PSC. This can be attributed to the work function of PANI < PEDOT:PSS which decreased $V_{OC}$ but enhanced hole extraction at the HTM/perovskite interface, thus increasing $J_{sc}$. Doping electrolyte solution with LiTFSI increased the work function of PANI, thus increasing $V_{OC}$ from 0.87 to 0.93V.
Chapter 1: Introduction

1.1 Background

Today’s world is energy driven and a clean renewable source of energy like sunlight is important to meet the growing energy demand for a sustainable future. Solar energy is considered as the ultimate source of energy for the Earth. Living beings including humans have been utilizing solar energy for various purposes such as warmth and food. Solar energy has been used in practical technological applications such as water heater and photovoltaics. All the other forms of energy such as wind, hydroelectricity is also dependent on the solar energy.

Solar energy motivates research in many technologies such as electric vehicles, smart grids, and electronics [4]. Conversion of solar energy into electricity by photovoltaics is one of the most promising approaches to solve global energy issues [5]. The best research-cell efficiency chart shows the progress in the efficiencies of solar cells using certain materials and technologies over four decades (Figure 1.1). The highest solar cell efficiency achieved is 46.0%. However, this was possible using a four-junction architecture based on III-V compound semiconductor materials such as GaAs and Indium selenide. Such tandem structures are very sophisticated, and the processing of solar cells based on III-V compound semiconductor materials lead to a high processing cost. This makes the technology very expensive. Crystalline silicon solar cells dominate the photovoltaic industry with a relatively expensive manufacturing process. Today’s research focuses on creating devices from low cost materials and simple solution processing [6]. There has been rapid progress on alternative light absorbing semiconducting materials for solar cell applications which includes copper indium gallium selenide (CIGS), cadmium telluride (CdTe), conjugated polymers, organic small molecules and dyes, and perovskites [7]. Organic-inorganic hybrid perovskite based solar cell technology has attracted a lot of interest as it competes with the dominant silicon solar cells in terms of power conversion efficiency, cost, and processing [8]. Their power conversion efficiencies (PCEs) have been
increased from 3.8% in 2009 to over 22% recently for n-i-p mesoscopic structure [9, 10].

Figure 1.1 Best Research-Cell Efficiency reported over last four decades [11].
Perovskite solar cell (PSC) started to be used as a photovoltaic material in 2009. It was used as an absorber for DSSC and achieved around 3-4% PCE [12]. There was great progress in PCE of PSC within the last 10 years up to 6.5% in 2011 [13], then more than 20% in 2015 [14], 22.1% in 2016 [15], and finally 23.3% in 2018 [16]. Figure 1.2 shows the increase in PCE (%) of perovskite solar cells with year. The advancement of efficient perovskite solar cells has been very quick. Further, the perovskites have the potential of low-cost manufacturability. This has attracted a lot of attention to make perovskite photovoltaics a commercial product and significant progress has already been made with startup companies heading towards commercializing perovskite solar modules [17-19]. Organometal halide perovskite materials demonstrate several advantages including excellent optical properties which can be tuned by managing chemical compositions, low exciton binding energy (∼45 meV), ambipolar charge transport [20] long charge carrier lifetime, and long electron–hole diffusion lengths [21, 22]. They have a tetragonal structure which becomes cubic once the size of organic cation is reduced, decreasing band gap from 2 to 1.5 eV, thus allowing absorption of broader band wavelengths of light. These properties make perovskite materials an excellent light harvesting material for thin-film photovoltaic applications [23]. Perovskite is a mineral species with a general formula of ABX3, where A and B are cationic species and X is a halide atom. The most widely used perovskite (CH3NH3PbI3) for solar cell applications consists of the organic cation methylammonium (CH3NH3), inorganic metal lead (Pb), and iodine (I) as the halogen atom.

Figure 1.2 Progress in efficiency of perovskite solar cells from 2006 to 2018.
Regarding an n-i-p perovskite solar cell, to fully crystallize an individual precursor component into a perovskite phase, several strategies have been adopted such as one-step deposition [24, 25], sequential two-step deposition [26] and vapor-phase deposition [27]. Among these, two-step deposition has been widely used for achieving high efficiency perovskite solar cells. In n-i-p structure, the two-step deposition technique consists of first spin coating a thin film of PbI\(_2\) layer on top of a mesoporous TiO\(_2\) layer, which is then dip-coated into methylammonium iodide solution in isopropyl alcohol. The reaction led to formation of dense, big cubic crystals of perovskite (CH\(_3\)NH\(_3\)PbI\(_3\)), causing a rougher perovskite thin film. Other problems caused by sequential two step deposition is the uncontrollable surface morphology of CH\(_3\)NH\(_3\)PbI\(_3\) which is detrimental to device reproducibility. The residual PbI\(_2\) in CH\(_3\)NH\(_3\)PbI\(_3\) thin films deteriorates device performance with lower short circuit current density, fill factor, and open circuit voltage. Some of these issues have been addressed in earlier reports by depositing a CH\(_3\)NH\(_3\)PbI\(_3\) capping layer on mesoporous TiO\(_2\) films via spin coating the PbI\(_2\) layer twice or using better coordinating dimethylsulfoxide (DMSO) as the solvent for higher film quality and surface coverage [26, 28-30]. To obtain smooth and dense films, dopants such as methylamine iodide (MAI) and tertbutylpyridine (TBP) have previously been doped into PbI\(_2\) precursor to form high quality perovskite film for efficient perovskite solar cells. Several reports have concluded that to obtain efficient perovskite solar cells, the perovskite CH\(_3\)NH\(_3\)PbI\(_3\) film should be smooth and dense with fewer structural defects [31, 32].

2,2',7,7'-Tetrakis (N,N-di-pmethoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) has been used as one of the state-of-the-art hole transport materials (HTM) [33], featuring spiro framework and four electron-rich arylamine substituents. However, the challenging synthesis routes and exorbitant cost of the spirobifluorene central core make spiro-OMeTAD a relatively expensive material. In addition, the PCE of PSCs highly depends on the sublimation grade of the spiro-OMeTAD [12, 34]. As a result, a wide number of HTMs including inorganic [35], polymer [36-38] metal organic compounds [39, 40] and small
organic molecule HTMs [33] have been synthesized and investigated. Small organic compounds are one of the most studied HTMs because they are structurally simple and easy to synthesize [41-52]. One strategy used for the design of small organic HTMs focuses on developing the central cores. Initially, spiro-like derivatives were developed as central cores for small organic molecule HTMs.

PCE of the p-i-n device is lower than that of the n-i-p device, however it is more preferred as it can be fabricated at a lower temperature (<100 °C) compared to 450 °C for the regular n-i-p structure that enables use of flexible substrates and the roll to roll production of the perovskite solar cells. Poly(ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is the most commonly used hole-transport layer (HTL) in p-i-n perovskite solar cells. The efficiency of perovskite solar cell employing PEDOT:PSS HTL has increased remarkably; however, various problems have been noticed. Most of all, the large particle size of PEDOT induces degradation of the device because the aggregation of particles causes defects. The high costs and low electrical conductivity limits use of PEDOT:PSS as an efficient HTL. In addition, the acidic property of PEDOT:PSS is detrimental to device stability. Carbon-based materials can help alleviate these limitations. Carbon black, carbon nanofibers, carbon nanotubes (CNTs), CNT-sponge, graphite and graphene have been successfully employed as hole transport materials (HTMs) in dye sensitized solar cells (DSSCs) [53, 54]. The carbon materials show promising conductivity and heat resistance [55]. Graphene oxide (GO) has been previously utilized in organic light-emitting diodes (OLEDs), polymer solar cells, and DSSCs [56]. Using reduced graphene oxide (RGO) as an HTM in p-i-n perovskite solar cells has led to a PCE of 10.8% [57]. GO as an HTL in perovskite solar cells with CH$_3$NH$_3$PbI$_3$$_x$Cl$_x$ absorber achieved an efficiency over 12% [58]. A composite of GO/PEDOT:PSS as HTL in p-i-n perovskite solar cells exhibited a PCE of 9.7% with stability improvement [59]. On the other hand, conducting polymers (CPs) such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PT) derivatives, and PEDOT have attracted much attention as promising candidates for HTMs in solar cells due to
their excellent electrocatalytic activity, simple synthesis procedure, and good electrical conductivity [60-64]. Carbon based materials are usually incorporated into the CPs to form nanocomposites, which possess synergistic properties of carbon materials and CPs. Adding GO into conducting polymers such as PANI, polypyrrole, polythiophene can result in enhanced electrical conductivity [65, 66]. GO is known as a partially oxidized two dimensional graphite layer, which has high electrical conductivity and long stability, but poor redox catalytic activity [65]. However, PANI is characterized by an excellent redox behavior, but with low electrical conductivity. The combination of positively charged PANI with negatively charged GO by a self-assembly technique led to high electron-conduction and charge-transfer ability [67].

As a first step for commercialization of p-i-n perovskite solar cell, its cost should be deduced. That could be achieved via finding cheap and stable alternative HTM to PEDOT:PSS. Inorganic hole conductors have been used for perovskite cells and employed successfully as a hole conducting material [68-70]. Transparent conducting polymers have high-conductivity and good stability which makes them promising candidates as alternate hole transport materials to PEDOT:PSS. Polyaniline is one of the most promising potential electronic conducting polymers as HTM in perovskite solar cells due to high conductivity, environmental stability, low cost, easy synthesis, and high degree of processability. In addition, it can be synthesized with high purity and transparency. Polymerization of aniline into PANI can be done chemically, electrochemically, photochemically or via enzyme-catalysis. The electrochemical polymerization method by cyclic voltammetry is the most preferred procedure to prepare PANI. The prepared polymer from this method has very high purity and good adhesion with the hydrophilic substrate compared to the chemically prepared PANI which contain impurities and has bad adhesion with substrate. Electrochemical polymerization allows controlling various parameters during polymerization such as oxidation state, thickness, adhesion, conductivity and transparency of PANI by changing the applied voltage, scan rate, polymerization
time, monomer and dopant concentration, dopant type and electrolyte temperature [3, 71-73].

Stability is one of the key issues of the PSC technology. Perovskites are prone to several environmental factors such as moisture and oxygen [74, 75], heat [76], prolonged sunlight illumination [77], ultraviolet light exposure [78], and mechanical rigidity [79]. Therefore, the research in perovskites are also dedicated to improve this stability and significant progress has been made [80, 81]. However, a standard protocol does not exist in the PSC research regarding the reporting of the perovskites stability [78]. One of the limiting factors is the water soluble property of the organic component of the perovskites making the technology susceptible to moisture [82]. This high susceptibility of the perovskites can be restrained by several methods such as modification of the constituent elements in the perovskites, device structures, the interfaces and the fabrication environment conditions [78].

1.3 Previous work

1.2.1 Perovskite Solar Cell

Organic-inorganic perovskites were first studied by Weber in 1978 [83, 84]. Perovskites were first used as photovoltaic absorber material in 2006 [85], where methylammonium lead halide functioned as sensitizer in mesoscopic TiO₂ thin film giving a PCE of ~2.2%. In 2009, Miyasaka et al. increased the PCE to 3.8% by using liquid electrolyte based DSSC which led to corrosion of the perovskites [12] while Im et al. increased to 6.5% in 2011 via optimization of perovskite thickness [13]. A breakthrough efficiency of 10% occurred in 2012 by replacing the liquid electrolyte with solid-state electrolyte spiro-OMeTAD as the HTM. This high efficiency was attributed to the corrosion prevention of the perovskites [86]. In 2013, perovskite deposition method was modified from one-step to two-step which enhanced the PCE of perovskite solar cell to ~15% [87]. In 2015, Yang et al. fabricated formamidinium lead iodide (FAPbI₃-based) PSCs with efficiency > 20% [14]. In 2017, Yang et al. showed that the concentration of deep defects can be significantly reduced by the use of iodide ions into the
organic cation solution. This approach led to a certified high efficiency of 22.1\% [88].

### 1.2.2 Doping of perovskite absorber in the n-i-p perovskite solar cell

The doping of perovskite with moisture from atmospheric humidity and the addition of water was recently considered to be one of the most important factors during perovskite crystallization. Recently, a number of reports on the use of humidity to improve perovskite morphology has been published. Im et al. obtained an improved perovskite morphology with a compact and dense film by incorporating H\(_2\)O or HBr (aq) as additive in CH\(_3\)NH\(_3\)PbBr\(_3\)/DMF precursor solution. [89]. In 2014, Yang et al. optimized doping with environmental humidity while fabricating perovskite solar cells and achieved an efficiency up to 19.3\% [90]. In 2015, Zhang et al. employed tertbutyl pyridine (TBP) as a dopant in PbI\(_2\) precursor and obtained uniform and dense perovskite film. An improved efficiency of 16.21\% was obtained, however, device stability was significantly affected by TBP [31]. In 2015, Namyoung et al. fabricated perovskite solar cells via Lewis base adduct of PbI\(_2\). 1:1:1 adduct of MAI•PbI\(_2\)•DMSO was formed by spin-coating the DMF solution containing equimolar MAI, PbI\(_2\) and DMSO, and using diethyl ether to remove the DMF solvent. They achieved an average PCE of 18.3\% and a maximum PCE of 19.7\% [32]. Wu et al. employed H\(_2\)O additive in PbI\(_2\) precursor and obtained a high quality perovskite film by decreasing the pin holes in the film [91]. Bert et al. demonstrated that the addition of some water into the perovskite precursors does not degrade the efficiency of perovskite solar cells [92]. The perovskite films were also exposed to the controlled moisture environment and perovskite grains with larger grain size and less defect density, were observed, which eventually led to superior device performance [30, 92-95]. Moisture has been shown to be crucial factor that can affect the crystallization and growth of perovskite films [93, 96-98]. Increase in perovskite film crystallinity was observed as the perovskite films were exposed to high humidity conditions. It was concluded that some reactive phases in the form of CH\(_3\)NH\(_3\)PbI\(_3\)•H\(_2\)O and (CH\(_3\)NH\(_3\))\(_4\)PbI\(_6\) .2H\(_2\)O were formed when the water molecules reacted with the
perovskites. These phases are formed by hydrogen bonding between water molecules and iodides, and hydrogen bonding between MA and water. However, these reactive phases are metastable and could easily dehydrate in air [96].

1.2.3 Hole transport materials alternative to Spiro-OMeTAD for the n-i-p PSC

Sun et al. reported a series of low-cost spiro[fluorene-9,9′-xanthene] (SFX) based HTMs exhibiting impressive PCEs over 19% [41, 99]. Recently, Wang et al. established a new spiro skeleton based on spiropentaphenylpyrazole-9,9′-thioxanthene for HTMs. They demonstrated that the PCE of PPyra-TXA (18.06%) outperforms that of spiro-OMeTAD [42]. Meanwhile, it has been demonstrated that the simple triarylamines such as carbazole and phenothiazine are good cores for constructing HTMs [43, 44, 100]. In addition, thiophene derivatives [45, 46, 101-105] such as cyclopentadithiophene [45, 101] and silolothiophene [105] have been introduced as central cores for small organic molecule HTMs because of their high hole mobility and electrical conductivity [33]. Nazeeruddin and co-workers have molecularly engineered the small molecule FDT (fluorene–dithiophene) HTM, yielding a PCE up to 20.2%. This work suggests that there exists stronger adhesion and improved interfacial coupling between FDT and perovskite owing to the existence of thiophene-iodine interaction. These results demonstrated that the performance of small organic molecule HTMs highly depends on the design of central cores [45].

1.2.4 Hole transport materials as dopants for PEDOT:PSS in the p-i-n PSC

Using reduced graphene oxide (RGO) as an HTM in p-i-n perovskite solar cells has led to a PCE of 10.8% [57]. GO as an HTL in perovskite solar cells with a CH3NH3PbI3-xClx absorber achieved an efficiency over 12% [58]. A composite of GO/PEDOT:PSS as an HTL in p-i-n perovskite solar cells exhibited a PCE of 9.7% with stability improvement [59]. On the other hand, conducting polymers (CPs) such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PT) derivatives, and PEDOT have attracted much attention as promising candidates.
for HTMs in solar cells due to their excellent electrocatalytic activity, simple synthesis procedure, and good electrical conductivity [60-64]. Carbon based materials are usually incorporated into the CPs to form nanocomposites, which possess synergistic properties of both carbon materials and CPs. Adding GO into conducting polymers such as PANI, polypyrrole, or polystyrene can result in enhanced electrical conductivity [65, 66]. GO is known as a partially oxidized two dimensional graphite layer, which has high electrical conductivity and long stability, but poor redox catalytic activity [65]. However, PANI is characterized by excellent redox behavior, but with low electrical conductivity. The combination of positively charged PANI with negatively charged GO by a self-assembly technique led to high electron-conduction and charge-transfer ability [67]. For DSSCs, the PANI/GO nanohybrids and nanocomposites have been used as an efficient counter electrode material [106-108]. There is no report on use of PANI/GO and PANI/PEDOT:PSS nanocomposites as HTMs for perovskite solar cells.

1.2.5 Electrochemically synthesized PANI as a HTM alternative to PEDOT:PSS for the p-i-n PSC

In 2014, Jeng et al. used NiO as a HTL by the spin-coating technique and achieved 7.8% PCE [109]. Two factors namely enhanced wetting and proper energy level alignment between CH$_3$NH$_3$PbI$_3$ perovskite and NiOx contribute to higher efficiency compared to PEDOT:PSS (3.9%). In 2014, GO was also employed as an HTL in PSC achieving an efficiency over 12% [58]. The developed morphology and crystallization of perovskite is characterized by homogenous large domains, improved surface coverage, highly textured perovskite crystal domains, and in-plane orientation, thus exhibiting improved PSC performance. In 2015, reduced graphene oxide (RGO) as an HTM in p-i-n PSCs led to a PCE of 10.8% [57]. This device was more reproducible and stable than the device fabricated using PEDOT:PSS and GO as an HTM. In 2015, Kim et al. fabricated efficient, fully vacuum–processed perovskite solar cells using N,N0-Di(1-naphthyl)-N,N0-diphenyl-(1,10-biphenyl)-4,40-diamine) NPB
combined with the interfacial layer of MoO$_3$ as hole transporting and hole extraction (injection) layers with 13.7% PCE [110]. Fully vacuum–processed perovskite solar cells accelerated the advancement of the perovskite solar cells, resulting in high efficiency and reproducibility. In 2015, Hyosung et al. used a poly [2,6-(4,4-bis-potassiumbutanylsulfonate-4H-cyclopenta-[2,1-b;3,4-b’]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (CPE-K) as an HTL for a p-i-n perovskite solar cell. A PCE of over 12% with enhanced device stability was demonstrated and the improvement was attributed to a number of reasons namely excellent wetting of the perovskite precursor on the CPE, superior hole selectivity between the perovskite and indium tin oxide (ITO) anode, and pH-neutral CPE-K [111]. In 2016, GO/PEDOT:PSS composite was used as an HTL in p-i-n perovskite solar cells and exhibited a PCE of 9.7% compared to 8.2% for the cell made of pristine PEDOT:PSS [59], exhibiting better efficiency and stability than the pristine PEDOT:PSS. In 2017, Lee et al. used chemically prepared polyaniline:poly (styrenesulfonate) (PANI:PSS) as an efficient hole transport material (HTM) in inverted planar perovskite solar cells (PSCs) achieving up to 11.67% [112]. PANI:PSS is a cheaper alternative to PEDOT:PSS; however, efficiency is low, the chemical synthesis of PANI is long, uses many materials, and the produced PANI contain many impurities which affects device performance and may needs purification.

1.3 Motivation

There is a need for

(1) High quality, defect free solution processed perovskite film,
(2) Simple and scalable synthesis of hole transport material, and
(3) Efficient charge extraction from perovskite absorbers, to enable high efficiency and stability of perovskite photovoltaics.

1.4 Objectives

The goal of this work was to engineer hole transport and absorber layers by

1.4.1 Doping of perovskite precursor solution using additives
1.4.2 Substituting conventional high cost spiro-OMeTAD with thiophene-based materials

1.4.3 Synergistic combination of PEDOT:PSS with GO and PANI, targeting stable perovskite solar cells with efficiency over 18%

1.4.4 Substituting conventional high cost PEDOT:PSS by facile synthesis of polyaniline electrochemically

1.5 Tasks

1.5.1 Investigate doping of perovskite precursor solution with additives for n-i-p PSC
   • Employ suitable dopant (TBAI₃, LiI, LiTFSI and BMImI) to dope PbI₂ precursor solution
   • Perform structural, optical and morphological characterizations of perovskite films
   • Fabricate and characterize n-i-p devices

1.5.2 Substituting conventional high cost spiro-OMeTAD by the facile synthesized of thiophene-based materials
   • Perform structural, optical and morphological characterizations of thin films of the thiophene based materials.
   • Fabricate and characterize pin devices

1.5.3 Synergistic combination of PEDOT:PSS with GO and polyaniline, targeting stable perovskite solar cells with efficiency over 20% for pin PSC
   • Prepare nanocomposites of PEDOT:PSS, GO, and PANI
   • Prepare thin films from the prepared nanocomposites
   • Perform structural, optical and morphological characterizations of the prepared films
   • Fabricate and characterize pin devices

1.5.4 Substituting conventional high cost PEDOT:PSS by facile synthesis of PANI
   • Synthesize PANI thin films electrochemically
• Perform structural, optical, and morphological characterizations of the synthesized films
• Fabricate and characterize pin devices
Chapter 2: Theory

2.1 Photovoltaic Cell

Solar photovoltaic (PV) is the fastest growing renewable energy technology and a worldwide installed PV capacity has reached more than 300 GWs by 2016. Photovoltaic is a way to collect energy from the sun by using solar cells that convert the sun’s energy into electricity via absorption of photons by a semiconductor material. Sunlight consists of packets of photons. Upon sunlight illumination, these photons are either absorbed or reflected or transmitted by the solar cell. The photons which are absorbed by the solar cell are only responsible for the current generation. The current generation is in the form of generation of charge carriers that are eventually extracted from the solar cell and feeds the load in the external circuit. One significant advantage of Solar PV is that it does not generate any pollution and greenhouse gases. PV in combination with batteries can be used in large energy applications such as automobiles and electric grids. A solar or photovoltaic cell is the building block of solar PV. These solar cells are connected in series and parallel to form photovoltaic modules and these modules are connected to form PV arrays.

2.1.1 First Generation Solar Cells

Crystalline silicon PV which consist of solar cells based on silicon semiconducting material is the first-generation solar cell technology. A crystalline silicon solar cell requires silicon of ultra-high purity. This ultra-high pure silicon requires sophisticated machines and energy intensive processes for production. A PV cell is made from a silicon wafer. The top of the wafer is diffused with a n-type dopant usually phosphorous while the base of the wafer is diffused with a p-type dopant usually boron. The p-side of the wafer is typically much thicker than the n-side as electrons have higher mobility than the holes. Therefore, a PV cell is simply a pn junction. When n-side and p-side are brought together in contact, due to concentration gradient, electrons from the n-side move into the p-side and vice versa. The electrons leave behind positive ions and holes leave behind
negative ions. This makes the junction area depleted of the carriers. Therefore, the junction area is called the depletion region. An electric field is created by the ions at the junction which drifts the electrons the other way around. This leads to the equilibrium of the carriers.

If the PV cell is placed in the sun, plenty of minority carriers will be generated as a result of photon absorption. In addition, an internal potential will be generated, decreasing the energy barrier at the depletion region. In this case a current will be generated and dominated by a drift of minority carriers (electrons in the p-type Si layer) to the n-type Si layer.

A PV cell also requires metal contacts and metallic grids to form electrical contacts with the semiconductor active material to extract and collect electrons after generation. These electrons eventually flow through the external circuit supplying the load.

Crystalline silicon has a band gap of 1.1 eV corresponding to a wavelength of 1127 nm, this means it can absorb all wavelengths shorter than 1127 nm. The optimum band gap for a semiconductor that balances absorption loss and thermalization loss is 1.5 eV. Silicon is cheap and abundant and has fewer processing issues, hence is the most common material for photovoltaic. Crystalline silicon PV provides a broad absorption range of solar spectrum and excellent carrier mobilities. However, the superior optoelectronic quality of the crystalline silicon PV comes with high pricing. The high price of this technology is since the manufacturing requires expensive and sophisticated machines and involves highly energy intensive steps.

2.1.2. Second Generation

2.1.2.1 Amorphous silicon

Amorphous silicon can be prepared on a stainless-steel ribbon over large areas using plasma-enhanced chemical vapor deposition. Like crystalline silicon, amorphous silicon can be doped to build p- and n- type layers. Amorphous silicon has a bandgap of ~ 1.7eV.

2.1.2.2 Polycrystalline silicon
Polycrystalline silicon or multicrystalline silicon basically consists of several crystal silicon grains instead of a single crystal for monocrystalline silicon. These grains are separated by grain boundaries. Although the optoelectronic quality of polycrystalline silicon is inferior to monocrystalline silicon, it is superior over amorphous Si with charge carrier mobilities of magnitudes of order higher. The bandgap of polycrystalline silicon is ~ 1.1eV.

Silicon solar cells require much thicker silicon films to absorb light efficiently. Thin-Film Technologies involves a new class of materials that are direct bandgap semiconductors and have high absorption coefficient. Thus the thin film solar cells can be made with absorbers with much lower thickness. This benefits from the manufacturing cost. In addition, they can also be made flexible in nature. Examples of such thin film technologies are Cadmium Telluride, Copper Indium Gallium Diselenide, and Gallium Arsenide.

2.1.2.3 CdTe: Cadmium Telluride

This thin-film technology has relatively higher solar spectrum absorption with lower manufacturing cost. It has achieved efficiency of up to 19%. The toxicity of cadmium and scarcity of tellurium limits using this solar cell.

2.1.2.4 CIGS: Copper Indium Gallium Diselenide

CIGS is another popular thin film technology and has already achieved power conversion efficiency of 20%. Gallium helps to increase the efficiency by broadening the absorption of solar spectrum. A limitation of this solar cell technology is the rarity of indium.

2.1.2.5 GaAs: Gallium Arsenide

Gallium arsenide possesses an optimum energy band gap of 1.42 eV and is an excellent semiconducting material for photovoltaic applications. The GaAs semiconducting materials exhibit a lattice mismatch between gallium and arsenide, therefore growth of GaAs is usually carried out using expensive molecular beam epitaxial methods to reduce lattice strain, thus making the overall fabrication process costly for large scale photovoltaic applications.
These second-generation solar cell technologies can be produced at a lower manufacturing cost. Further these technologies benefit from the reduced module masses and requirement of less supporting structures during rooftop module placements compared to the first generation. The disadvantages of the second generation are the lower efficiency compared to the silicon wafer based solar cells, instability of amorphous silicon, and the high toxicity.

2.1.3 Third Generation

The third generation of solar cells have quite a different cell structure and operation mechanism compared to a traditional pn- junction.

2.1.3.1 Nanocrystalline Solar Cells: These types of solar cells are based on a nanocrystalline films with grain sizes in the range of nanometers. The nanocrystals can be based on silicon, CdTe or CIGS on substrates usually made of silicon or organic conductors.

2.1.3.2 Photo electrochemical cells (Graetzel cell): These types of solar cells produce electricity or hydrogen based on a process similar to the electrolysis of water.

2.1.3.3 Dye sensitized hybrid solar cells: (DSSC)s are organic-inorganic hybrid technology showing promise as a very low-cost technology [113-115]. This technology has the advantage of easy manufacturing and components from abundant materials. Invented by Michael Grätzel and Brian O'Regan in 1991, the current world record efficiency is ~13-15%. This high efficiency is due to efficient hole transport via liquid electrolytes (I/I₃⁻) (Figure 2.1); however, leakage of the electrolyte leads to poor stability. Some solid-state hole conductors (polymer or inorganic solids) were used as hole transporters for DSSC, but they achieved low efficiency (~ 6%). Working principles for dye-sensitized solar cells (Figure 2.1) involve photon absorption (ηₐ) in dye molecules, followed by electron injection from the dye to TiO₂, then electron transport through TiO₂ to the photoanode, and finally electron transport back to dye molecules by electrolyte I/I₃⁻.
Dye sensitized solar cells are an attractive replacement for existing technologies. They could be used in many applications like rooftop solar collectors, working even in low-light conditions, and being potentially rechargeable. The trouble with DSSCs is the leakage of the electrolyte solution which affects stability in addition to the degradation of the electrodes by the electrolyte.

### 2.1.3.4 Polymer Solar Cells

In this technology, PC60BM is used as electron acceptor, with charge transfer from conjugate polymers to a C60 acceptor of 100%. Current world record efficiency for a tandem polymer solar cell is ~10.6%. Its processing is solution-based and low cost. There are two structures: the normal structure (Figure 2.2) with poor stability and the inverted structure with improved stability.
The working principle of polymer solar cells is as follows (Figure 2.3):

1) **Photon absorption** ($\eta_A$): photon is absorbed by active organic donor materials leading to an excited state.
2) **Exciton formation** ($\eta_{ex}$): excited state undergoes structure reorganization with thermalization loss, forming an electron-hole pair, called exciton.
3) **Exciton diffusion** ($\eta_{diff}$): excitons move by diffusion processes to a region where charge separation occurs.
4) **Exciton dissociation** ($\eta_{ed}$): excitons separate into free electron and hole- this is possible at sharp potential at donor-acceptor interface, however this process is not well understood.
5) **Charge transport** ($\eta_{tr}$): free charge carriers transport to electrode (holes to the anode and electrons to the cathode) with help of internal field.
6) **Charge collection** ($\eta_{cc}$): collected at corresponding electrodes.
chemically synthesized, with a low material cost. The problems with polymer solar cells involve lower efficiency compared to silicon (wafer-based) solar cells, in addition to the poor stability as efficiency decreases over time due to environmental effects.

A p-n junction is formed when a p-type semiconducting material is joined to an n-type semiconducting material. Formation of p-type and n-type semiconducting materials is achieved by the doping of respective intrinsic semiconducting material. This will lead to an excess of holes which will be majority carrier in p-type material, and an excess of electrons which will be majority charge carriers in the n-type material. Holes are minority carriers in n-type while electrons are minority carriers in p-type materials.

\[
\begin{align*}
n &\sim N_D \\
p &\sim n_i^2/N_D \\
p &\sim N_A \\
n &\sim n_i^2/N_A \\
n = \text{concentration of electrons in the n-type semiconductor} \\
p = \text{concentration of holes in the p-type semiconductor} \\
n_i = \text{intrinsic carrier density} \\
N_A \text{ and } N_D = \text{density of acceptors and donors}
\end{align*}
\]

In a typical p-n junction, due to a concentration gradient of electrons between n-type and p-type, the electrons from n-type diffuse towards p-type material. Similarly, holes having a high concentration in p-type material diffuse towards n-type material. Majority carriers with energies above the barriers can diffuse across the junction while the very few number of minority carriers will drift across the junction. In equilibrium, they balance with no net current. In the case of a solar cell, as a result of optical excitation, there will be plenty of photogenerated minority carriers in the p-type material. Voltage is not externally applied, but is generated internally, decreasing the barrier at the depletion region. Thus, current is generated and dominated by a drift of minority carriers.

The diffusion currents of density for electrons (\(J_{n,\text{diff.}}\)) and holes (\(J_{p,\text{diff.}}\)) are given as:

\[
dn(x)
\]
\[ J_{n,\text{diff}} = q D (n) \frac{dn (x)}{dx} \]
\[ J_{p,\text{diff}} = - q D (p) \frac{dn (x)}{dx} \]

D(n) = diffusion coefficient for electrons
D(p) = diffusion coefficient for holes, respectively
n = electron concentration
p = hole concentration
q = electron charge.

The energy band diagram of a p-n junction solar cell (Figure 2.4) shows that the work function \((E_{fp})\) of the p-region is higher than the intrinsic level \((E_i)\) because of the high concentration of holes, and the work function \((E_{fn})\) of the n-region is lower because of the high concentration of electrons. When there is no junction between p- and n-type semiconductor materials, then no energy bending is observed. However, when p- and n-type semiconductors come together to form a junction, a depletion region is formed at the junction and the two fermi levels of the n- and p-type materials align in the same level resulting in a contact potential difference leading to energy band bending (energy barrier) at the junction between p- and n- regions. When excited with photons, electrons from a valence band (VB) and are excited towards a conduction band (CB), creating a hole in the valence band. The electron-hole pairs in the CB and VB are then separated into free electrons and free holes at the junction due to the internal electric field which is caused by the potential difference between the two regions (built in potential \((V_{bi})\)). The negatively charged free electrons flow through the n-side and positively charged free holes flow through the p-side and get collected at the cathode and anode, respectively.
Figure 2.4 energy band diagram of a p-n junction solar cell [119]

The depletion region formed at the junction of p- and n-type layers is due to the diffusion of opposite charges towards the junction as a result of a concentration gradient. The width of the depletion region is determined by the doping concentration of p- (N_A) and n- (N_D) layers under thermal equilibrium for a homojunction:

\[
W = \sqrt{\frac{2eV_{bi}}{q} \left( \frac{1}{N_A} + \frac{1}{N_D} \right)}
\]

where \( \varepsilon \) is the dielectric permittivity of the semiconductor, \( q \) is the elementary charge having value of 1.602e-19, and \( V_{bi} \) is the built in potential between the quasi fermi levels of p- and n-layers.

**Electrical Model of a Solar Cell**

Dark currents (no illumination) of a diode are normally approximated by “single diode model”:

\[
J_D(V) = J_0 \left( e^{\frac{qV}{nk_B T}} - 1 \right)
\]

\( V \) = applied voltage to the diode (V)
\( J_D \) = dark current density of the diode (A/cm²)
\( J_0 \) = saturation current density (10⁻¹¹ A/cm²) of the diode
\( n \) = ideality factor (n=1-2) of the diode
\( k_B \) = Boltzmann constant (1.38 x 10⁻²³ J/°K)
I_D = A x J_D where A is area of the diode (cm²)

Illuminated currents (under illumination) of a diode are normally approximated by,

\[ J_L(V') = J_D - J_{PH} = J_0 (e^{\frac{qV}{kT}} - 1) - J_{PH} \]

where \( J_{PH} \) and \( J_P \) are the photogenerated current and photogenerated current density.

**Short circuit current (I_sc)**: This is the current of the short circuit device (V=0) under a standard light illumination. It is the number of photogenerated charges that are collected by the electrode and is directly proportional to the amount of absorbed light, charge generation, transport and collection.

\[ I_{sc} = \int_{\lambda_0}^{\lambda_1} e \cdot N_{ph}(\lambda) \cdot EQE(\lambda) d\lambda \]

Where EQE(\( \lambda \)) and \( N_{ph}(\lambda) \) are the external quantum efficiency and photon flux density, respectively, at a wavelength \( \lambda \) in the incident solar (AM 1.5G) spectrum. \( \lambda \) is the cutoff absorption wavelength of cell.

**Open circuit voltage (V_oc)**: Voltage of the device under open circuit condition (I=0) under a standard light illumination is described by:

\[ V_{OC} = \frac{n k T}{q} \ln \left( \frac{I_{PH}}{I_0} \right) \]

where \( n \) is the ideality factor of the solar cell, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( e \) is the electric charge, \( I_{ph} \) is the photocurrent density and \( I_0 \) is the saturation current density.

\( V_{OC} \) is limited by bandgap, offset between donor HOMO (Highest Occupied Molecular Orbital) and acceptor LUMO (Lowest Unoccupied Molecular Orbital), and charge recombination. In polymer solar cells, \( V_{OC} \) is limited by the difference of acceptor LUMO and donor HOMO (Figure 2.5a).
$V_{OC} = \frac{1}{e} \left( LUMOA_{cceptor} - HOMOD_{onor} \right)$  \hspace{1cm} \text{(Maximum upper limit)}

$V_{OC} = \frac{1}{e} \left( LUMOA_{cceptor} - HOMOD_{onor} - 0.3eV \right)$  \hspace{1cm} \text{(Empirical value)}

For p-i-n small molecule and perovskite solar cells, $V_{OC}$ is the energy difference between the fermi level of p- and n-layer (Figure 2.5b).

\[ I_{SC} = I_L(V=0) \]
\[ V_{OC} = V(I_L=0) \]
\[ P_m = I_m \times V_m \] \hspace{1cm} \text{(maximum power point)}

**Fill factor (squareness, FF):** One gets higher FF through achieving balanced transport of electron and hole carriers, reduced recombination losses, ohmic contribution of the electrode and the contact. FF is defined as:

\[ FF = \frac{P_m}{I_{SC}V_{OC}} = \frac{I_m \times V_m}{I_{SC}V_{OC}} \]

**Solar cell efficiency ($\eta$):** Solar cell efficiency is defined as the ratio of the output power produced from the solar cell to the incident light power ($P_s$) under a standard illumination condition. Therefore, it basically gives information on maximum power output of the solar cell. The solar cell efficiency is dependent on
three factors: open circuit voltage ($V_{OC}$), short circuit current ($J_{SC}$), and fill factor (FF).

$$\eta = \frac{I_m V_m}{P_s} = \frac{I_{SC} V_{OC} FF}{P_s}$$

Figure 2.6 J-V curve of a solar cell showing its photovoltaic parameters.

Solar cells have parasitic resistances which can be modeled as parallel shunt resistance ($R_{SH}$) and series resistance ($R_S$). If the solar cell behaves as an ideal cell, $R_{SH}$ should be infinite implying no alternative pathways for current to flow, while $R_S$ should be zero implying no voltage drop before the load. Fill factor (FF) basically depends on these parasitic resistances. FF can be increased by increasing $R_{SH}$ and decreasing $R_S$. Parasitic resistances reduce $I_{SC}$, $V_{OC}$, and FF of solar cells. The effect of series and shunt resistances on the fill factor is often much more than their effect on $V_{OC}$ and $I_{SC}$ (Figure 2.7).

Figure 2.7 Efficiency of solar cell is reduced by the two parasitic resistances, shunt and series resistances.
\[ R = \frac{V}{I} = \frac{V}{A/cm^2} = \Omega cm^2 \]

\[ I = \frac{V - IR_s}{R_{sh}} + I_0 \left( \exp\left[\frac{q(V - IR_s)}{nkT}\right] - 1 \right) - I_{PH} \]

\[ I_{SC} \approx -\frac{R_{sh}}{R_s + R_{sh}} I_{PH} \approx -I_{PH} \]

\[ \frac{V_{OC}}{R_{sh}} + I_0 \exp\left[\frac{qV_{OC}}{nkT}\right] = I_{PH} \]

For calculation of the shunt resistance, the inverse of the slope of the linear region of the IV curve in the third quadrant (reverse-bias) determines the value of \( R_{SH} \) (Figure 2.8). While the series resistance is determined by the inverse of the slope of the IV curve in the first quadrant (forward-bias). The values of these series and shunt resistances differ under dark and illumination conditions.

![Figure 2.8 Estimation of shunt resistance and series resistance from dark IV curve](image)

In the dark, \( I_{ph} = 0, R_{sh} \gg R_s \), so current flows through \( R_{sh} \) can be ignored. At larger voltage, the resistance of the diode can be ignored.
Under illumination conditions, the series and shunt resistances, $R_S$ and $R_{SH}$, are determined from the slopes of the I-V curve at $V_{OC}$ and $I_{SC}$, respectively (Figure 2.9).

### 2.2 Solar cell terminologies and characterization parameters

Emission (and absorption) of infrared radiation occurs by all objects with a temperature above absolute zero. The intensity of the radiation becomes higher and the peak wavelength becomes shorter with increase in temperature (Figure 2.10). The sun exhibits an equivalent temperature of 5800 K and a peak wavelength of 530 nm (green light). The solar spectrum basically ranges from ultraviolet to beyond IR wavelength region.
Figure 2.10 Radiation Curves (the higher the body's temperature, the more radiation emitted and the shorter wavelength of the emission) [120].

Solar spectrum explains the difference between AM0 solar spectrum and AM1 or AM1.5 (The dips in the curves shown in Figure 2.11). Sunlight passes through the atmosphere and part of that light gets absorbed by the different gases (H₂O, CO₂, O₂, O₃, N₂) in the atmosphere. The fingerprint of the gases in the atmosphere can be seen in the spectral irradiance of the sunlight on the surface of the earth (AM1 or AM1.5) as energy coupling from electromagnetic wave to the resonant modes of the molecule leads to absorption of electromagnetic field.
Figure 2.11 Solar irradiation spectra showing radiation at the extra-terrestrial and earth [2]

**Air mass**: This is the ratio of the optical path length to the sun to optical path length considering the sun overhead. The air mass value changes during day time, all year round, and in different locations. As a result, AM1.5 is usually considered a standard solar spectrum for device characterization and solar cell calculations. Solar irradiance outside of the earth’s atmosphere is referred as air mass zero (AM0). Solar irradiance at the noon hour at the equator of the earth is referred to as the air mass 1 (AM1). Total power of sunlight just outside of the earth’s atmosphere is 1366 W/m². When measuring solar cells in a lab, often a sunlight simulator (Xe arc lamp) equipped with an AM1.5 filter and calibrated power of 1000 W/m² (100 mW/cm²) is used.
Figure 2.12 a) Different air mass on the earth relative to the Sun’s position [121] b) Different air mass on the earth within the day

\[ n_{AM} = \frac{OA}{OB} = \frac{1}{\sin(\gamma')} \]

**Solar simulator – Xe Arc Lamp:** Majority of the light is generated within a pinpoint-sized cloud of plasma situated where the electron stream leaves the face of the cathode towards the anode. Exponential decay of luminous intensity can be observed when moving from cathode to anode (Figure 2.13).

A Xenon Arc lamp with filters approximates the AM1.5 spectrum characteristics of an artificial light source generating a spectral match (Figure 2.14) with spatial uniformity over the illumination area and stability over time.
The AM1.5 filter cannot get rid of the peaks in 750-1000nm, so we need to use reference solar cells. Selection of the reference photodetector depends on the absorption spectra of the solar cell being tested as following (Figure 2.15):

- 350 nm -700 nm (S1133): a-Si, DSSC, polymer
- 350 nm - 900nm (S1133-01): CIGS, CDTe, polymer, GaAs
- 350 nm - 1100nm (S1133-14): Si
Optical response of solar cells: Spectral quality of a solar cell can be evaluated by its quantum efficiency characteristic. External quantum efficiency of a solar cell at a given wavelength is the ratio between number of electrons collected at the electrodes \( n_e \) to the number of photons shined onto the surface of solar cell \( n_{ph} \). Internal quantum efficiency (IQE) of a solar cell is the ratio between the number of electrons collected at the electrodes to the number of photons absorbed into the solar cells (exclude the reflection \( R \) and transmission \( T \) from the front surface of the solar cell).

\[
EQE(\lambda) = \frac{n_e(\lambda)}{n_{ph}(\lambda)}
\]

\[
IQE(\lambda) = \frac{EQE(\lambda)}{1 - R(\lambda) - T(\lambda)}
\]

\[
EQE(\lambda) = K \times NEQE(\lambda)
\]

\[
K = \frac{J_{sc}}{\int e \cdot \Phi(\lambda) \cdot NEQE(\lambda) \ d\lambda}
\]

\( J_{sc} \) is the short circuit current of the cell obtained under \( \Phi(\lambda) \) illumination (often \( \Phi_{AM1.5}(\lambda) \)).

2.3 perovskite solar cell device architecture and working principle

Perovskite refers to a group of materials which has same crystal structure as calcium titanate (CaTiO3), discovered by German mineralogist Gustav Rose and named after Russian mineralogist L.A. Perovski. Perovskite crystals can have (a) cubic phase and (b) less symmetrical orthorhombic phase (Figure 2.16) [124]. Class of perovskites can be represented by formula ABX₃. For perovskite photovoltaics, the large cation “A” is methylammonium (MA) or formamidinium (FA) or Cs or some combination; cation “B” is Pb or Sn and anion “X” is halogen mostly I or Br or Cl or some combination.

Organometal halide perovskite materials demonstrate several advantages including excellent optical properties which can be tuned by managing chemical
compositions, low exciton binding energy (∼45 meV), ambipolar charge transport [20], long charge carrier lifetime, and long electron–hole diffusion lengths [21, 22]. They have a tetragonal structure which becomes cubic once the size of organic cation is reduced, decreasing band gap from 2 to 1.5 eV, thus allowing absorption of broader band wavelengths of light. These properties make perovskite materials an excellent light harvesting material for thin-film photovoltaic applications [23].

The first process that takes place in a semiconducting photovoltaic material is light absorption which creates a splitting of the electrons and holes in quasi Fermi levels $E_{Fn}$ and $E_{Fp}$, respectively. The next process is charge separation which requires to contact each quasi Fermi level independently by charge-selective contacts. Consequently, the selection of these selective contacts determines the photovoltage limit [125]. An intrinsic light absorbing semiconductor is usually sandwiched by doped n-type and p-type charge selective contacts.

Figure 2.16 Perovskite crystal structures: (a) cubic phase and (b) less symmetrical orthorhombic phase [126]. Energy band diagram at open circuit conditions for PSC (c) In dark and (d) under illumination. [127]
Figure 2.16 shows the energy band diagram of perovskite solar cell in dark and under illumination. Under dark conditions, the Fermi level $E_{F0}$ is in equilibrium along the complete device. A built-in potential $V_{bi}$ is produced as the n-type and p-type selective contacts present low and high work functions, respectively. In the light absorbing layer, the bands are inclined due to the intrinsic nature of the absorbing layer with an acting electrical field. Consequently, this electrical field produces the contact selectivity which is responsible to push electrons to the n-type contact and holes to the p-type contact. In this case, the drift current has a significant role in charge separation and collection processes.

Under illumination conditions at open circuit, the flat band conditions are produced by the splitting of Fermi levels. The open circuit voltage is limited by the work functions of the selective contacts.

There are two structures for Perovskite solar cells (PSC): the regular structure (n-i-p PSC) and the inverted structure (p-i-n PSC) as shown in Figure 2.17. Figures 2.17 (a) and (b) show the regular and inverted structures of Perovskite solar cell, respectively. Figures 2.17 (c) and (d) show the energy level diagrams of the regular and inverted perovskite solar cell, respectively. Photons are absorbed by the absorber (perovskite, CH$_3$NH$_3$PbI$_3$) layer leading to an excited state. Photogenerated electrons move to the electron transport layer (TiO$_2$ in n-i-p PSC and PCBM in p-i-n PSC). Photogenerated holes move to the hole transport layer (Spiro-OMeTAD in n-i-p PSC and PEDOT:PSS in p-i-n PSC), then charges are collected at electrodes.
Figure 2.17 (a) regular and (b) inverted structures of perovskite solar cell. Energy level diagram of (c) regular and (d) inverted perovskite solar cell.

2.4 Electrochemically synthesized Polyaniline

The different oxidation states of PANI [3]:

1. Pernigraniline Base, fully oxidized (Violet), not conducting
2. Leucoemeraldine Base, fully reduced (Yellow), not conducting
3. Emeraldine Base, half oxidized (Blue), not conducting
4. Emeraldine Salt, p-type doped emeraldine base (Green), the only conducting form of PANI
y = 1 (leucoemeraldine), 0.5 (emeraldine) and 0 (pernigraniline) as base forms

Emeraldine salt (ES), PANI/HA

Figure 2.18. The different oxidation states of PANI [3].

**Doping of Emeraldine Base into Emeraldine Salt**

As shown in the equations in Figure 2.1, when emeraldine base is protonated, a dication (bipolaron) is formed. Bipolaron is not stable due to the presence of two successive similar charges on the same site, so it is dissociated into two polarons (more stable thermodynamically). A polaron is delocalized by resonance [3].
Electrochemical Polymerization by Cyclic Voltammetry

An electrochemical cell as shown in Figure 2.20 consists of three electrodes dipped into an electrolyte solution and attached to a computer controlled potentiostat. The cleaned ITO substrate is the working electrode. Pt wire is used as an auxiliary (counter) electrode and an Ag/AgCl is a reference electrode in an aqueous solution containing aniline monomer and an inorganic acid as a dopant. A potential is applied. Potentiostat injects electrons into the counter electrode leading to a potential difference between the reference and the working electrodes. This potential difference results in oxidation of aniline into anilinium cations at the working electrode, generating a current flow to the counter electrode via solution. Potentiostat measures the current flow between the working and counter electrodes, and potential is constant at the reference electrode, so it can measure and adjust the potential at working electrode [3, 71, 128].
Figure 2.20 Electrochemical cell for electrochemical polymerization by cyclic voltammetry [3]

The mechanism of electrochemical polymerization of aniline is shown in Figure 2.21. Aniline is oxidized into a cation radical, and cation radicals are coupled at the p-position. The dimer is oxidized into a radical, and is coupled with another cation radical. This step is the propagated forming of emeraldine base. Emeraldine base is protonated into emeraldine salt [3].

**Step 1. Oxidation of Monomer**

\[
\begin{align*}
\text{Ph} - \text{NH}_2 & \xrightarrow{H^+} \text{Ph}^+ \text{N}^- \text{H}^- \\
\text{Ph}^+ \text{N}^- \text{H}^- & \rightleftharpoons \text{Ph}^+ \text{N}^- \\
\text{Ph}^+ \text{N}^- & \rightleftharpoons \text{Ph}^+ \text{N}^- \text{H}^-
\end{align*}
\]

**Step 2. Radical Coupling and Rearomatization**

\[
\begin{align*}
\text{Ph}^+ \text{N}^- \text{H}^- + \text{Ph}^+ \text{N}^- \text{H}^- & \rightarrow \text{Ph}^+ \text{N}^- \text{N}^- \text{H}^- \\
\text{Ph}^+ \text{N}^- \text{N}^- \text{H}^- & \rightarrow \text{Ph}^+ \text{N}^- \text{N}^- \text{H}^- \\
\text{Ph}^+ \text{N}^- \text{N}^- \text{H}^- & \rightarrow \text{Ph}^+ \text{N}^- \text{N}^- \text{H}^- + H^+
\end{align*}
\]
2.5 Operating Principles of Characterizing Techniques

2.5.1 Electrochemical Measurement of Bandgap ($E_g$)

Electrochemical doping provides a good way to measure the bandgap. To do so, bring the voltage down to HOMO, find the onset of the current, which is the top of the $\pi$ band. Lower the voltage and keep watching until it reaches LUMO level, find onset of the current that is the $\pi^*$ band. The difference between these two onsets is the bandgap. Figure 2.22 shows the oxidation potential at the positive scan and reduction potential at the negative scan for a thin film of Ru-PPyBBIM measured by cyclic voltammetry.

Figure 2.22 Steady state cyclic voltammetry for a thin film of Ru-PPyBBIM showing its oxidation potential at the positive scan and reduction potential at the negative scan [129]
Ferrocene is always used as an external reference for measuring HOMO and LUMO of the polymer under test (Figure 2.23).

Figure 2.23 Real experimental measurements - Reduction

LUMO is measured from the reduction potential as following:

$$E_{\text{LUMO(Polymer)}} = E_{\text{HOMO(Ferrocene)}} - E_{\text{RED(Polymer)}} + E_{\text{OX(Polymer)}}$$

HOMO is measured from the oxidation potential as following:

$$E_{\text{HOMO(Polymer)}} = E_{\text{HOMO(Ferrocene)}} - E_{\text{OX(Polymer)}} + E_{\text{OX(Ferrocene)}}$$

2.5.2 UV-Vis Spectroscopy

In this phenomenon of interaction of molecules with ultraviolet and visible lights, samples absorb energy in the form of ultraviolet, visible, or near infrared light to excite these electrons from ground states to excited states. It analyzes the light absorption of perovskite films across the UV, visible and NIR of electromagnetic spectrum. Excitation of electrons by light absorption involves transition of an electron from an electronic ground state to higher energy state, which is usually from HOMO to LUMO, or valence band to conduction band.
The light sources of UV-Vis spectroscopy instrument are deuterium arc lamps and tungsten lamps which generate wavelengths in the range of 280 – 1100 nm. Figure 2.24 shows a schematic diagram of the UV-Vis system. When a sample is illuminated, electrons are excited corresponding to the energy difference between electronic transitions inside the molecule (e.g., bonding and antibonding). The amount of light absorbed depends on the thickness and purity of the absorber. Any change in the band gap of the absorbing materials leads to blue or red shift of the absorbance peak.
2.5.3 X-ray diffraction (XRD)

This technique is used for characterization of crystalline materials, as crystals reflect X-ray beams at certain angles of incidence. When the interference of X-ray beams as they leave the crystal is constructive, then Braggs law could be applied.

\[ n\lambda = 2dsin\Theta \]

\( \lambda \) = wavelength of X-ray, \( d \) = space between atomic layer, \( \Theta \) = angel of incidence

Figure 2.25 X-ray diffraction from crystallographic planes in a crystal [131]

X-rays are part of the electromagnetic spectrum, with wavelengths shorter than Ultraviolet light. X-ray crystallography is an important characterization technique that is employed to determining the atomic and molecular crystal structure based on the diffraction of incident X-rays by the crystallographic planes in the crystal. Wavelength of X-rays is of the same order as the spacing in the grating (in crystals the typical interatomic spacing ~ 2-3 Å), so X-rays could be diffracted by crystal structures.

Crystallite size can be calculated using Scherrer Formula:

\[ t = \frac{0.9\lambda}{B \cos \theta_B} \]
2.5.4 Scanning Probe Microscopy (Atomic Force Microscopy)

This technique monitors the interactions between a probe and a sample surface via mapping of force distribution. Atomic forces involve the Van der Waals Force–dipoles of individual particles, electrostatic or Coulombic Forces–ionic bonds, and capillary and adhesive forces (liquid meniscus and tip contamination). Cantilever is a key component in AFM. Hooke’s Law: $F = -kx$ is the force applied to the sample ($k$ is the cantilever spring constant and $x$ is the tip displacement). Resonant Frequency: $(2\pi f)^2 = \frac{k}{m}$ ($f$ is resonant frequency of cantilever, $k$ is the cantilever spring constant, and $m$ is the mass on the cantilever).

Figure 2.26 (From “Elements of X-ray Diffraction”, B.D. Cullity, Addison Wesley)

Figure 2.27 (a) Schematic of an atomic force microscope (b) Force-distance curve with tip-sample separation distance indicating different regimes of imaging [132]
Cantilever and Basic AFM Principle

AFM depends on the interaction between tip and sample which involves scanning a sharp tip mounted on a cantilever across an object’s surface and measuring the forces between the tip and surface. A laser beam is emitted towards a cantilever and the reflected beam is detected by a photodetector. While the tip is scanning on the film surface in tapping mode, the cantilever goes up and down, so beam reflection changes accordingly and topography can be estimated (Fig. 2.27a). AFM resolution is only determined by the size of the probe-sample interaction volume, so it can be at a scale of picometers (10-12 m). It is also affected by tip dimension, detection system, operating conditions & controls. In real systems, it can reach atomic resolution (can see an atom, typically 1 – 5 angstroms in diameter). The optical microscope is limited by diffraction from light wavelength (if you use deep UV light, it can be 200 nm). It has many measurement capabilities such as topography and material composition and characteristics. Also, tips can be used to create small structures on samples (nanolithography). AFM has easy operating conditions as it can be performed in vacuum, air (gas), and liquid.

2.5.5 Kelvin probe force microscopy (KPFM):

Figure 2.28 Electronic energy levels of the sample and tip (a) tip and sample without contact (b) tip and sample with electrical contact (c) tip and sample with external dc bias
Energy levels of HTL need to be well matched with that of the CH$_3$NH$_3$PbI$_3$ perovskite to facilitate efficient hole transfer. To investigate the barrier of back recombination at the perovskite/HTM interface and within the particles of the hole transport material, kelvin probe force microscopy (KPFM) was measured together with atomic force microscopy (AFM) using a noncontact atomic force microscopy method which uses a conducting tip as a Kelvin probe to measure surface potential.

When the semiconducting material (sample) and the tip come into contact, there will be contact potential difference ($E_{CPD}$) between them, and electrons will flow from the material with lower work function ($E_{FS}$) to that with the higher work function ($E_{FT}$), and there will be electrostatic force between them. This electrostatic force is nullified by applying an external bias. When the external bias equals the CPD, the work function of the sample could be estimated (Figure 2.29) using the equation:

$$V_{CPD} = \frac{\phi_{tip} - \phi_{sample}}{-e}$$

(1)

where $\phi_{tip}$ is the work function of the tip and $\phi_{sample}$ is the work of the sample.

When the external voltage is applied to the tip or to the sample it changes their work functions. Hence, based on equation (1) the sign of $V_{CPD}$ will be different in the two cases. The dc voltage difference (direction) $V_{CPD}$ is thus given for the two cases as:

$$V_{Sample}^{CPD} = \frac{\phi_{tip}}{-e} - \left( \frac{\phi_{Sample}}{-e} + V_{Ext} \right) = V_{CPD} - V_{Ext}$$

(2)

$$V_{Tip}^{CPD} = \left( \frac{\phi_{Tip}}{-e} + V_{Ext} \right) - \left( \frac{\phi_{Sample}}{-e} \right) = V_{CPD} + V_{Ext}$$

(3)

where Equations (2) and (3) are for the cases of voltage applied to the sample and the tip, respectively. After the nullifying procedure, we obtain $V_{Ext} = \pm V_{CPD}$, where the ‘+’ and ‘-’ refer to the external bias applied to the sample and the tip, respectively.
2.5.6 The Incident Photon to Current (IPCE)

The IPCE or external quantum efficiency (EQE) is defined as the ratio of number of output electrons to the number of input photons. Figure 2.29 shows the experimental setup to measure External Quantum efficiency (EQE) of solar cells. It is measured using a Xenon arc lamp (solar simulator) focused to a monochromator. Two lenses are used to focus the monochromatic light to the active area of the solar cell. NREL calibrated photo-diodes are used as a reference for EQE measurements.

![Experimental Setup to measure External Quantum efficiency (EQE) of solar cells](image)

A diffraction gating is used to split the white light into different wavelengths of light. The output of the monochromator is a single wavelength of light and this light is focused on to the solar cell under test with the help of focus lenses. A voltage monitoring unit (VMU) of a semiconductor parameter analyzer is programmed in time sampling mode. A transimpedance amplifier converts low current signal output from the solar cell into voltage and further amplifies the signal. Finally, the corresponding output voltage at each wavelength is recorded using the parameter analyzer. Following the same methods, output voltage at each wavelength is recorded for the solar cell under testing and reference solar cells, so the EQE of the solar cell under testing is calculated using NREL certified EQE data for the reference cell.

\[
\text{EQE}_{\text{solar cell}} = \left( \frac{V_{\text{solar cell}}}{V_{\text{ref}}} \right) \times \text{EQE}_{\text{ref}}
\]
2.5.7 Transient Photoconductivity Spectroscopy

This measures the time of charge transport and back recombination of materials with low mobility. Kinetics of charge transport and recombination greatly affect photovoltaic parameters of solar cells including short circuit current, open circuit voltage, fill factor, and efficiency. Charge carriers should be collected to the electrodes (charge transport time, $\tau_d$) with the internal electric field before their recombination within the cell (recombination time, $\tau_l$). Measurement resolution should be in nanoseconds for thin films.

Transient Photovoltage Spectroscopy

The device is applied to a short pulse at open circuit conditions (using high impedance of 1MΩ) and under illumination. Lifetime of the charge carriers are calculated from TPV. The schematic of TPV measurement and its decay curve is obtained through 1MΩ resistance (Figure 2.30 (a) & (b)).

![Schematic of transient photovoltage (TPV) measurement and (b) TPV decay](image)

Figure 2.30 (a) Schematic of transient photovoltage (TPV) measurement and (b) TPV decay
The voltage decay in TPV is given by:

\[ \Delta V = \Delta V_0 \exp\left(-\frac{t}{\tau}\right) \]

This equation was fitted with a mono-exponentially decaying function to calculate the loss time \( \tau \) of the device.

**Transient Photocurrent Spectroscopy**

When the device is applied to a short pulse under a short circuit condition to generate carriers, then TPC gives the collection time of the generated carriers. The transient current is determined by calculating the current through the small resistance using ohm's law. The TPC setup and transient photocurrent decay is produced across the 50 Ω resistor. The obtained decay completely drops to its zero (Figure 2.31).

![Figure 2.31](image)

Figure 2.31 (a) Schematic of transient photocurrent and (b) transient photocurrent decay
Chapter 3: Experimental Procedures

3.1 Materials

Methylammonium iodide (CH3NH3I) was purchased from Dyesol. PbI2 (99%) was obtained from Acros organics. FAI, MABr, mesoporous TiO2 (30NRD) and FK209 were purchased from Dyesol. PbBr2 and CsI were ordered from TCI. Anhydrous dimethyl sulfoxide (DMSO) (>99.9%) and γ-butyrolactone (>99%) were purchased from Sigma Aldrich. Clevios™ P VP AI 4083 PEDOT:PSS was ordered from Heraeus. PC60BM and Rhodamine were purchased from Nano-C and Sigma Aldrich. LiTFSI, LiI and BMImI were obtained from Sigma Aldrich. FTO coated glass substrates were purchased from Hartford Glass Company. Tetra-n-butylammonium triiodide (TBAI3) and titanium diisopropoxide were obtained from Sigma-Aldrich, and bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) was obtained from Fluka. Graphene Oxide was obtained from Graphene Supermarket. Ag was ordered from Kurt J. Lasker. All the materials were used as received.

3.2 Device fabrication

3.2.1 Doping of perovskite precursor solution using additives.

Perovskite solar cells were fabricated on fluorine doped tin dioxide (FTO) coated substrates (1.5 cm _ 1.5 cm). FTO substrates were etched with a diluted HCl solution (1 ml HCl in 10 ml DI water) and zinc powder. The etched substrates were then cleaned via sonication in soapy water, DI-water, acetone and isopropanol for 25 min, respectively, followed by treatment with oxygen plasma. A thin layer of compact TiO2 (0.15 M titanium diisopropoxide in ethanol) was spin coated at 4500 rpm for 45 s followed by annealing at 200 °C for 10 min. A thin layer of mesoporous TiO2 scaffold (150–200 nm) was deposited by spin coating at 5000 rpm for 30 s using a commercial TiO2 paste (30 NRD, Dyesol) diluted in ethanol with a weight ratio of 1 : 6, followed by annealing at 460 °C for 30 min. Substrates coated with TiO2 were immersed in 25 mM TiCl4 aqueous solution and annealed at 70 °C for 30 min followed by washing with DI water and ethanol. Finally, they were annealed at 460 °C for 30 min. PbI2 (462 mg PbI2 + 12 mg additive per ml DMF) solutions with different additives (LiI, LiTFSI and
BMImI) were prepared by stirring for 2 h on a hot plate at 70 °C inside a glovebox. PbI₂ solutions were spin coated at 4000 rpm for 45 s followed by annealing at 70 °C for 30 min. They were then dip coated into a CH₃NH₃I (10 mg ml⁻¹ isopropanol) solution for 1.5 min followed by immediately spin coating perovskite films at 6000 rpm for 10 s for drying. Finally, perovskite films were annealed at 100 °C for 15 min. Spiro-OMeTAD was used as a hole transport layer. It was prepared by mixing 86 mg of (2,20,7,70-tetrakis(N,N-diphenylamino)spiro[7,3-fluorene]-9,9-spirobifluorene) (spiro-MeOTAD), 34 ml of 4-tert-butylpyridine, 19 ml of a stock solution of 520 mg/ml lithium bis(trifluoromethylsulfonyl)imide in acetonitrile, and 12.5 ml of a stock solution of 50 mg tris(2-(1Hpyrazol-1-yl)-4-tert-butylpyridine)–cobalt(III) (FK209, Dynamo) dissolved in 0.2 ml chlorobenzene. Spiro-MeOTAD was spin coated outside the glove box on the top of the perovskite layer at 4000 rpm for 40 s. Samples were then transferred to an evaporator for Ag deposition (120 nm) as the top electrode. A schematic for the fabrication of perovskite solar cell by dip coating (Fig. 3.1).

Figure 3.1 Schematic showing fabrication of nip perovskite solar cell by dip coating (two step method).
3.2.2 Dithieno[3,2-b:2',3'-d]pyrrole-based Hole Transport Materials for Perovskite Solar Cells with Efficiencies over 18%

Perovskite solar cells were fabricated on fluorine-doped tin dioxide (FTO) coated substrates (1.5 cm × 1.5 cm). FTO substrates were etched by diluted HCl solution (1 ml HCl in 10 ml DI water) and Zinc powder. The etched substrates were then cleaned via sonication in soap water, DI-water, acetone and isopropanol for 25 min, respectively, followed by treatment with oxygen plasma. A thin layer of compact TiO$_2$ (0.15 M titanium diisopropoxide in ethanol) was spin coated at 4500 rpm for 45 sec followed by annealing at 200 °C for 10 min. A thin layer of mesoporous TiO$_2$ scaffolds was deposited by spin coating at 5000 rpm for 30 sec using a commercial TiO$_2$ paste (30 NRD, Dyesol) diluted in ethanol at a weight ratio of 1: 6, followed by annealing at 450 °C for 30 min. Substrates coated with TiO$_2$ are immersed in 25 mM TiCl$_4$ aqueous solution and annealed at 70 °C for 30 minutes, followed by washing with DI water and ethanol, and finally annealed at 450 °C for 30 min. The mixed perovskite precursor solutions contain FAI/PbI$_2$/MABr/PbBr$_2$ (mole ratio is 1/1.1/0.2/0.2) in anhydrous DMF/DMSO (v/v = 4/1). To improve the quality of perovskite film, CsI (1.5 M) was added to the above solution. The volume ratio of FAI/PbI$_2$/MABr/PbBr$_2$ and CsI is 5 / 95. The mixed solution was stirred at 60 °C for half of hour. A two-step program at 1000 and 6000 rpm for 10 and 30 s respectively was employed for spinning. During the second spinning process, a 100 μL chlorobenzene was dripped on the substrate 15s before the coating is completed. Films with Cs-containing perovskite turned dark immediately after spin coating. The substrates were then annealed (usually at 100 °C) for 1 h in a nitrogen filled glove box. After the perovskite annealing, the substrates were cooled down for few minutes and a Spiro-OMeTAD solution (70 nm in chlorobenzene) was spin coated at 4000 rpm for 20 s. Spiro-OMeTAD was doped with Li-TFSi and FK209 and TBP. The Spiro-OMeTAD additive molar ratios were 0.5, 0.03 and 3.3 for Li-TFSI, FK209 and TBP, respectively. Note that, the concentration of H16 and H18 is the same as that of Spiro-OMeTAD used. Samples were then transferred to the evaporator for Au deposition (80 nm) as the top electrode.
3.2.3 Synergistic combination of PEDOT:PSS with graphene oxide and polyaniline, targeting stable perovskite solar cells with efficiency over 18%

Perovskite solar cells were fabricated on patterned indium tin oxide (ITO) coated glass substrates, which were cleaned by sonication in detergent water, DI-water, acetone and isopropanol for 25 min each followed by oxygen-plasma treatment. Thin layers of different HTMs including pristine PEDOT:PSS, pristine GO, PANI/GO composite with the optimized ratio (1:2), PANI/PEDOT:PSS composite with the optimized ratio (1:2), and PANI/PEDOT:PSS/GO composite with the optimized ratio (1:1:1) were spin coated at 4500 rpm for 1 min on top of cleaned ITO substrates. Next came annealing at 120 °C for 20 min. Perovskite solution was prepared from an equimolar mixture of 581 mg PbI$_2$ and 209 mg CH$_3$NH$_3$I dissolved in a 1 ml mixture solvent comprising of DMSO and γ-butyrolactone in 3:7 vol. ratio. The prepared perovskite precursor solution was stirred on a hotplate inside the glovebox for about 2 h at 70 °C. Perovskite solution was spin coated on top of thin films of different HTMs at 750 rpm for 20 s and then at 4000 rpm for 1 min, which were dripped with 160 μL toluene after 20 s during the second spinning step. The films were then annealed at 80 °C for 10 min. PC$_{60}$BM solution with a concentration of 20mg/ml in chlorobenzene was then coated onto the perovskite layer at 2000 rpm for 40 s followed by annealing at 80 °C for 5 min. Rhodamine solution (0.5 mg/ml in isopropanol) was then spin coated on top of PC$_{60}$BM layer at 4000 rpm for 40 s inside glovebox. Finally, 100 nm of silver was deposited as a top electrode by thermal evaporation. The active area of solar cells was 0.16 cm$^2$, as defined by the shadow mask. Figure 3.2 is a schematic showing the fabrication of the p-i-n perovskite solar cell.
3.2.4 Substituting conventional high cost PEDOT:PSS by facile synthesis of polyaniline

Perovskite solar cells were fabricated on ITO coated substrates (1.5 cm × 1.0 cm). ITO substrates were cleaned by sonication in soapy water, DI-water, acetone, and isopropanol for 25 min each, then treated with plasma. A thin layer of PANI was synthesized electrochemically by cyclic voltammetry on the cleaned ITO substrates. Electro-polymerization of aniline was carried out using these cleaned ITO substrates as a working electrode with a total exposure area of 1 cm². Pt wire was used as an auxiliary (counter) electrode and a Ag/AgCl as a reference electrode in an aqueous solution containing 0.5M aniline monomer and 0.8M HNO₃ as a dopant via cyclic voltammetry at a potential interval range from (-0.2 to 1.1V), sweep rate of 25 mVs⁻¹ for 1 cycle using a computer controlled potentiostat. After electro-polymerization, the PANI film was washed with distilled water followed by annealing at different temperatures (60, 100, 140 °C) for about 10 min. PEDOT:PSS was spin coated at 4500 rpm for 1.0 minutes on a cleaned ITO substrate. A perovskite solution consisting of 581mg PbI₂ and
209mg CH₃NH₃I was dissolved in a 1ml solvent consisting of DMSO and γ-butyrolactone with 3:7 ratio. This prepared solution was stirred on a hotplate inside the glovebox for about 2 hr at 70 °C. The perovskite solution was spin coated on top of PANI and PEDOT:PSS films at 750 rpm for 20 sec, followed by spinning at 4000 rpm for 1 min. The films were then annealed at 80 °C for 10 min. PC₆₀BM solution with a concentration of 20mg/ml in chlorobenzene was spin coated on the top of perovskite layer at 2000 rpm for 40 sec followed by annealing at 80 °C for 5 min. Rhodamine solution with 0.5 mg/ml in isopropanol was spin coated on the top of PC₆₀BM layer at 4000 rpm for 40 sec inside glove box. Finally, 100 nm of silver was deposited as a top electrode.

3.3 Characterization
Characterization was performed for perovskite films and the different hole transport materials (HTMs). Perovskite films were characterized using UV-VIS spectroscopy, XRD, AFM topography, CS-AFM and KPFM. HTMs were characterized for their HOMO and LUMO, AFM topography, CSAFM, and contact angel. The fabricated devices were characterized using J-V characteristics, EQE and transient measurements. AFM topography and KPFM images were obtained using an Agilent 5500 scanning probe microscope (SPM) equipped with MAC III controller. J-V characteristics of solar cells were measured in forward and reverse bias using an Agilent 4155C semiconductor parameter analyzer under illumination (Xenon arc lamp, Newport, light intensity ~100 mW/cm² (AM 1.5). A reference cell calibrated by the National Renewable Energy Laboratory (NREL) was used to adjust the distance between the lamp and the sample to be sure that light intensity is 100 mW/cm².

3.3.1 UV-Vis spectroscopy
UV-vis absorption spectra of perovskite films were recorded using an Agilent 8453 UV-vis spectrophotometer, it has a UV source (mercury lamp) and a source for visible and near infrared radiation (tungsten lamp) as shown in Fig 3.3.
Figure 3.3 Schematic of UV-Visible absorption spectroscopy [133]

A mirror reflects the light from the tungsten and the mercury lamps on to a filter. The beam from the filter passes through a monochromator grating, the output light falls on the sample is and compared with the reference. ITO/glass slides were the reference (or blank). Absorbance spectra were in the range from 200 to 1100 nm.

3.3.2 Electrochemical measurement of bandgap (E\textsubscript{g})

Cyclic voltammetry (CV) for measuring the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the synthesized Polyaniline (PANI) will be measured using a potentiostat/galvanostat (Ametek VERSASTAT3-200). It will be performed in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu\textsubscript{4}NPF\textsubscript{6}) in acetonitrile. Platinum wire is used as a counter electrode, the synthesized PANI on ITO will be the working electrode and silver/silver chloride will be the reference electrode (Figure 3.4). Voltage is swept at a scan rate of 25 mVs\textsuperscript{-1} at room temperature and in nitrogen gas environment. Ferrocene is used as an external reference.
3.3.3 X-ray Diffraction (XRD)

XRD was measured using a Rigaku SmartLab diffractometer which contained a goniometer for rotating the source, sample and detector (Figure 3.5). The source contained a copper tube (2.2 kW Cu-Kα) and generated x-rays of wavelength 1.54 Å by applying an accelerating voltage of 44 keV. For n-i-p perovskite solar cells (PSCs), the samples used for XRD measurements were perovskite films deposited on FTO/TiO₂ slides while for p-i-n PSCs, samples were perovskite films deposited on ITO/PEDOT:PSS slides. XRD spectra were recorded at 2θ values from 5° to 60°. Samples were put horizontally inside the instrument, while the source and detector were rotating along the sample z-axis using the goniometer. X-ray diffraction gave a plot of the diffracted x-ray beam intensity as a function of 2θ.
3.3.4 Atomic Force Microscopy

An Agilent 5500 scanning probe microscope was used for measuring the topography of thin films of absorber and hole transport materials. Imaging was performed using Picoview 1.14.2 software provided by Agilent Technology and images were processed using Gwyddion software (Figure 3.6). Measurement was performed in tapping mode using a silicon tip coated with Cr/Pt (Budget Sensors, Multi 75E-G), with 75 KHz resonant frequency and 3 N/m force constant. For a better image resolution and less damage of the film surface, the tip was oscillated above its resonance frequency at 150 to 200 Hz using a lock-in amplifier (MAC III controller), thus the tip-sample interaction force maintained in the net attractive regime [134, 135]. Topography was measured for perovskite films prepared using the two step method before and after doping with different additives and crystallized using thermal annealing inside the glove box. Also, AFM used for measuring topography of different hole transport materials including PEDOT:PSS, Graphene oxide, and polyaniline.
3.3.5 Kelvin Probe Force Microscopy (KPFM):

KPFM was measured along with atomic force microscopy (AFM) using a conducting tip as a Kelvin probe to measure surface potential. The CPD between the tip and sample is measured along with the topography. An electrical oscillation is provided to excite the tip which then induces an electrostatic force between the tip and sample. The thus produced electrostatic force is then nullified by dc voltage offset applied on the scanning tip at every pixel on the sample. Surface potential mapping of perovskite films and different hole transport materials was performed by using an Agilent SPM 5500 atomic force microscope equipped with a MAC III controller (comprising three lock-in amplifiers). A Budget Sensors Multi 75- EG tip was used which has a platinum/iridium conductive coating. Lock-in 1 was used to keep the tip oscillating at its mechanical resonance (75 KHz) while lock-in 2 was used to apply AC (3-4 kHz) bias with a certain DC offset (0.5 - 3.0 V) to the tip, so the electrostatic force between the sample and tip could be nullified by the additional DC feedback.
(KPFM servo). The amplitude output of lock-in 1 was directly proportional to the electrostatic force between sample and tip as the amplitude output of lock-in 1 was connected to the input of lock-in 2 [136]. A block diagram of Kelvin probe force microscopy (KPFM) is show in Figure 3.7.

![Block diagram of Kelvin probe force microscopy (KPFM)](image)

Figure 3.7 Block diagram of Kelvin probe force microscopy (KPFM) [137].

3.3.6 Current sensing atomic force microscopy (CS-AFM)

CS-AFM was measured in contact mode using an Agilent 5500 scanning probe microscope equipped with a MAC-III controller and Pt/Ir coated Si tip. The conducting probe makes contact with the scanned film and measures the current variation across the surface with fixed bias. Carriers were injected from a conducting Pt/Ir coated AFM tip into the films of perovskite and the different hole transport materials, then were collected at the grounded ITO/FTO electrode. The current was measured using a built-in preamplifier with 1 nAV⁻¹ sensitivity. The images were taken at 0.3 V bias to avoid tip-induced local oxidation/reduction and impurities on the surface of the film.
3.3.7 Current Density-Voltage (J-V)

The J-V characteristics of the perovskite solar cells were measured under an illumination intensity of ~100 mW/cm$^2$ (AM1.5) using solar simulator (Xenon lamp, Newport) along with Agilent 4155C semiconductor parameter analyzer (Figure 3.8). The illumination intensity was calibrated using a National Renewable Energy Laboratory (NREL) photo-detector (S1133-14). Measurements were done in the forward and reverse bias.

![Figure 3.8 Photograph of current-voltage measurement setup](image)

3.3.8. External Quantum Efficiency Measurement

EQE was measured using a Xenon lamp (Newport) connected to a monochromator (Newport). The light from the monochromator (Cornerstone™ 260 1/4 m) was focused onto the active area of the solar cell using two convex lenses in series (Figure 3.9). The solar cell calibrated by the National Renewable Energy Laboratory (NREL) was used as a reference for measurements. The monochromator consisted of a grating to analyze the light from the Xenon lamp into its wavelengths to output every wavelength with 0.35 nm accuracy. The wavelength range from the monochromator was 350-800 nm with an interval of 5 nm. The small current from the cell under test was converted into voltage and
amplified by a lock-in amplifier connected to the cell then recorded by the Agilent 4155C semiconductor parameter analyzer. Newport EQE software output voltage versus time for each wavelength. EQE measurements were done for the reference cell (S1133-14) from NREL then for the fabricated perovskite solar cells.

3.3.9 Transient Photocurrent/Photovoltage Spectroscopy

Transient measurements will be performed by focusing a pump laser pulse on the device generated by a Nitrogen Laser (a crisp pulse at 337 nanometers) coupled with a Model 1011 dye laser as the excitation source (repetition rate ~ 4 Hz, pulse duration < 1 ns) (Figure 3.10). The wavelength of the pulse was selected as close to the absorption peak of the perovskite film to reach a uniform generation and fall on the solar cell from the FTO side. Oscilloscope was used to measure the pulse width of the dye laser through the response of the photodiode (rise time less than 1 ns, spectral range 280 - 1100 nm) that was used as an excitation source to the device. Charge transport time and charge carrier lifetime were obtained from transient photocurrent (TPC) and transient photovoltage...
(TPV). TPC is measured under short circuit conditions (by a very low resistor at 50 Ω) while TPV is measured under open circuit condition (by a huge resistor at 1 MΩ). Charge transport time and charge carrier lifetime are obtained by fitting the decay function with mono-exponential equation $A \exp(-t/\tau)$ where $\tau$ is the charge carrier lifetime.

Figure 3.10 Schematic diagram of transient photoconductivity measurement system.

During TPV measurements, an external light source with 1-2 sun conditions was illuminated in the device to obtain steady state conditions by an external halogen lamp source. The open circuit voltage level depends upon the solar cell illumination current density following the equation:

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

$n =$ ideality factor,
$k =$ Boltzmann constant,
$T =$ temperature,
$q =$ elementary charge,
$J_L =$ illumination current density,
$J_0 =$ reversed saturation current density.

Solar cell illumination current density depends on background light intensity, so $V_{OC}$ depends on background light intensity. Therefore, carrier
lifetime depends on carrier concentration. Carrier concentration was varied using different intensities of the white light source and carrier density concentration correlated with the charge carrier lifetime.

3.3.10 Conductivity Measurements

A two-contact electrical conductivity set-up was used for measuring conductivities of the three HTMs. Samples were prepared using glass substrates cleaned via sonication in soapy water, DI-water, acetone, then isopropanol for 25 min, respectively. Thin layers of three HTMs were prepared by spin coating at 1000 rpm for 1 min from solutions with the same concentrations used for fabricating the devices. Finally, an 80 nm thick Ag back contact was deposited by thermal evaporation. The conductivity (σ) was determined by using the following equation.

\[ \sigma = \frac{L}{Rwd} \]

Here, \( L \) is the channel length (0.05 mm), \( w \) is the channel width (0.2 μm), \( d \) is the thickness of HTM film (thicknesses of the prepared films were measured with a DekTak profilometer), and \( R \) is the resistance.

3.3.11 Mobility Measurements

Hole mobility of the studied HTMs was recorded by space-charge-limited currents (SCLCs). First, PEDOT: PSS was spin coated onto the substrates and then annealed on a hotplate at 120 °C for 30 min, forming a thin layer (< 100 nm). After that, HTMs were deposited via spin coating at 2000 rpm for 30 s. Finally, a 150 nm thick Ag back contact was deposited onto the HTM layer. The thicknesses of the HTMs were measured by using a Dektak profilometer. The current density of devices was measured with a Keithley 2400 Source-Measure unit. Hole mobility was calculated by the following equation

\[ J = \frac{9}{8} \mu \varepsilon \varepsilon_r \frac{V^2}{d^3} \]
Chapter 4: Results and Analysis

4.1 Doping of perovskite precursor solution using additives.

4.1.1 Increased Efficiency for Perovskite Photovoltaics via Doping the PbI$_2$ Layer with TBAI$_3$

4.1.1.1 UV-visible and XRD spectra of perovskite films before and after doping with TBAI$_3$

The UV–vis absorbance spectra of pristine and TBAI$_3$-doped perovskite (CH$_3$NH$_3$PbI$_3$) films (Figure 4.1a). Both pristine and doped perovskite films showed characteristic broad absorption across visible and near-infrared region, exhibiting a low optical bandgap of $\sim$1.5 eV, as determined from the absorption onset. The TBAI$_3$-doped perovskite films showed nearly similar but slightly enhanced absorbance compared with the pristine perovskite film. To confirm the crystallization of the perovskite phase, XRD measurements were conducted on perovskite films. Figure 4.1b shows the XRD spectra of pristine and TBAI$_3$-doped perovskite films deposited on top of FTO/c-TiO$_2$/meso-TiO$_2$. XRD measurements show strong characteristic peaks of the perovskite phase at 14.09° (110), 28.4° (220), and 31.8° (310), indicating the formation of pure perovskite (CH$_3$NH$_3$PbI$_3$) phase. However, a small peak at 12.65° was observed in the pristine perovskite film which corresponds to the PbI$_2$ phase. Addition of TBAI$_3$ additive to the PbI$_2$ layer leads to a significant decrease in the peak at 12.65° from the final perovskite film along with a remarkable increase in peak intensity of the (110) plane at 14.09°. Higher peak intensity of the 110 plane suggests a higher crystalline fraction in the perovskite film. That is because the TBAI$_3$ additive acts as a polar Lewis base at which the heteroatom in the ammonium group (e.g., nitrogen) donates electrons to the Lewis acid Pb$^{2+}$ in PbI$_2$, producing the Lewis base adduct of PbI$_2$. This increases the solubility of PbI$_2$ in DMF solvent and enhances its reaction with methylamine iodide, leading to a perovskite film with higher crystallinity [32].
Figure 4.1 (a) UV–vis absorbance spectra and (b) XRD patterns of pristine and TBAI$_3$ (8 mg/mL)-doped perovskite (CH$_3$NH$_3$PbI$_3$) films deposited on top of FTO/c-TiO$_2$/meso-TiO$_2$.

4.1.1.2 AFM topography images of perovskite films before and after doping with TBAI$_3$

AFM topography images of perovskite (CH$_3$NH$_3$PbI$_3$) films before and after adding TBAI$_3$ to the precursor PbI$_2$ solution (Figure 4.2). Morphology of the prepared films after adding TBAI$_3$ dopant was observed to be dense and composed of crystalline grains having particle size in the range ~200–300 nm. It was observed that the pristine perovskite film (prepared without any additives) morphology showed agglomeration of perovskite particles, causing a rougher film with a higher Rms roughness of 39.6 nm as compared to TBAI$_3$-doped perovskite films which had a lower Rms roughness of 34.6 nm. The higher film roughness in the pristine perovskite films may hinder charge transport in the film and across the interface at the perovskite/charge transport layer.
Figure 4.2 Tapping mode AFM topography images of pristine and TBAI$_3$ (8 mg/mL)-doped perovskite (CH$_3$NH$_3$PbI$_3$) films annealed at 100 °C for 15 min.

4.1.1.3 Optimization of doping degree of perovskite solution with TBAI$_3$

J-V characteristics of perovskite solar cells made from pristine and perovskite films doped with different concentrations (6, 8, 10 mg/ml) of TBAI$_3$ in the PbI$_2$ precursor (Figure 4.3). Table 4.1 shows photovoltaic parameters including short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF) and efficiency ($\eta$) obtained from the fabricated solar cells. It was observed that by increasing concentration of TBAI$_3$ additive in perovskite films, there was enhancement in $J_{sc}$, $V_{oc}$ and $\eta$ up to 8mg/ml compared to solar cells made from pristine perovskite films, beyond 8mg/ml, these parameters start to decrease. An optimum efficiency ($\eta$) of 14.85% was observed for the 8 mg/ml TBAI$_3$ doped perovskite-based device, which is significantly improved as compared to the efficiency of 11.18% obtained from device made from pristine perovskite films.

Figure 4.3 (a) Forward and (b) reverse current density-voltage (J-V) characteristics of perovskite solar cells made from pristine and different concentration (6, 8, 10 mg/ml) of TBAI$_3$ doped perovskite films.
Table 4.1 PV parameters of fabricated perovskite solar cells made from pristine and different concentration (6, 8, 10 mg/ml) of TBAI$_3$ doped perovskite films.

<table>
<thead>
<tr>
<th>Devices</th>
<th>Scan</th>
<th>$J_{sc}$ (mAcm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>Forward</td>
<td>20.25</td>
<td>0.87</td>
<td>0.43</td>
<td>7.6%</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>20.12</td>
<td>0.99</td>
<td>0.56</td>
<td>11.18%</td>
</tr>
<tr>
<td>6 mg/ml TBAI$_3$</td>
<td>Forward</td>
<td>22.48</td>
<td>1.00</td>
<td>0.41</td>
<td>9.28%</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>21.27</td>
<td>1.03</td>
<td>0.54</td>
<td>11.75%</td>
</tr>
<tr>
<td>8 mg/ml TBAI$_3$</td>
<td>Forward</td>
<td>23.45</td>
<td>0.99</td>
<td>0.47</td>
<td>10.92%</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>23.52</td>
<td>1.07</td>
<td>0.59</td>
<td>14.85%</td>
</tr>
<tr>
<td>10 mg/ml TBAI$_3$</td>
<td>Forward</td>
<td>21.16</td>
<td>0.98</td>
<td>0.43</td>
<td>9.00%</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>21.59</td>
<td>1.03</td>
<td>0.55</td>
<td>12.27%</td>
</tr>
</tbody>
</table>

4.1.1.4 J–V characteristics and EQE spectra of solar cells made of perovskite films before and after doping with TBAI$_3$

J–V characteristics and EQE spectra of perovskite solar cells made from pristine perovskite film and film doped with the optimized concentration of TBAI$_3$ (8 mg/mL) in perovskite (Figure 4.4). Table 4.2 shows photovoltaic parameters such as short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), and efficiency ($\eta$) obtained from the fabricated solar cells. It was observed that upon addition of TBAI$_3$ additive to perovskite films, there was significant enhancement in $J_{sc}$ and $V_{oc}$ as compared to solar cells made from pristine perovskite films. A highest efficiency of 14.85% was observed for the 8 mg/mL TBAI$_3$-doped perovskite-based device, which was significantly higher than the efficiency of 11.18% obtained from the device made from pristine perovskite films. The EQE spectrum (Figure 4.4c) showed enhanced EQE (%) for the TBAI$_3$-doped perovskite film-based device in the range of 350–750 nm, and the $J_{sc}$ values from EQE were well in agreement with $J_{sc}$ obtained from the J–V characteristics. The increase in $J_{sc}$ for the TBAI$_3$-doped sample can be attributed to the formation of pure perovskite phase having high crystalline fraction and smoother morphology, which could lead to improved charge transport and
collection in the device, as compared to the pristine perovskite film-based device. The adsorption of ammonium cation from the additive (TBAI₃) on the TiO₂ surface enhances injection of electrons from the conduction band of perovskite into the conduction band of TiO₂, resulting in an enhancement in Jsc. When CH₃NH₃PbI₃ is adsorbed on the TiO₂ surface, electrons are accumulated in the conduction band of TiO₂, leading to a positive shift in the Fermi level (Ef) of TiO₂ (Figure 4.5) and causing a suppression in electron recombination [31]. The positive shift in TiO₂ Fermi level and reduced recombination can lead to higher Voc as observed in the TBAI₃-doped perovskite solar cells.

Figure 4.4 (a) Forward and (b) reverse current density–voltage (J–V) characteristics and (c) EQE spectra of perovskite solar cells made from pristine and TBAI₃ (8 mg/mL)-doped perovskite films.
Table 4.2 Photovoltaic Parameters of Fabricated Perovskite Solar Cells Made from Pristine and TBAI<sub>3</sub> (8 mg/mL)-Doped Perovskite Films

<table>
<thead>
<tr>
<th>Devices</th>
<th>Scan</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mAcm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>FF</th>
<th>η (%)</th>
<th>EQE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>Forward</td>
<td>20.25</td>
<td>0.87</td>
<td>0.43</td>
<td>7.6</td>
<td>77.92</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>20.12</td>
<td>0.99</td>
<td>0.56</td>
<td>11.18</td>
<td></td>
</tr>
<tr>
<td>8 mg/ml TBAI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Forward</td>
<td>23.45</td>
<td>0.99</td>
<td>0.47</td>
<td>10.92</td>
<td>92.46</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>23.52</td>
<td>1.07</td>
<td>0.59</td>
<td>14.85</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.5 Schematic energy diagram showing the positive shift in Fermi level (E<sub>f</sub>) of TiO<sub>2</sub> upon addition of TBAI<sub>3</sub> additive to PbI<sub>2</sub> precursor solution.

4.1.1.5 Transient and stability measurements of solar cells made of perovskite films before and after doping with TBAI<sub>3</sub>

Charge transport time and charge carrier lifetime of pristine and TBAI<sub>3</sub> (8 mg/mL)-doped perovskite film-based devices were obtained (Table 4.3) by fitting the transient photocurrent and transient photovoltage decay curves with mono-exponential function A exp(−t/τ). Transient photocurrent and transient photovoltage decay curves are shown in Figure 4.6a,b. It was observed that the charge transport time for perovskite solar cells doped with TBAI<sub>3</sub> is faster than that of the pristine perovskite solar cells. As shown in Table 4.3, a charge transport time of 6.8 μs was obtained for the solar cells containing TBAI<sub>3</sub> compared to 14 μs for the cells made from pristine perovskite film. It was in agreement with the higher J<sub>sc</sub> values as observed in J−V characteristics of solar
cells prepared from doped TBAI₃-based perovskite film. The charge carrier lifetime is longer for perovskite solar cells prepared by perovskite film doped with TBAI₃ additive in comparison to pristine perovskite film-based solar cells. A charge carrier lifetime of 10.77 µs was obtained for the cells containing TBAI₃ in the PbI₂ precursor compared to a charge carrier lifetime of 7.1 µs for the cells prepared without any additive. A long charge carrier lifetime can reduce charge recombination and allow more charge extraction in the device, which can lead to a higher open circuit voltage, as observed in the TBAI₃-doped perovskite film-based device.

![Figure 4.6](image)

Figure 4.6 (a) Transient photocurrent and (b) transient photovoltage decay of perovskite solar cells made from pristine and TBAI₃ (8 mg/mL)-doped perovskite films. (c) Device stability of perovskite solar cells made from pristine and TBAI₃ (8 mg/mL)-doped perovskite films.

Table 4.3 Fitted Charge Transport Lifetime and Charge Carrier Lifetime of Perovskite Solar Cells Made from Pristine and TBAI₃ (8 mg/mL)-Doped Perovskite Films

<table>
<thead>
<tr>
<th>Devices</th>
<th>Charge transport time (µs)</th>
<th>Charge carrier life time (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>14.0</td>
<td>7.1</td>
</tr>
<tr>
<td>TBAI₃ (8 mg/ml)</td>
<td>6.8</td>
<td>10.77</td>
</tr>
</tbody>
</table>

Device stability in air for the perovskite solar cell doped with 8 mg/mL TBAI₃ in the precursor PbI₂ and perovskite solar cell made from pristine perovskite film (Figure 4.6c). It shows a decrease in device efficiency with
respect to time of exposure in air having relative humidity of 40% at room temperature. This device stability study in air also includes the effect of temperature, moisture, and light on the performance of the perovskite solar cell with time. It was observed that the TBAI$_3$-doped perovskite film-based device showed an efficiency decrease of 71% after exposure to air for 10 days, while the solar cell made from pristine perovskite film exhibited a much larger.

4.1.2 Higher Efficiency Perovskite Solar Cells Using Additives of LiI, LiTFSI and BMImI in the PbI$_2$ Precursor

4.1.2.1 UV-visible and XRD spectra of perovskite films before and after doping with LiTFSI, LiI and BMImI additives.

Figure 4.7a shows UV-Vis spectra of perovskite films prepared in the same condition of device fabrication from PbI$_2$ solutions doped with LiTFSI, LiI and BMImI additives. The UV-Vis spectra indicate a broad absorption band across the visible region with two significant peaks at 470 nm and 790 nm. The characteristic absorption shoulder near 740 nm for MAPbI$_3$ perovskite increases with the addition of the additives where BMImI has the highest peak absorbance, followed by LiI and LiTFSI. No additive exhibited the lowest peak absorbance. Absorbance is directly proportional to the external quantum efficiency (EQE) of the solar cells. The higher absorbance of the additive incorporated MAPbI$_3$ perovksite is supported by the EQE data of the perovskite solar cells with the highest EQE percent for BMImI, followed by LiI and LiTFSI versus lowest EQE percent for no additive perovskite. The increase in the absorbance maybe resulted from the generation of new energy levels after the addition of LiI, LiTFSI and BMImI additives. This decreases the bandgap of perovskite materials [138], which broadens its absorption spectrum range giving rise to a higher Jsc.

Figure 4.7b shows XRD measurements of perovskite films prepared by doping the PbI$_2$ solution with an optimized concentration of additives LiI, LiTFSI and BMImI (12mg/1ml). The peaks at the 2-theta values of 14.08°, 28.41°, 31.85°, and 43.19° corresponding to the tetragonal crystal structure of halide perovskite are assigned to (110), (220), (310), and (330) planes of CH$_3$NH$_3$PbI$_3$,
respectively [92, 139]. The peak at 12.12° is assigned to the (001) plane of PbI$_2$, suggesting incomplete conversion of perovskite. The incomplete conversion from precursor to perovskite has been previously reported in sequential deposition method adopted for perovskite formation [139-141].

Adding LiI, BMImI and LiTFSI to the PbI$_2$ layer leads to the disappearance of the peak at 12.65° compared to the perovskite film without adding additive. This suggests that a complete conversion of PbI$_2$ into perovskite has occurred while adding the above dopants into the PbI$_2$ precursor. This was attributed to polar additives which acted as polar Lewis bases that donate electrons to the Lewis acid Pb$^{2+}$ in the PbI$_2$. This produced the Lewis base adduct of PbI$_2$ and increased the solubility of PbI$_2$. The enhanced solubility due to additives leads to formation of a much smoother PbI$_2$ film compared to un-doped film. The same amount of time was used for the dip-coating of the spin-coated PbI$_2$ film into the MAI solution. Since the doped MAPbI$_3$ film had no dominant PbI$_2$ peaks as observed in un-doped MAPbI$_3$, it implies that the reaction time between doped PbI$_2$ and MAI was lower versus the un-doped PbI$_2$ indicating the enhancement in the reaction between the two. Thus the amount of PbI$_2$ residue was reduced and the perovskite crystallinity was enhanced [8, 138].

![Figure 4.7](a) UV-Vis absorption spectra and (b) XRD spectra of FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$ films before and after adding additives LiI, LiTFSI and BMImI in the PbI$_2$ layer.
4.1.2.2 AFM Topography Images of Perovskite Films Before and After Doping with LiTFSI, LiI and BMImI Additives

AFM topography images (Fig. 4.8) show that adding lithium and imidazolium iodide derivatives in the PbI$_2$ layer increased the crystal size. Perovskite films where the precursor PbI$_2$ layer was doped by LiI, BMImI and LiTFSI have a larger crystal size than that without any additive, especially in the case of the BMImI dopant. The increased perovskite crystal size is in good agreement with XRD patterns as the crystal growth is highly regulated by the formation of adduct of MAI, PbI$_2$ and the dopants which act as polar Lewis bases. This adduct formation increased the solubility of PbI$_2$ and enhanced its reaction with the methylamine iodide, thus enhancing crystal growth resulting in perovskite films with larger crystal size for higher crystallization [8, 138]. The crystal growth follows the order of BMImI > LiTFSI > LiI. LiTFSI has heteroatoms which are electron donating, thus making LiTFSI a stronger Lewis base than LiI. BMImI is a heterocyclic aromatic compound which not only contains heteroatoms, but also has a conjugated $\pi$ system (electrons are delocalized throughout the ring). Thus BMImI is very electron rich and a stronger Lewis base than LiI and LiTFSI.

![AFM images of perovskite before and after adding additives](image)

Figure 4.8 AFM images (5x5 µm) of perovskite before and after adding additives
(a) no additive, (b) BMImI, (c) LiI, (d) LiTFSI in the PbI$_2$ layer
4.1.2.3 KPFM of Perovskite Films Before and After Doping with LiTFSI, LiI and BMImI Additives.

The back recombination barrier between titanium dioxide and the perovskite layer and within the grains of the perovskite layer could be studied through KPMF measurements. The device performance strongly depends on the alignment of energy levels of the electron transport material (TiO$_2$) with those of the perovskite layer doped with different additives. The KPFM was conducted on the TiO$_2$ and different MAPbI$_3$ layers on planar samples. Surface potential images (Figure 4.9a-e) and (Figure 4.9f) show the surface potential distribution of TiO$_2$, pristine perovskite and doped perovskite films. The surface potential of perovskite film (Figure 4.9b) is not homogeneous when adding dopants into the PbI$_2$ precursor solution which means there are some regions have higher potential than the others. This led to a downward band bending in the energy band diagram. Thus the minority carrier electrons in the p-type absorber layer will be attracted from the regions with higher surface potential towards those with the lower surface potential [142-145]. This enhances minority carrier collection and provides an effective current pathway for minority carriers to reach the n-type layer. The surface potential of the perovskite film doped with BMImI has the highest surface potential. The surface potential distributions (Figure 4.9f) show that all the absorber perovskite films have a surface potential larger than that of the TiO$_2$ electron transport layer. The TiO$_2$ has an average surface potential value of 0.352 V. The surface potentials of perovskite films increased as a result of doping [BMImI (0.674 V) > LiI (0.515 V) > LiTFSI (0.426 V) > no additive (0.422 V)]. The higher surface potential of absorber increased the driving force of electron injection from perovskite to TiO$_2$ leading to a higher Jsc. This agrees with the Jsc values BMImI > LiI > LiTFSI > no additive in the J-V curves in Figures 4.11a and b.
Figure 4.9 2D surface potential of (a) TiO₂, (b) pristine perovskite (no additive), perovskite doped by (c) LiTFSI, (d) LiI, and (e) BMImI in the PbI₂ precursor

(f) Their surface potential distribution of perovskite (CH₃NH₃PbI₃)

4.1.2.4 CS-AFM images of perovskite films before and after doping with LiTFSI, LiI and BMImI additives.

To understand the role of the additives in perovskite films via doping the PbI₂ precursor solution, CS-AFM measurements for the pristine and doped perovskite films were carried out on their surfaces. CS-AFM results of different perovskite films (Figure 4.10). The pristine perovskite film has a lower average
value of surface current with the average value of 0.36 nA (fig. 4.10a) than that of the doped perovskite films. As shown in Table 4.4, the average values of surface current of perovskite films were 0.47 nA, 1.02 nA, and 1.16 nA when doping the PbI₂ precursor solution with LiTFSI (fig. 4.10b), LiI (fig. 4.10c), and BMImI (fig. 4.10d), respectively. These results suggest an improvement in the Jsc in the final perovskite solar cells after doping the PbI₂ precursor solutions with LiTFSI, LiI, and BMImI. The average values of surface current of perovskite films follows the order of BMImI > LiI > LiTFSI > no additive, which matches the order of Jsc in the J-V curves of figs. 4.11a and b.

![Figure 4.10 CS-AFM images of perovskite films (a) pristine and doped by (b) LiTFSI, (c) LiI and (d) BMImI on top of Glass/FTO/TiO₂.](image)

Table 4.4 Surface current of perovskite films before and after doping the PbI₂ layer with additives.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td>No additive</td>
<td>0.36 nA</td>
</tr>
<tr>
<td>12mg/ml LiTFSI</td>
<td>0.47 nA</td>
</tr>
<tr>
<td>12mg/ml LiI</td>
<td>1.02 nA</td>
</tr>
<tr>
<td>12 mg/ml BMImI</td>
<td>1.16 nA</td>
</tr>
</tbody>
</table>
4.1.2.5 Optimization of Doping Degree of Perovskite Solution with LiTFSI, LiI and BMImI Additives

J-V characteristics of perovskite solar cells made from pristine and perovskite films doped with different concentrations (6, 9, 12, 15 mg/ml) of BMImI in the PbI2 precursor are shown in Figure 4.11. Table 4.5 shows photovoltaic parameters including short circuit current density ($J_{SC}$), open circuit voltage ($V_{OC}$), fill factor (FF) and efficiency ($\eta$) obtained from the fabricated solar cells. It was observed that by increasing concentration of BMImI additive in perovskite films, there was enhancement in $J_{SC}$, $V_{OC}$, and $\eta$ up to 12 mg/ml compared to solar cells made from pristine perovskite films. Beyond 12mg/ml, these parameters start to decrease. An optimum efficiency ($\eta$) of 18.00% was observed for the 12 mg/ml BMImI doped perovskite based device, which is significantly improved as compared to the efficiency of 11.30% obtained from device made from pristine perovskite films.

Figure 4.11 (a) Forward and (b) reverse current density-voltage (J-V) characteristics of perovskite solar cells made from pristine and different concentration (6, 9, 12, 15 mg/ml) of BMImI doped perovskite films
Table 4.5 Photovoltaic parameters of fabricated perovskite solar cells made from pristine and different concentration (6, 9, 12, 15 mg/ml) of BMImI doped perovskite films

<table>
<thead>
<tr>
<th>BMImI</th>
<th>Bias</th>
<th>Jsc (mAcm⁻²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>Forward</td>
<td>19.15</td>
<td>0.86</td>
<td>0.46</td>
<td>7.58</td>
</tr>
<tr>
<td>------</td>
<td>Reverse</td>
<td>20.45</td>
<td>0.91</td>
<td>0.48</td>
<td>8.93</td>
</tr>
<tr>
<td>6mg/ml</td>
<td>Forward</td>
<td>23.05</td>
<td>0.94</td>
<td>0.40</td>
<td>8.67</td>
</tr>
<tr>
<td>------</td>
<td>Reverse</td>
<td>20.95</td>
<td>0.91</td>
<td>0.61</td>
<td>11.63</td>
</tr>
<tr>
<td>9mg/ml</td>
<td>Forward</td>
<td>23.44</td>
<td>0.92</td>
<td>0.39</td>
<td>8.41</td>
</tr>
<tr>
<td>------</td>
<td>Reverse</td>
<td>24.16</td>
<td>0.98</td>
<td>0.60</td>
<td>14.21</td>
</tr>
<tr>
<td>12mg/ml</td>
<td>Forward</td>
<td>24.03</td>
<td>0.98</td>
<td>0.51</td>
<td>12.1</td>
</tr>
<tr>
<td>------</td>
<td>Reverse</td>
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<td>1.04</td>
<td>0.7</td>
<td>18.00</td>
</tr>
<tr>
<td>15mg/ml</td>
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<td>24.16</td>
<td>0.96</td>
<td>0.52</td>
<td>12.06</td>
</tr>
<tr>
<td>------</td>
<td>Reverse</td>
<td>22.83</td>
<td>1.04</td>
<td>0.63</td>
<td>14.96</td>
</tr>
</tbody>
</table>

J-V characteristics of perovskite solar cells made from pristine and perovskite films doped with different concentrations (6, 9, 12, 15 mg/ml) of LiI in the PbI₂ precursor are shown in Figure 4.12. Table 4.6 shows photovoltaic parameters including short circuit current density (Jsc), open circuit voltage (Voc), fill factor (FF) and efficiency (η) obtained from the fabricated solar cells. It was observed that by increasing concentration of LiI additive in perovskite films, there was enhancement in Jsc, Voc, and η up to 12 mg/ml compared to solar cells made from pristine perovskite films. Beyond 12mg/ml, these parameters start to decrease. An optimum efficiency (η) of 17.01% was observed for the 12 mg/ml LiI doped perovskite based device, which is significantly improved as compared to the efficiency of 11.30% obtained from device made from pristine perovskite films.
Figure 4.12 (a) Forward and (b) reverse current density-voltage (J-V) characteristics of PSCs made from pristine and different concentration (6, 9, 12, 15 mg/ml) of LiI doped perovskite films.

Table 4.6 Photovoltaic parameters of fabricated PSCs made from pristine and different concentration (6, 9, 12, 15 mg/ml) of LiI doped perovskite films

<table>
<thead>
<tr>
<th>LiI</th>
<th>Bias</th>
<th>( J_{sc} ) (mA cm(^{-2}))</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>Forward</td>
<td>19.15</td>
<td>0.86</td>
<td>0.46</td>
<td>7.58</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>20.45</td>
<td>0.91</td>
<td>0.48</td>
<td>8.93</td>
</tr>
<tr>
<td>6mg/ml</td>
<td>Forward</td>
<td>23.2</td>
<td>0.98</td>
<td>0.5</td>
<td>11.40</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>22.2</td>
<td>0.99</td>
<td>0.56</td>
<td>12.31</td>
</tr>
<tr>
<td>9mg/ml</td>
<td>Forward</td>
<td>23.26</td>
<td>0.98</td>
<td>0.5</td>
<td>11.40</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>22.42</td>
<td>1.01</td>
<td>0.58</td>
<td>13.13</td>
</tr>
<tr>
<td>12mg/ml</td>
<td>Forward</td>
<td>22.92</td>
<td>1.00</td>
<td>0.58</td>
<td>13.33</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>23.36</td>
<td>1.10</td>
<td>0.66</td>
<td>17.01</td>
</tr>
<tr>
<td>15mg/ml</td>
<td>Forward</td>
<td>22.15</td>
<td>0.98</td>
<td>0.48</td>
<td>10.42</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>23.77</td>
<td>1.01</td>
<td>0.58</td>
<td>13.92</td>
</tr>
</tbody>
</table>

J-V characteristics of perovskite solar cells made from pristine and perovskite films doped with different concentrations (6, 9, 12, 15 mg/ml) of LiTFSI in the PbI\(_2\) precursor are shown in Figure 4.13. Table 4.7 shows photovoltaic parameters including short circuit current density \( (J_{sc}) \), open circuit voltage \( (V_{oc}) \), fill factor \( (FF) \) and efficiency \( (\eta) \) obtained from the fabricated solar cells. It was observed that by increasing concentration of LiTFSI additive in
perovskite films, there was enhancement in $J_{SC}$, $V_{OC}$, and $\eta$ up to 12 mg/ml compared to solar cells made from pristine perovskite films. Beyond 12mg/ml, these parameters start to decrease. An optimum efficiency ($\eta$) of 15.60% was observed for the 12 mg/ml LiTFSI doped perovskite based device, which is significantly improved as compared to the efficiency of 11.30% obtained from device made from pristine perovskite films.

![Graph](a) Pristine 6mg/ml LiTFSI 9mg/ml LiTFSI 12mg/ml LiTFSI 15mg/ml LiTFSI

![Graph](b) Pristine 6mg/ml LiTFSI 9mg/ml LiTFSI 12mg/ml LiTFSI 15mg/ml LiTFSI

Figure 4.13 (a) Forward and (b) reverse J-V characteristics of PSCs made from pristine and different concentration of LiTFSI doped perovskite films.

Table 4.7 PV parameters of fabricated PSCs made from pristine and different concentration (6, 9, 12, 15 mg/ml) of LiTFSI doped perovskite films

<table>
<thead>
<tr>
<th>LiTFSI</th>
<th>Bias</th>
<th>$J_{SC}$ (mAcm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>------</td>
<td>Forward</td>
<td>19.15</td>
<td>0.86</td>
<td>0.46</td>
<td>7.58</td>
</tr>
<tr>
<td>------</td>
<td>Reverse</td>
<td>20.45</td>
<td>0.91</td>
<td>0.48</td>
<td>8.93</td>
</tr>
<tr>
<td>6mg/ml</td>
<td>Forward</td>
<td>20.71</td>
<td>0.95</td>
<td>0.58</td>
<td>11.41</td>
</tr>
<tr>
<td>6mg/ml</td>
<td>Reverse</td>
<td>21.06</td>
<td>1.01</td>
<td>0.61</td>
<td>12.98</td>
</tr>
<tr>
<td>9mg/ml</td>
<td>Forward</td>
<td>22.67</td>
<td>0.98</td>
<td>0.51</td>
<td>11.33</td>
</tr>
<tr>
<td>9mg/ml</td>
<td>Reverse</td>
<td>22.82</td>
<td>1.03</td>
<td>0.58</td>
<td>13.63</td>
</tr>
<tr>
<td>12mg/ml</td>
<td>Forward</td>
<td>22.94</td>
<td>1.02</td>
<td>0.58</td>
<td>13.57</td>
</tr>
<tr>
<td>12mg/ml</td>
<td>Reverse</td>
<td>23.14</td>
<td>1.07</td>
<td>0.63</td>
<td>15.60</td>
</tr>
<tr>
<td>15mg/ml</td>
<td>Forward</td>
<td>22.89</td>
<td>1.02</td>
<td>0.56</td>
<td>13.07</td>
</tr>
<tr>
<td>15mg/ml</td>
<td>Reverse</td>
<td>23.26</td>
<td>1.06</td>
<td>0.61</td>
<td>15.04</td>
</tr>
</tbody>
</table>
The previous results confirmed that the optimum concentration for these mentioned dopants is 12mg/ml; beyond this concentration, performance decrease gradually. This may be caused by the precursor PbI\textsubscript{2} solution become fully saturated while adding 12mg/ml dopant, and any further solute added to the solution doesn’t dissolve. This results in rough contaminated film which may hinder charge transport in the film and across the interface at the perovskite/charge transport layer.

4.1.2.6 J-V Curves and IPCE Spectra of Solar Cells made of Perovskite Films Before and After Doping with LiTFSI, LiI and BMIImI Additives.

J-V curves and IPCE spectra of perovskite films prepared using the pristine PbI\textsubscript{2} solution and that doped with an optimized concentration of additives LiTFSI, LiI and BMIImI (12mg/ml) are shown in Figure 4.14. Various additive concentrations including 6 mg/ml, 9 mg/ml, 12 mg/ml, 15 mg/ml were studied to find the optimal concentration. As shown in the supporting information, 12mg/ml was found as the optimal concentration for additives LiTFSI, LiI and BMIImI. The photovoltaic performance of perovskite solar cells was increased by doping PbI\textsubscript{2} with LiTFSI, LiI and BMIImI additives. Adding lithium and imidazolium iodide derivatives in the PbI\textsubscript{2} layer leads to an increase in all the photovoltaic parameters including J\textsubscript{sc}, V\textsubscript{oc}, fill factor (FF), and efficiency (\(\eta\)). Table 4.8 shows photovoltaic parameters of fabricated perovskite solar cells before and after adding different additives in the PbI\textsubscript{2} layer. The highest device efficiency was found to be 18% when adding BMIImI additive in the precursor PbI\textsubscript{2} solution. Adding LiI and LiTFSI additives results in enhancement in efficiency (\(\eta\)) of the fabricated devices up to 17.01% and 15.6%, respectively, compared to 11.3% for the device fabricated from the pristine PbI\textsubscript{2} solution. J\textsubscript{sc} was improved from 23.01 mAcm\textsuperscript{2} for the device fabricated using pristine PbI\textsubscript{2} solution when compared to 23.14, 23.36, and 24.70 mAcm\textsuperscript{2} for the devices fabricated using LiTFSI, LiI, and BMIImI doped PbI\textsubscript{2} precursor solutions. The J\textsubscript{sc} of the fabricated solar cells are well matched with KPFM and CS-AFM results. The J\textsubscript{sc} of the fabricated solar cells made of doped perovskite films is higher than those fabricated with the
pristine perovskite films with the order of BMImI > LiI > LiTFSI > no additive. KPFM results confirmed that the doped perovskite films have higher surface potential than the un-doped films, which increases the driving force of electron injection from perovskite to TiO\textsubscript{2} thus increasing J\textsubscript{sc}. CS-AFM results showed that the doped perovskite films have higher surface current than that of the undoped film. In addition, the increase in J\textsubscript{sc} after doping with Li\textsuperscript{+} derivatives may be attributed to the adsorption of the small Li\textsuperscript{+} cation on the surface of TiO\textsubscript{2}. This positively charged Li\textsuperscript{+} cation has electron withdrawing property that enhances electron injection from perovskite to TiO\textsubscript{2} thus improving J\textsubscript{sc}. The N heteroatoms of BMImI have the electron donor property. When they are adsorbed on the TiO\textsubscript{2} surface, electrons are accumulated in the conduction band of TiO\textsubscript{2} leading to an enhancement of J\textsubscript{sc} and a positive shift in the Fermi level (E\textsubscript{F}) of TiO\textsubscript{2}. Thereby, suppression of electron recombination occurs. The V\textsubscript{OC} has been increased from 1.02 V for devices without doping to 1.07, 1.04, and 1.1 V after adding the additives LiTFSI, BMImI, and LiI, respectively [8]. Table 4.8 shows the great enhancement in FF to 0.63, 0.66, and 0.7 after adding the additives LiTFSI, LiI and BMImI, respectively, into the PbI\textsubscript{2} precursor solution compared to a FF of 0.48 for the pristine PbI\textsubscript{2} solution. The photovoltaic parameters in Figures 4.14a and b are in good agreement with results from XRD measurements, UV-VIS spectra and AFM images.

The external quantum efficiency (EQE) in Figure 4.14c is higher than 90\% in the wavelength range of 480-650 nm for the BMImI additive in the PbI\textsubscript{2} solution. All the EQE spectra showed an enhancement after adding BMImI, LiI and LiTFSI additives in the PbI\textsubscript{2} layer with the values of 91.69\%, 89.39\%, 83.49\%, respectively, compared to 70.97\% for the control cell without any additives. The EQE increases are in good agreement with the J-V characteristics, UV-Vis spectra, KPFM, and CS-AFM results. The enhancement in EQE was attributed to the adsorption of positive cations, especially the small Li\textsuperscript{+} cations from LiTFSI, LiI, and BMImI on the TiO\textsubscript{2} surface which enhanced electron injection to the TiO\textsubscript{2}. Since the BMImI doping led to the highest efficiencies, we conducted the reproducibility on the BMImI based devices (Figure 4.14d). The
highest efficiencies among the 20 cells are 18\% with an average at about 16.3\%. Hysteresis, i.e., discrepancy that exists between forward and reverse voltage sweeping during current-voltage measurement is dominant in perovskites and one of the reasons attributed to it in most of the reports is ion migration due to excess ions as interstitial defects [146-148]. In regard to this mechanism, it can be proposed that the doped perovskites have more ionic characteristics, as the dopants are ionic and can be segregated into positively charged and negatively charged ionic species making the ion migration characteristics in the doped perovskites more pronounced. The accumulation of the excess ions can facilitate the polarization of the perovskite to make the hysteresis even more severe as seen in the doped perovskite solar cells.

Figure 4.14 (a) Forward and (b) reverse JV characteristics and (c) EQE of PSCs doped with different additives in the PbI$_2$ layer. (d) Repeatability of PSC doped with BMImI
Table 4.8 Photovoltaic parameters of fabricated perovskite solar cells before and after adding different additives in the PbI₂ layer.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Scan</th>
<th>( J_{sc} ) (mAm⁻²)</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>( \eta ) (%)</th>
<th>EQE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No additive</td>
<td>Forward</td>
<td>22.87</td>
<td>0.94</td>
<td>0.47</td>
<td>10.1</td>
<td>70.97%</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>23.01</td>
<td>1.02</td>
<td>0.48</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>LiTFSI</td>
<td>Forward</td>
<td>22.94</td>
<td>1.02</td>
<td>0.58</td>
<td>13.57</td>
<td>83.49%</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>23.14</td>
<td>1.07</td>
<td>0.63</td>
<td>15.6</td>
<td></td>
</tr>
<tr>
<td>BMImI</td>
<td>Forward</td>
<td>24.03</td>
<td>0.98</td>
<td>0.51</td>
<td>12.1</td>
<td>91.69%</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>24.70</td>
<td>1.04</td>
<td>0.7</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>LiI</td>
<td>Forward</td>
<td>22.92</td>
<td>1.00</td>
<td>0.58</td>
<td>13.33</td>
<td>89.39%</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>23.36</td>
<td>1.10</td>
<td>0.66</td>
<td>17.01</td>
<td></td>
</tr>
</tbody>
</table>

4.1.2.7 Transient and Stability Measurements of Solar Cells made of Perovskite Films Before and After Doping with LiTFSI, LiI and BMImI Additives

Charge transport time and charge carrier lifetime were obtained from transient photocurrent (TPC) and transient photovoltage (TPV) measurements of perovskite solar cells prepared by doping the PbI₂ precursor solution with LiI, LiTFSI and BMImI additives, respectively (Figures 4.15a and b). The transient photocurrent and photovoltage were generated by a nanosecond pulse of a dye laser incident on solar cells under short circuit conditions (by a very low resistor at 50 Ω) and open circuit condition (by a huge resistor at 1 MΩ). No background light was applied. Charge transport time and charge carrier lifetime were obtained by fitting the decay function with mono-exponential equation \( A \exp(-t/\tau) \) where \( \tau \) is the charge carrier life time. As shown in Table 4.9, charge carrier lifetimes of 7.78 µs, 9.10 µs and 9.91 µs were obtained for the cells containing BMImI, LiTFSI, and LiI in the PbI₂ precursor, respectively. These are longer than the charge carrier life time of 5.94 µs for the cell without any additive. The longer charge carrier lifetime for additives-based cells can be attributed to the increase in \( V_{oc} \) and larger perovskite grain size that can reduce trap states and recombination,
thus improving the FF. The charge transport times of 0.84 µs, 2.59 µs and 5.24 µs (Table 4.9) were obtained for the cells containing BMImI, LiI and LiTFSI in PbI₂ precursor, respectively. These are shorter than that of 8.41 µs for the cell without any additive. This is as a result of adsorption of positive cations of dopants on the surface of TiO₂. Especially the small Li⁺ cations that penetrate deeply into the mesoporous nanocrystalline TiO₂ films form an ambipolar Li⁺ - e⁻ with the electrons on the conduction band of TiO₂. This improved electron transport in the nanocrystalline TiO₂ network and enhanced the charge transport time is consistent with the Jsc and EQE results. These results match well with UV-Vis spectra, KPFM, and CS-AFM results as discussed earlier.

![Figure 4.15](image_url)

Figure 4.15 (a) TPC and (b) TPV decay of PSCs before and after adding LiI, BMImI and LiTFSI additives in the PbI₂ precursor. (c) Their efficiencies with respect to exposure time to ambient condition (relative humidity 40%)

Table 4.9 Charge transport parameters of fabricated perovskite solar cells before and after adding different types of additives in PbI₂ layer

<table>
<thead>
<tr>
<th>Additive</th>
<th>Charge transport time (µs)</th>
<th>Charge carrier lifetime (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No additive</td>
<td>8.41</td>
<td>5.94</td>
</tr>
<tr>
<td>LiTFSI</td>
<td>5.24</td>
<td>9.10</td>
</tr>
<tr>
<td>BMImI</td>
<td>0.84</td>
<td>7.78</td>
</tr>
<tr>
<td>LiI</td>
<td>2.59</td>
<td>9.91</td>
</tr>
</tbody>
</table>

Efficiency of the LiTFSI, LiI, and BMImI doped and pristine perovskite solar cells over time with exposure to ambient condition (relative humidity 40%) is shown in Figure 4.15c. The cells were not encapsulated and characterized at
periodic intervals. It was observed that the doped perovskite solar cells showed a much higher stability than the pristine cells. The BMImI, LiI and LiTFSI doped perovskite solar cells exhibited an efficiency decrease of 57%, 60%, and 91% respectively after exposure to air for 70 days versus 93% decrease for pristine perovskite solar cell after only 24 days. This stability enhancement in LiI and LiTFSI incorporated perovskite solar cells may be attributed to the hygroscopic property of the additives. These additives may serve as desiccant materials that will help prevent moisture degradation to the perovskite active material. Improved stability in BMImM incorporated perovskite solar cell can be attributed to the presence of the active [N] heteroatom of the heterocyclic imidazolium group with electron donating property. Any organic compound containing a C-H bond can be degraded when exposure to light and heat giving rise to free radicals. The [N] heteroatom present in BMImI can enable it to act as heat and light stabilizer by binding of the [N] atom with the carbon radical via donating an electron, thus blocking its propagation into more free radicals and improving its stability [8].

J-V characteristics of perovskite solar cells made from 12mg/ml BMImI doped perovskite solar cells compared to perovskite devices doped with mixture of LiI, LiTFSI, and BMImI are shown in Figure 4.16. Table 4.10 shows photovoltaic parameters including short circuit current density (J_sc), open circuit voltage (V_oc), fill factor (FF), and efficiency (η) obtained from the fabricated solar cells. Results show that the best device performance (18.53%) could be obtained when doping the PbI_2 precursor solution with 12mg/ml BMImI only.

![Figure 4.16](image-url)  
**Figure 4.16** (a) Forward and (b) reverse J-V characteristics of PSCs made from perovskite doped with different concentrations of LiTFSI, LiI, and BMImI
Table 4.10 Photovoltaic parameters of fabricated PSCs made from PbI₂ precursor solutions doped with different concentrations of LiTFSI, LiI, and BMImI

<table>
<thead>
<tr>
<th>Additive</th>
<th>Scan</th>
<th>( J_{sc} ) (mAcm(^{-2}))</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12mg/ml BMImI</td>
<td>Forward</td>
<td>24.03</td>
<td>0.98</td>
<td>0.51</td>
<td>12.10</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>24.70</td>
<td>1.04</td>
<td>0.7</td>
<td>18</td>
</tr>
<tr>
<td>12mg BMImI + 12mg LiI/ml</td>
<td>Forward</td>
<td>24.35</td>
<td>0.91</td>
<td>0.45</td>
<td>9.89</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>24.41</td>
<td>1.06</td>
<td>0.66</td>
<td>17.18</td>
</tr>
<tr>
<td>4mg BMImI + 4mg LiI + 4mg LiTFSI/ml</td>
<td>Forward</td>
<td>24.57</td>
<td>0.95</td>
<td>0.5</td>
<td>11.71</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>24.69</td>
<td>1.03</td>
<td>0.67</td>
<td>17.02</td>
</tr>
<tr>
<td>12mg BMImI + 12mg/ml LiI + 12mgLiTFSI/ml</td>
<td>Forward</td>
<td>24.40</td>
<td>0.96</td>
<td>0.53</td>
<td>12.37</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>24.55</td>
<td>1.02</td>
<td>0.62</td>
<td>15.47</td>
</tr>
</tbody>
</table>

4.2 Dithieno[3,2-b:2',3'-d]pyrrole-based Hole Transport Materials for Perovskite Solar Cells with Efficiencies over 18%

4.2.1 Electrochemical measurement of HOMO and LUMO of Spiro-OMeTAD and the thiophene based HTMs

Electrochemical properties of H16 and H18 were investigated by cyclic voltammetry (CV) in the DCM solution containing 0.1 M tetrabutylammonium perchlorate (TBAP, 0.1 M) as the supporting electrolyte. Redox peaks of H16 and H18 are reversible, suggesting high electrochemical stability of both HTMs (Figure 4.17) [149]. As shown in table 4.11, HOMO values of H16 and H18 were calculated to be -4.97 and -4.96 eV, respectively, which are slightly higher than that of spiro-OMeTAD (-5.13 eV). Therefore, the open circuit voltage of PSCs based on H16 and H18 may be lower than that of spiro-OMeTAD. On the other hand, the HOMO values of H16 and H18 are much higher than that of mixed-ion (FAI/MABr/PbI/PbBr/CsI) perovskite (-5.65 eV vs vacuum) [150, 151], providing enough driving force for hole transport.
Table 4.11 Optical and electrochemical properties of H16, H18 and spiro-OMeTAD

<table>
<thead>
<tr>
<th>Dye</th>
<th>$E_0$-0/eV</th>
<th>HOMO/V vs NHE</th>
<th>LUMO/V vs NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>H16</td>
<td>2.65</td>
<td>-4.97</td>
<td>-2.32</td>
</tr>
<tr>
<td>H18</td>
<td>2.65</td>
<td>-4.96</td>
<td>-2.31</td>
</tr>
<tr>
<td>spiro</td>
<td>2.65</td>
<td>-5.13</td>
<td>-2.10</td>
</tr>
</tbody>
</table>

$E_0$-0 is the energy gap between the HOMO and LUMO; $^d$HOMO was recorded by cyclic voltammetry of HTMs; $^e$LUMO was calculated from HOMO–$E_0$-0.

Figure 4.17 (a) Cyclic voltammetry (b) energy level diagram of the three HTMs

4.2.2 Electrical Conductivity and Hole Mobility of the Different HTMs

To estimate the photovoltaic performance of H16 and H18, two key parameters including conductivity and hole mobility were recorded. The conductivities of the doped HTMs were determined using a two-contact electrical conductivity set-up (Glass/HTM/Ag). The semi-log current density-voltage ($J$-$V$) characteristics for in-plane, hole-only devices based on the H16, H18 and spiro-OMeTAD are shown in Figure 4.18a. The obtained conductivity for H16, H18 and spiro-OMeTAD was $9.79 \times 10^{-5}$, $7.92 \times 10^{-5}$ and $8.76 \times 10^{-5}$ S.cm$^{-1}$, respectively. The conductivity of H16 is slightly higher than that of spiro-OMeTAD, while that of H18 is slightly lower than spiro-OMeTAD.

Hole mobility of HTMs was investigated by the space-charge-limited current (SCLC) method using the Mott-Gurney equation [152]. Their $J$–$V$ curves and fitting results are shown in Figure 4.18b. The hole mobility of H16, H18 and
spiro-OMeTAD was determined to be $5.55 \times 10^{-4}$, $2.33 \times 10^{-4}$ and $2.87 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. Clearly, the hole mobility of H16 is much higher than that of H18. This may relate to molecular ordering in the HTM layer. As shown in the inset pictures of Figure 4.13b, H18 displays a cross geometry from the top view of the molecule, while H16 exhibits a planar structure. Therefore, the molecular of H16 could form a higher packing, which can improve the hole transport process at the perovskite-HTM interface.

![Image](image.png)

Figure 4.18 (a) Semi-log current density-voltage characteristics and (b) Square root of current density-voltage curves for H16, H18 and spiro-OMeTAD with chemical doping; the inset pictures are the top view of H16 and H18

### 4.2.3 Measuring J-V Characteristics, EQE, and Stability of Solar Cells made of the Three HTMs

The forward and reverse $J-V$ curves of solar cells fabricated using Spiro-OMeTAD, H16 and H18, respectively are shown in Figures 4.19a and b. The champion data of H16, H18 and spiro-OMeTAD are also presented in Table 4.12. In this work, cesium-containing triple cation perovskite solar cells [45] were fabricated to estimate the photovoltaic performance of the target HTMs. Around 150 nm thick H16 films were deposited on the perovskite film, which was fabricated by one-step method using the Cs/MA/FA perovskite precursor solution [153].

The Incident Photon to Current (IPCE) of the champion PSCs are displayed in Figure 4.19c and Table 4.12. The integrated photocurrent follows the trend of $H16 >$ spiro-OMeTAD $>$ H18, which is consistent with $J$-
Vcharacteristics. The integrated $J_{SC}$ of the champion devices is slightly lower than the measured $J_{SC}$ due to a spectral mismatch between solar simulating system and the EQE light. However, in view of the same conditions in the test, our approach is reliable for fair evaluation of the photovoltaic performance of the three HTMs discussed in this work. The trend of integrated $J_{SC}$ is consistent with the measurements.

The difference of DTP cores for H16 and H18 significantly influenced photovoltaic performance of the DTP-based HTMs. The H16-based PSCs exhibited a short-circuit current density ($J_{SC}$) of 23.28 mA cm$^{-2}$, an open-circuit voltage ($V_{OC}$) of 1.108 V and a fill factor (FF) of 70.42%, yielding a PCE of 18.16% under an AM 1.5G illumination (100 mWcm$^{-2}$). This value is nearly on par with the PCE of the state-of-art HTM spiro-OMeTAD (18.27%), which displays a $J_{SC}$ of 22.92 mA cm$^{-2}$, a $V_{OC}$ of 1.123 V, and a FF of 70.97. In contrast, H18 displays a relatively lower photovoltaic performance with a PCE of 15.29%. Similar hysteresis behaviors were observed for the three HTMs, which indicates that the hysteresis behavior is not arising from the HTM, but from the intrinsic property of the perovskite layer. Perovskite has ionic characteristics and can be segregated into positively charged and negatively charged ionic species leading to ion migration. The accumulation of the excess ions can facilitate the polarization of the perovskite to make the hysteresis. The average forward-reverse PCE follows the trend of spiro-OMeTAD (16.96%) > H16 (16.91%) > H18 (14.08%). In short, our results clearly show that the photovoltaic performance of H16 is comparable to that spiro-OMeTAD. Considering that H16 can be obtained through a facile synthetic route, H16 is better than spiro-OMeTAD.
Figure 4.19 (a) Forward and (b) reverse J-V characteristics, and (c) IPCE with the integrated $J_{sc}$ of the champion devices based on H16, H18 and spiro-OMeTAD; (d) Stability test of the H16, H18 and Spiro-OMeTAD based PSCs.

Table 4.12 PV parameters of the PSCs based on H16, H18 and spiro-OMeTAD

<table>
<thead>
<tr>
<th>HTMs</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mAcm$^{-2}$)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>IPCE (%)</th>
<th>$R_s^a$ (Ω·cm$^2$)</th>
<th>$R_{sh}$ (Ω·cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H16-Rev</td>
<td>1.108</td>
<td>23.28</td>
<td>70.42</td>
<td>18.16</td>
<td>91.00</td>
<td>7.23</td>
<td>3192.81</td>
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<tr>
<td>H16-For</td>
<td>1.084</td>
<td>23.12</td>
<td>61.98</td>
<td>15.53</td>
<td>12.58</td>
<td>15.58</td>
<td>3252.07</td>
</tr>
<tr>
<td>H18-Rev</td>
<td>1.088</td>
<td>22.38</td>
<td>62.82</td>
<td>15.29</td>
<td>87.08</td>
<td>11.16</td>
<td>1744.59</td>
</tr>
<tr>
<td>H18-For</td>
<td>1.048</td>
<td>22.41</td>
<td>54.85</td>
<td>12.88</td>
<td>15.17</td>
<td>601.06</td>
<td>601.06</td>
</tr>
<tr>
<td>spiro-Rev</td>
<td>1.123</td>
<td>22.92</td>
<td>70.97</td>
<td>18.27</td>
<td>87.59</td>
<td>7.40</td>
<td>3297.26</td>
</tr>
<tr>
<td>spiro-For</td>
<td>1.082</td>
<td>22.66</td>
<td>63.84</td>
<td>15.65</td>
<td>9.58</td>
<td>3347.70</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $R_s$ and $R_{sh}$ are given by the PCE measurement system

Furthermore, the cell stability without encapsulation of H16, H18 and Spiro-OMeTAD based PSCs were investigated. The non-encapsulated devices were stored under ambient air condition with a humidity of 20%. The non-
encapsulated device based on H16 and H18 retained 98.90% and 90.80%, respectively, of its initial PCE after storage for two weeks in the dark compared to 98.25% for the Spiro-OMeTAD based device (Figure 4.19d). Note that the data was obtained with 4-Tert-butylpyridine (TBP) as additive, which has a negative effect on the long-term stability of devices [154].

FF is another important photovoltaic parameter responsible for the difference in device performance between H16 and H18. Apparently, the FF of J-V curve (reverse) for H18 (FF = 62.82) is lower than H16 (FF = 70.42). It has been demonstrated that FF is sensitive to the photoactive layer/electrode interface, which can be determined by the series resistance ($R_s$) and shunt resistance ($R_{sh}$). In this work, $R_s$ and $R_{sh}$ were directly extracted from the $J−V$ curves [155].

As presented in Table 4.12, the $R_s$ of H16 is 7.23 Ω·cm$^2$, which is much lower than that of H18 (11.16 Ω·cm$^2$). This comparison suggests that hole transfer between perovskite layer and H16 is better than that between perovskite layer and H18. This is consistent with the hole-mobility measurement results. In addition, as H16 was replaced by H18, the $R_{sh}$ decreased from 3192.81 to 1744.59 Ω·cm$^2$, implying that there are more charge recombination and leakage currents [156]. Due to the smaller $R_s$ and higher $R_{sh}$, the FF of the H16 based PSC (0.70) was much higher than that of H18 (0.62). Note that the FFs of H16 based PSCs are close to those of spiro-OMeTAD, which can be explained by their comparable $R_s$ and $R_{sh}$.

### 4.2.4 Reproducibility of the Solar Cells Fabricated Using the Different HTMs

To investigate the reproducibility of the devices with the three HTMs, 30 devices in several different batches were fabricated. As comparison, the H16 based PSCs exhibited higher reproducibility than H18. More than 90% of the 30 devices using H16 obtained a PCE higher than 16% (Figure 4.20).
4.2.5 AFM Topography and CS-AFM Images of the Three HTMs

To understand the effect of the different hole transport materials on the photovoltaic parameters, we measured their morphology using atomic force microscopy (AFM). All AFM samples have the same structure FTO/TiO$_2$/Perovskite/HTM, which was prepared in the same processing conditions as mentioned in experimental sections. The film of H18 (Figure 4.21c) has a higher Rms (roughness) of 4.68 nm compared to that of H16 (Figure 4.21b), with a Rms of 3.25 nm and spiro-OMeTAD (Figure 4.21a) with RMS of 4.48 nm. Apparently, the H16 HTM layer is smoother than the spiro-OMeTAD, while H18 film is the roughest HTM. The higher film roughness hinders charge transport in the film and across the interface at the perovskite/hole transport layer, thus decreasing the $J_{SC}$ [6, 8]. These results are in good agreement with $J-V$ characteristics which showed that $J_{SC}$ of PCS made of H16 > spiro-OMeTAD > H18.
The current sensing CS-AFM images were presented in Figures 4.21d-f. Results revealed that the surface current of the HTMs follow the trend of H18 < spiro-OMeTAD < H16, with the surface current values of -50.1 < -50.4 < -51.2 PA, respectively. Also, this result is in good agreement with conductivity measurements.

4.2.6 Transient Measurements for the Solar Cells made of the Different HTMs

To scrutinize the charge recombination behavior in the new HTM based PSCs, we recorded the transient photovoltage (TPV, Figure 4.22a) of the studied devices. The charge carrier life time of H16, H18 and spiro-OMeTAD based PSCs were determined to be 32.22, 31.55 and 42.77 µs, respectively. A longer life time means a reduced charge recombination, contributing to a higher V_{OC} in devices. This can explain the higher V_{OC} obtained for H16 based PSCs as compared to those containing H18.
Also, the transient photocurrent of PSCs was recorded (TPC, Figure 4.22b) based on the different HTMs. TPC is closely related to the conductivity of the HTMs since different HTMs cause different photocurrent decay time [157].

The charge transport time of 1.31, 2.31 and 1.96 $\mu$s were found for H16, H18 and spiro-OMeTAD based PSCs, respectively. Apparently, H16 based devices show a faster charge transport as compared to H18 and spiro-OMeTAD based ones. Therefore, perovskite solar cells using H16 as a HTM outperforms H18 and spiro-OMeTAD with respect to the $J_{SC}$. Noted that, the hole mobility and homogeneity of HTM film can affect the hole transport property in the devices [158].

The fast hole transport in H16 based PSCs originates from a combination of relatively higher hole mobility and smoother film. In contrast, H18 shows a slower charge transport, which is the integrated outcome of lower hole mobility and less homogeneous surface.

![Figure 4.22](image.png)

Figure 4.22 (a) Normalized Transient photovoltage (TPV) and (b) Transient photocurrent (TPC) of nip perovskite solar cells made of the H16, H18 and spiro-OMeTAD.
4.3 Synergistic Combination of PEDOT:PSS with Graphene Oxide and Polyaniline, Targeting Stable Perovskite Solar Cells with Efficiency over 18%

Perovskite solar cell device structure using different hole transport layers namely GO, PEDOT:PSS, GO/PANI, PEDOT:PSS/PANI, and GO/PEDOT:PSS/PANI nanocomposites are shown in Figure 4.23.

![Diagram of Perovskite Solar Cell Device Structure](image)

Figure 4.23 Structure of p-i-n PSCs using different HTMs: GO, PEDOT:PSS, GO/PANI, PEDOT:PSS/PANI, and GO/PEDOT:PSS/PANI nanocomposites

4.3.1 Cyclic Voltammetry (CV) Analysis for Measuring HOMO and LUMO of PEDOT:PSS, Graphene Oxide and Polyaniline

The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of PEDOT:PSS, graphene oxide (GO), and Polyaniline (PANI) were measured using cyclic voltammetry (CV) experiments carried out on a potentiostat/galvanostat (Ametek VERSASTAT3-200). In a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu4NPF6) in acetonitrile as an electrolyte with Platinum wire (Sigma Aldrich) as counter electrode, thin films of PANI, GO and PEDOT:PSS deposited onto ITO substrates as a working electrode and Ag/AgCl as reference electrode were used
for the measurements. Voltage was swept at a scan rate of 25 mVs\(^{-1}\) at room temperature and in nitrogen gas environment. Ferrocene was used as an external reference. Oxidation potentials of ferrocene, oxidation and reduction potentials of PEDOT:PSS, GO and PANI are shown in Figure 4.24. HOMO and LUMO values were calculated using the following equations.

\[
E_{\text{HOMO(Polymer)}} = E_{\text{HOMO(Ferrocene)}} - E_{\text{OX(Polymer)}} + E_{\text{OX(Ferrocene)}}
\]

\[
E_{\text{LUMO(Polymer)}} = E_{\text{HOMO(Ferrocene)}} - E_{\text{RED(Polymer)}} + E_{\text{OX(Polymer)}}
\]

Table 4.13 shows the HOMOs and LUMOs of the three hole transport materials (HTMs). The calculated HOMO energy levels were -4.4 eV for PEDOT:PSS, -5.0 and -5.5 eV for GO and -5.1 eV for PANI that are higher than that of CH\(_3\)NH\(_3\)PbI\(_3\) at -5.5 eV. They also are transparent with large bandgaps indicating that their energy levels match with perovskite materials and can be used as HTMs in the p-i-n perovskite solar cell. It was reported that HOMO level of PEDOT:PSS (-5.0 eV) which match with ITO energy level (-4.7 eV) to act as a HTM [159]. However our CV measurements show two observations. First, the HOMO energy level of PEDOT:PSS (-4.4 eV) doesn’t match with the ITO. Second, the broadness of the oxidation peak of PEDOT:PSS which may be attributed to presence of other energy levels and their oxidation peaks overlapped together generating one broad peak. This is because PEDOT:PSS is a doped copolymer containing many organic molecules with different energy levels. In all cases, the CV measurements ensure that the oxidation potentials of PANI and GO are higher than that of PEDOT:PSS, so their HOMO levels are lower than that of PEDOT:PSS. GO has two oxidation peaks and two reduction regions confirming that it has two band gaps. The HOMO of GO was found to be lower than those of PANI and PEDOT:PSS, thus indicating its potential to increase the open circuit voltage, Voc. HOMO of PANI (-5.1 eV) as shown in Figure 4.24 is in between the two HOMOs of GO (-5.0 eV and -5.5 eV) as shown in Figure 4.24c, thus GO/PANI as HTL is expected to induce better charge transport and solar cell
performance when compared to pristine GO. Similarly, HOMO of PANI (-5.1 eV) as shown in Figure 4.24d is in between that of PEDOT:PSS (-4.4 eV) (Figure 4.24b) and CH$_3$NH$_3$PbI$_3$ (-5.5 eV), suggesting better charge transport and solar cell performance with PEDOT:PSS/PANI composite as HTL compared to pristine PEDOT:PSS. Much better charge transport and device performance is expected by mixing the three mentioned HTMs together forming GO/PEDOT:PSS/PANI composite as HTL in pin perovskite solar cell.

![Cyclic voltammetry for measuring (a) oxidation potential of ferrocene and HOMO & LUMO of (b) PEDOT:PSS, (c) graphene oxide and (d) polyaniline](image)

**Figure 4.24** Cyclic voltammetry for measuring (a) oxidation potential of ferrocene and HOMO & LUMO of (b) PEDOT:PSS, (c) graphene oxide and (d) polyaniline

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{\text{OX}}$ (V)</th>
<th>$E_{\text{RED}}$ (V)</th>
<th>$E_{\text{HOMO}}$</th>
<th>$E_{\text{LUMO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrocene</td>
<td>0.3</td>
<td>----</td>
<td>-4.8</td>
<td>----</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>-0.1</td>
<td>-0.85</td>
<td>-4.4</td>
<td>-3.85</td>
</tr>
<tr>
<td>GO</td>
<td>0.5</td>
<td>-1.5</td>
<td>-5.0</td>
<td>-2.8</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>-2.0</td>
<td>-5.5</td>
<td>-1.8</td>
</tr>
<tr>
<td>PANI</td>
<td>0.6</td>
<td>-1.15</td>
<td>-5.1</td>
<td>-3.05</td>
</tr>
</tbody>
</table>

**Table 4.13** CV measurements for Ferrocene, PEDOT:PSS, GO and PANI
4.3.2 UV-Vis Absorbance Spectra of CH$_3$NH$_3$PbI$_3$ Perovskite Films Deposited on top of Pristine PEDOT:PSS, GO and their Composites with PANI.

UV-Vis absorbance spectra of CH$_3$NH$_3$PbI$_3$ perovskite films on top of different hole transport materials were recorded using Agilent 8453 UV-Vis spectrophotometer G1103A. UV-Vis spectra of perovskite film prepared on top of HTL of pristine PEDOT:PSS, pristine GO, GO/PANI composite, PEDOT:PSS/PANI composite, and GO/PEDOT:PSS/PANI composite are shown in Figure 4.25. The HTLs and the perovskite films were prepared following the same procedure as the device fabrication. All the perovskite films on top of the different hole transport materials show a broad absorption across the visible region with two prominent peaks at 470nm and 790nm in absorption spectra. Results indicate that there is no significant change in the absorbance of the perovskite films deposited on different HTLs which is in good agreement with cyclic voltammetry measurements. This ensures that the composites of PEDOT:PSS, GO and PANI are transparent and they neither absorb nor have any effect on the bandgap of CH$_3$NH$_3$PbI$_3$ film. The shoulder band and the onset at ~800 nm that correlates to the optical band gap of ~1.55 eV was observed in all of the absorption spectra of CH$_3$NH$_3$PbI$_3$ perovskite on the different HTLs.

![Figure 4.25 UV-Vis absorbance spectra of CH$_3$NH$_3$PbI$_3$ perovskite films deposited on top of pristine PEDOT:PSS, GO and their composites with PANI](image-url)
4.3.3 XRD of Perovskite Films Deposited on top of the different HTMs and Contact Angles of water droplets on their surfaces.

XRD patterns were recorded to understand the effect of different HTMs on perovskite film crystallinity. Figure 4.26a shows XRD patterns of perovskite films prepared on top of the different HTMs with pristine PEDOT:PSS, GO and composites of GO/PANI, PEDOT:PSS/PANI, and GO/PEDOT:PSS/PANI. The strong Bragg peaks at 14.11°, 28.42°, 31.82°, and 43.09° are assigned to (110), (220), (310), and (330) of CH$_3$NH$_3$PbI$_3$. These characteristic peaks correspond to tetragonal crystal structure of halide perovskite with high crystallinity [8, 160].

The PbI$_2$ peak at 12.12° was not observed in any of the XRD spectra indicating complete conversion of PbI$_2$ to perovskite. The XRD patterns show that adding PANI to PEDOT:PSS significantly enhanced perovskite crystallinity as seen from the high diffraction intensity of the characteristics peaks. Perovskite crystallinity is the highest in GO, therefore adding GO to the PEDOT:PSS/PANI composite has significantly improved the perovskite crystallinity. The XRD results suggest that both PANI and GO can help to obtain perovskite films with higher crystallinity. Previous reports suggested that hydrophobic surface facilitates the formation of good quality perovskite polycrystalline films in comparison to hydrophilic surfaces [161].

To study the hydrophobicity of the HTMs, contact angle measurement was used. Figure 4.26b shows optical microscopy images of water droplets on the surfaces of the different HTM films deposited on ITO surface. Results show that the contact angle of the pristine HTMs follow the trend GO > PANI > PEDOT:PSS with the values 53°, 33°, and 16°, respectively. Contact angle of water droplet on a film of the HTMs is an indication of hydrophobicity and surface tension. This result supports the higher contact angle of 29° achieved for the HTM with PEDOT:PSS mixed with GO and PANI compared to pristine PEDOT:PSS, indicating more hydrophobicity. More hydrophobic HTM will lead to a higher surface tension at the interface between HTM and perovskite, resulting in a highly crystalline perovskite layer at 14.11° and 28.42°. On the other hand,
the more hydrophilic HTM leads to a lower surface tension at the interface between HTM and perovskite resulting in less crystalline perovskite layer [161].

These results are in good agreement with XRD patterns where GO/perovskite had the highest crystallinity, PEDOT:PSS/perovskite had the lowest crystallinity and higher crystallinity of HTM with PEDOT:PSS mixed with GO and PANI compared to pristine PEDOT:PSS.

Figure 4.26 a) XRD patterns of CH$_3$NH$_3$PbI$_3$ perovskite films deposited on top of PEDOT:PSS, PEDOT:PSS/PANI, GO, GO/PANI and GO/PEDOT:PSS/PANI b) Contact angles of the different HTMs on ITO glass substrates.

4.3.4 AFM Topography Images of the Different HTMs and Perovskite Films Deposited on top of each of them.

AFM measurements of different HTLs and perovskite films on top were carried out and their topographical images are shown in Figures 4.27a-e. The different HTLs and perovskite films were prepared in the same conditions for XRD measurements. The root mean square (Rms) values of surface roughness of PEDOT:PSS and GO were found at 1.59 nm and 1.203 nm, respectively, in an area of 4 µm × 4 µm. Topographical images (Figs. 4.27c-e) show that PANI is distributed homogeneously when added to PEDOT:PSS and GO. However, there is a slight increase in Rms at 7.24 nm, 3.92 nm and 2.31 nm for the GO/PANI,
PEDOT:PSS/PANI and GO/PEDOT:PSS/PANI composite films, respectively. To further study the effects of different HTMs and understand the distinct changes in XRD patterns, the AFM topography of perovskite films on top of these HTMs was measured as depicted in figures 4.27f-j. CH$_3$NH$_3$PbI$_3$ perovskite films on pristine GO (Figure 4.27f) and PEDOT:PSS (Figure 4.27g) HTLs exhibited pin-holes on perovskite film that can act as defects to induce severe degradation in device performance. These can trap charge carriers, decrease charge transport and short circuit current. Adding PANI to GO decreased pin-holes in the HTL (Figure 4.27c vs 4.27a) resulting in more homogeneous large grain perovskite films (Figure 4.27h vs 4.27f). The films are smoother (Rms=12.79 nm, fig. 4.27h) with larger crystalline domains than those on the pristine GO (Rms=16.4 nm, Figure 4.27f). The larger crystal size may be attributed to the slow evaporation of solvent molecules from the rough surface of GO/PANI, which traps or adsorbs a large amount of solvent. The residual solvent molecules assisted the inter-diffusion of PbI$_2$ and MAI components into each other resulting in slow crystallization of perovskite phase and formation of large particles. Adding PANI to PEDOT:PSS also resulted in a smoother perovskite film (Rms=13.22 nm, Figure 4.27i) with closely packed surface topography compared to that on the pristine PEDOT:PSS (Rms=20.7 nm, Figure 4.27g). These results are expected to assist perovskite solar cells with improved charge transport and higher power conversion efficiency after adding PANI in the PEDOT:PSS and GO layers. The smoothest perovskite films could be prepared on top of the GO/PEDOT:PSS/PANI composite layer (Rms=12.47 nm, Figure 4.27j). The higher perovskite film roughness may cause issues for depositing an electron transport layer (ETL) and top electrode, hindering charge transport and collection across the interface of perovskite/ETL/top electrode.
Figure 4.27 Tapping mode AFM topography images of (a) pristine GO, (b) pristine PEDOT:PSS, (c) GO/PANI composite (2:1), (d) PEDOT:PSS/PANI composite (2:1), (e) GO/PEDOT:PSS/PANI composite (1:1:1) and CH$_3$NH$_3$PbI$_3$ perovskite (PVK) films deposited on top of each of them (f-j).
4.3.5 CS-AFM Images of the Different HTMs.

To understand the role of the conductivity of PANI and GO, CS-AFM measurements on the pristine and composite HTLs were carried out. CS-AFM images of the thin films of different HTMs are shown in Figure 4.28. The pristine PEDOT:PSS film has the lowest average value with a surface current of 0.16 nA (Figure 4.28a), while pristine GO and pristine PANI films exhibited 1.21 nA (Figure 4.28b) and 0.59 nA (Figure 4.28c), respectively. The average surface current of individual HTL follows the trend PEDOT:PSS < PANI < GO, and hence the same trend in conductivity. PANI with higher conductivity than PEDOT:PSS, when added into PEDOT:PSS, enhanced the surface current of PEDOT:PSS to 0.43 nA (Figure 4.28d) and hence conductivity. Similarly, GO when added into PANI increased the conductivity and surface current of PANI to 1.16 nA (Figure 4.28e). The GO/PEDOT:PSS/PANI (1:1:1) composite HTL achieved a surface current of 1.1 nA (Figure 4.28f) which is higher than the individual PEDOT:PSS and composite PEDOT:PSS/PANI (2:1). These results suggest improvement in short circuit current of the perovskite solar cell when doping PEDOT:PSS with PANI and GO.

Figure 4.28 CS-AFM images of (a) pristine PEDOT:PSS, (b) pristine GO, (c) pristine PANI (d) PEDOT:PSS/PANI composite (2:1), (e) GO/PANI composite (2:1) and (f) GO/PEDOT:PSS/PANI composite (1:1:1) on top of Glass/ITO/HTL
4.3.6 Semi-log Current-Voltage Characteristics for Measuring the Conductivities of the Different HTM Films

The CS-AFM images in Figure 4.29 showed that surface currents of prepared films are non-homogeneous. Some regions exhibit a very high conductivity, while other regions exhibit low conductivity especially for the pristine PANI and pristine GO films. The poor adhesion of the hydrophobic PANI nanoparticles with the hydrophilic ITO substrates leads to a surface not fully covered with the HTM, resulting in very low current. The gaps between the micro-flakes in GO films resulted with a very low or almost zero current, while other regions had a very high current. This causes difficulty in measuring the conductivity accurately. Figure 4.29 shows the semi-log current-voltage (IV) curves of different HTMs. The conductivity (\(\sigma\)) was determined by using the following equation [162]:

\[
\sigma = \frac{L}{Rwd}
\]

where, \(L\) is the channel length (0.05 mm), \(w\) is the channel width (0.2 \(\mu\)m), \(d\) is the film thickness and \(R\) is the resistance. Thicknesses of the prepared films were measured with a DekTak profilometer.

The pristine GO films have a very poor conductivity of \(1.06 \times 10^{-5}\) S.cm\(^{-1}\) due to the gaps among the large flakes (Figure 4.29 and Table 4.14). The pristine PANI films have a relatively low conductivity of \(9.17 \times 10^{-4}\) S.cm\(^{-1}\) caused by the poor adhesion with ITO substrate. The pristine PEDOT:PSS exhibited a slightly higher conductivity at \(4.03 \times 10^{-3}\) S.cm\(^{-1}\). Adding PANI to the pristine PEDOT:PSS led to a much higher conductivity of \(1.66 \times 10^{-2}\) S.cm\(^{-1}\) for the PEDOT:PSS/PANI (2:1) films. Similarly, adding PANI to the pristine GO films significantly increased the conductivity to \(7.56 \times 10^{-2}\) S.cm\(^{-1}\) in the GO/PANI (2:1) films because PANI could fill the gaps among the GO microplates/particles and the GO could improve the film adhesion to substrates. The highest conductivity was achieved in the GO/PEDOT:PSS/PANI (1:1:1) films, which exhibited a conductivity at 0.814 S.cm\(^{-1}\), attributed to the film compactness.
Figure 4.29 Semi-log current-voltage characteristics of different HTM films

Table 4.14 Conductivites of the different HTMs

<table>
<thead>
<tr>
<th>HTM</th>
<th>GO</th>
<th>PANI</th>
<th>PEDOT:PSS</th>
<th>PEDOT:PSS/PANI (2:1)</th>
<th>GO/PANI (2:1)</th>
<th>GO/PEDOT: PSS/PANI (1:1:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity ($\sigma$) (S.cm$^{-1}$)</td>
<td>$1.06 \times 10^{-5}$</td>
<td>$9.17 \times 10^{-4}$</td>
<td>$4.03 \times 10^{-3}$</td>
<td>$1.66 \times 10^{2}$</td>
<td>$7.56 \times 10^{2}$</td>
<td>0.814</td>
</tr>
</tbody>
</table>
Figure 4.30 2D Surface potential of (a) Glass/ITO/PEDOT:PSS/MAPbI$_3$ and Glass/ITO/HTL where HTL is (b) Pristine PEDOT:PSS (c) Pristine GO (d) PEDOT:PSS/PANI composite (2:1) (e) GO/PANI composite (2:1) (f) GO/PEDOT:PSS/PANI composite (1:1:1)
4.3.7 KPFM Measurements of the Different HTMs and Perovskite Film

Energy levels of HTL need to be well matched with that of the CH$_3$NH$_3$PbI$_3$ perovskite to facilitate efficient hole transfer. To investigate this, KPFM measurements were carried out to determine the surface potential. Surface potential distribution of perovskite film and different HTMs including pristine PEDOT:PSS, pristine GO, PEDOT:PSS/PANI composite (2:1), GO/PANI composite (2:1) and GO/PEDOT:PSS/PANI composite (1:1:1) is shown in Figure 4.31. The surface potential distributions were acquired from KPFM images (Figure 4.30). The pristine PEDOT:PSS, pristine GO, PEDOT:PSS/PANI (2:1), GO/PANI (2:1) and PANI/PEDOT/GO (1:1:1) all exhibited a high average surface potential at -0.243 V, -0.606 V, -0.422 V, -0.435 V, and -0.573 V, respectively. These are higher than that of perovskite film with -0.757 V, which indicates that all the HTLs of interest can function as efficient HTMs to transfer holes from the perovskite to HTMs. Surface potential distributions show that the pristine GO film has the lowest average surface potential (-0.606 V) and the pristine PEDOT:PSS film with the highest (-0.243 V). These results indicate that perovskite solar cells fabricated using pristine GO as HTM can achieve the highest V$_{OC}$, while those fabricated using pristine PEDOT:PSS can lead to the lowest V$_{OC}$. This is consistent with the experimentally obtained V$_{OC}$ (Figure 4.35a,b and Table 4.17), which will be discussed later. Doping the HTLs with PANI results in a decrease in the average PEDOT:PSS surface potential from -0.243 to -0.422 V. This result is in good agreement with energy level diagram shown in Figure 4.32. GO has the lowest value of HOMO (-5.3 eV) [163], PEDOT:PSS has the highest value of HOMO (-5.0 eV) [164, 165], PANI has its HOMO value (-5.1 eV) between those of GO and PEDOT:PSS. Adding GO to PEDOT:PSS/PANI composite leads to additional decrease in the average surface potential from -0.422 to -0.573 V. This is expected to further enhance the V$_{OC}$ of the devices fabricated using GO/PEDOT:PSS/PANI compared to that pristine PEDOT:PSS and PEDOT:PSS/PANI composite.
Figure 4.31 Surface potential distribution of the CH3NH3PbI3 perovskite film and different pristine and composite HTMs namely pristine PEDOT:PSS, pristine GO, PEDOT:PSS/PANI composite (2:1), GO/PANI composite (2:1) and GO/PEDOT:PSS/PANI composite (1:1:1)

Figure 4.32 Schematic diagram showing energy levels of ITO, CH3NH3PbI3 perovskite and different HTMs including PEDOT:PSS, PANI and GO

4.3.8 AFM Topography Images of Pristine PANI and J-V Characteristics of Perovskite Solar Cells made from Pristine PANI as a Hole Transporting Material.

The tapping mode AFM topography image of pristine PANI film and J-V characteristics of perovskite solar cells made from pristine PANI as HTM are shown in Figure 4.33. It can be seen that PANI particles are agglomerated, resulting in a rough film with numerous gaps that can trap charge carriers
indicating a device with low Jsc. Table 4.15 shows photovoltaic parameters including short circuit current density (Jsc), open circuit voltage (Voc), fill factor (FF) and efficiency (η) obtained from the fabricated perovskite solar cells with PANI as HTM. It was observed that PANI could be used as an HTM for the inverted perovskite solar cell which is in good agreement with cyclic voltammetry measurements; however, the efficiency was very low (3.33%). This low efficiency can be attributed to the poor adhesion and contact between the hydrophobic PANI polymer chains and the hydrophilic ITO substrate. These results suggest that pristine PANI alone is not suitable as an HTM but rather should be doped or mixed with other HTMs to achieve better photovoltaic performance.

![AFM topography image of pristine PANI](image1.png)

**Figure 4.33** a) Tapping mode AFM topography images of pristine PANI, b) Forward and reverse current density-voltage (J-V) characteristics of perovskite solar cells made from pristine PANI as a hole transporting material

Table 4.15 Photovoltaic parameters of fabricated perovskite solar cells made from pristine PANI as a hole transporting material.

<table>
<thead>
<tr>
<th>HTM</th>
<th>Scan</th>
<th>Jsc  (mAcm⁻²)</th>
<th>Voc  (V)</th>
<th>FF</th>
<th>η   (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine PANI</td>
<td>Forward</td>
<td>6.64</td>
<td>0.88</td>
<td>0.57</td>
<td>3.33%</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>9.78</td>
<td>0.73</td>
<td>0.45</td>
<td>3.23%</td>
</tr>
</tbody>
</table>
4.3.9 Optimizing the Ratio of PEDOT:PSS, GO, and PANI in the HTM Composite to Achieve Solar Cell with better PV Parameters

J-V characteristics of perovskite solar cells made from pristine PEDOT:PSS, pristine GO, PEDOT:PSS/PANI composite with different ratios (3:1, 2:1, and 1:1), and the different GO/PANI composite ratios (3:1, 2:1, and 1:1) as HTMs are shown in Figure 4.34., and Table 4.16 summarizes the photovoltaic parameters. It was observed that by increasing the concentration of PANI as additive into PEDOT:PSS, there was enhancement in Jsc (from 18.54 to 22.23 mAcm$^{-2}$) and $\eta$ (from 12.547 to 16.29%) for PEDOT:PSS/PANI ratio of 2:1. By the same way, increasing the concentration of PANI as additive in GO as HTM results in an enhancement in Jsc (from 15.69 to 20.39 mAcm$^{-2}$) and $\eta$ (from 6.24 to 14.35%) when GO/PANI ratio of 2:1. This Jsc enhancement is attributed to the high conductivity of PANI and the enhanced hole transfer achieved via adding the PANI HOMO (-5.1 eV) as shown by CS-AFM and CV results, respectively. The enhancement in $\eta$ is not only due to the higher Jsc, but also there is a noticeable improvement in FF resulting from the balanced charge transport after adding PANI. A slight enhancement in $V_{OC}$ was observed when adding PANI to PEDOT:PSS which is in good agreement with cyclic voltammetry measurements that ensured the HOMO of PANI (-5.1 eV) is lower than that of PEDOT:PSS, with a measured value of (-4.4 eV) or the reported value of (-5.0 eV). Beyond the ratio (2:1) of the composites, PEDOT:PSS/PANI and GO/PANI led to a decrease in $\eta$ which may be because of the high concentration of PANI resulting in a poorer adhesion and contact between the HTM and ITO.
Figure 4.34 JV characteristics of perovskite solar cells: (a) Forward and (b) Reverse characteristics of PEDOT:PSS and PEDOT:PSS/PANI composites (3:1, 2:1, and 1:1) as HTMs. (c) Forward and (d) Reverse characteristics of GO and GO/PANI composites (3:1, 2:1, and 1:1) as HTMs.

Table 4.16 Photovoltaic parameters of fabricated PSCs with pristine PEDOT:PSS, pristine GO, the different PEDOT:PSS/PANI composite ratios (3:1, 2:1, and 1:1) and the different GO/PANI composite ratios (3:1, 2:1, and 1:1) as HTMs

<table>
<thead>
<tr>
<th>HTM</th>
<th>Scan</th>
<th>Jsc (mAcm⁻²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pristine PEDOT:PSS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forward</td>
<td></td>
<td>18.31</td>
<td>0.92</td>
<td>0.65</td>
<td>11.02</td>
</tr>
<tr>
<td>Reverse</td>
<td></td>
<td>18.54</td>
<td>0.95</td>
<td>0.71</td>
<td>12.54</td>
</tr>
<tr>
<td><strong>PEDOT:PSS/PANI (3:1)</strong></td>
<td></td>
<td>20.67</td>
<td>0.92</td>
<td>0.66</td>
<td>12.51</td>
</tr>
<tr>
<td>Forward</td>
<td></td>
<td>20.07</td>
<td>0.99</td>
<td>0.72</td>
<td>14.23</td>
</tr>
<tr>
<td>Reverse</td>
<td></td>
<td>22.23</td>
<td>0.99</td>
<td>0.74</td>
<td>16.29</td>
</tr>
<tr>
<td><strong>PEDOT:PSS/PANI (2:1)</strong></td>
<td></td>
<td>19.90</td>
<td>1.00</td>
<td>0.69</td>
<td>13.64</td>
</tr>
<tr>
<td>HTM</td>
<td>Reverse</td>
<td>Forward</td>
<td>Forward</td>
<td>Forward</td>
<td></td>
</tr>
<tr>
<td>--------------------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>Pristine GO</td>
<td>15.69</td>
<td>14.82</td>
<td>15.69</td>
<td>14.82</td>
<td></td>
</tr>
<tr>
<td>GO/PANI (3:1)</td>
<td>16.54</td>
<td>16.18</td>
<td>19.60</td>
<td>22.86</td>
<td></td>
</tr>
<tr>
<td>GO/PANI (2:1)</td>
<td>20.39</td>
<td>19.60</td>
<td>20.39</td>
<td>22.86</td>
<td></td>
</tr>
<tr>
<td>GO/PANI (1:1)</td>
<td>15.25</td>
<td>20.23</td>
<td>20.23</td>
<td>20.23</td>
<td></td>
</tr>
</tbody>
</table>

4.3.10 J-V Characteristics and IPCE Spectra of p-i-n Perovskite Solar Cells made of the Different HTMs, Repeatability of the Device made of GO/PEDOT:PSS/PANI Composite (1:1:1) as HTL, and Stability Compared to the Device made of Pristine PEDOT:PSS.

J-V characteristics, incident photon-to-current efficiency (IPCE) spectra, repeatability, and reproducibility of CH$_3$NH$_3$PbI$_3$ perovskite solar cells using different pristine and composite HTMs are shown in Figure 4.35 and table 4.17. Perovskite solar cells containing the pristine PEDOT:PSS HTL achieved a PCE of 12.97%, which was much higher than 6.24% for pristine GO HTL, although pristine GO was observed to have higher conductivity than the pristine PEDOT:PSS. The lower PCE from GO based devices may be caused by the large particle size of GO (flake size = 0.3 – 0.7 microns). The gaps in bulky GO films block charge transport pathways, trap charge carriers and decrease device efficiency, which is supported by conductivity measurements in figure 4.35 and table 4.17 (supporting information). However, the device with the pristine GO HTL exhibits a higher $V_{OC}$ (1.02 V) than that of the pristine PEDOT:PSS (0.95 V) which is supported by the surface potential studies. Adding PANI to PEDOT:PSS and GO significantly improved $J_{SC}$. Perovskite solar cells using GO/PANI and PEDOT:PSS/PANI achieved PCE of 14.35% and 16.29%, respectively. These are much higher than those from the pristine PEDOT:PSS and GO HTLs,
respectively. The improvement for PEDOT:PSS/PANI cells is due to PANI bringing a new HOMO energy level between the HOMO of PEDOT:PSS and that of perovskite, which facilitates hole extraction. This is also in accordance to the CS-AFM and conductivity results. The enhancement of efficiency in GO/PANI based cells can be attributed to the higher conductivity (shown in Figure 4.35) of GO/PANI film and efficient hole extraction. The higher conductivity is achieved by filling up the gaps between the micro-flakes of GO by PANI that results in a more compact HTL, thus providing provide a better charge transport pathway. Also, the interactions between positively charged sulfonated PANI and negatively charged GO accelerate the hole transfer and extraction from perovskite to ITO.

The introduction of a new HOMO energy level (-5.1 eV) by PANI between GO (-5.3 eV) and ITO (-4.7 eV), enhances the J_sc. Similar mechanisms can be applied to the PEDOT:PSS/PANI composite. The introduction of -SO_3H groups on the phenyl ring of the positively charged PANI (p-type) increases its electron withdrawing property and this further enhances charge transfer as reported previously [166].

The GO/PANI (2:1) composite has a higher conductivity than PEDOT:PSS/PANI (2:1) (Figure 4.35), however cells fabricated using GO/PANI (2:1) showed a lower J_sc than those fabricated with the PEDOT:PSS/PANI (2:1) composite. The reason is that the work function of PEDOT:PSS is higher than that of GO, which increases the driving force of hole transfer at the interface between the perovskite and HTL. This leads to a higher J_sc and lower V_oc in the cells fabricated by PEDOT:PSS/PANI (2:1), which is confirmed by transient photocurrent measurements (Figure 4.38). The highest efficiency of 18.12% was achieved by mixing all the three HTMs into a GO/PEDOT:PSS/PANI (1:1:1) composite as HTL. The key contribution of the addition of GO and PANI into PEDOT:PSS is the improvement in both V_oc and J_sc. Although CS-AFM results showed that the GO/PEDOT:PSS/PANI (1:1:1) composite led to a slightly lower surface current than that of GO/PANI (2:1), the cells with GO/PEDOT:PSS/PANI (1:1:1) as HTL had higher J_sc than the cell with GO/PANI (2:1). The
GO/PEDOT:PSS/PANI film has a lower ratio of large size GO particles which makes it more compact compared to the GO/PANI (2:1) film by decreasing the gaps in the film. This helps to improve charge transport and prevent charge carrier isolations. This is in good agreement with conductivity results (Figure 4.29).

The IPCE spectra (Figure 4.35c) are in good agreement with the J_sc values obtained from the J-V characteristics. IPCE has been enhanced after adding PANI and GO to PEDOT:PSS. IPCE is ~ 90% in the wavelength range of ca. 400-750 nm for perovskite solar cells comprising a combined dopant of PANI and GO in the PEDOT:PSS HTL. This is much higher than the values of 60.55% and 78.34% for those with the pristine GO and PEDOT:PSS, respectively, as HTLs. The highest achieved IPCE is 92.89% from solar cells using the GO/PEDOT:PSS/PANI (1:1:1) composite as an HTL, and the integrated short circuit current density (J_sc) for this condition under the standard reference spectrum is 22.20 mAcm\(^{-2}\) compared to 22.98 mAcm\(^{-2}\) for the response measured under the simulator. Figure 4.35d shows the repeatability test for the devices fabricated using GO/PEDOT:PSS/PANI (1:1:1) as HTL. The average efficiency of the 16 cells was about 17%, with the highest efficiency of 18.12%.

The normalized efficiency of perovskite solar cells made of pristine PEDOT:PSS and GO/PEDOT:PSS/PANI (1:1:1) as HTMs versus time upon exposure to air and relative humidity of 20% at room temperature is shown in Figure 4.35e. The cells were not encapsulated and characterized at periodic intervals. It was observed that the device containing the composite HTM showed a much higher stability than the pristine cells. The cells based on the PEDOT:PSS HTM exhibited 60% efficiency decrease after just 8 days compared to 40 days for the cell based on GO/PANI/PEDOT (1:1:1) HTM. The device containing GO/PANI/PEDOT (1:1:1) HTM exhibited an efficiency decrease of 75% after 80 days exposure, compared to complete degradation for the device made of pristine PEDOT:PSS HTM. This stability enhancement as a result of doping PEDOT:PSS with GO and PANI might be due to the use of PANI that is claimed to have one of the highest environmental stability among conducting polymers with metallic
characteristics and in addition, PANI and GO prohibit direct contact of ITO with highly acidic PEDOT:PSS [57, 167].

Figure 4.35 (a) Forward and (b) reverse J-V characteristics, and (c) IPCE of PSCs made from the different HTMs. (d) Repeatability of the device made of GO/PEDOT/PANI composite (1:1:1) as HTL. (e) Efficiency of GO/PEDOT:PSS/PANI based PSC with respect to time (RH 20%).
Table 4.1 Photovoltaic parameters of perovskite solar cells made with different HTMs of pristine PEDOT:PSS, pristine GO, PEDOT:PSS/PANI composite (2:1), GO/PANI composite (2:1) and GO/PEDOT:PSS/PANI composite (1:1:1).

<table>
<thead>
<tr>
<th>HTM</th>
<th>Bias</th>
<th>Jsc (mAcm(^{-2}))</th>
<th>Voc (V)</th>
<th>FF</th>
<th>η (%)</th>
<th>IPCE (%)</th>
<th>Jsc from IPCE (mAcm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>Forward</td>
<td>14.82</td>
<td>1.00</td>
<td>0.33</td>
<td>4.93</td>
<td>60.55</td>
<td>14.24</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>15.69</td>
<td>1.02</td>
<td>0.39</td>
<td>6.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Forward</td>
<td>18.31</td>
<td>0.92</td>
<td>0.65</td>
<td>11.02</td>
<td>78.34</td>
<td>18.09</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>18.54</td>
<td>0.95</td>
<td>0.71</td>
<td>12.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GO/PANI (2:1)</td>
<td>Forward</td>
<td>19.60</td>
<td>1.00</td>
<td>0.62</td>
<td>12.1</td>
<td>83.61</td>
<td>19.77</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>20.39</td>
<td>1.02</td>
<td>0.69</td>
<td>14.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEDOT:PSS/PANI (2:1)</td>
<td>Forward</td>
<td>20.07</td>
<td>0.99</td>
<td>0.72</td>
<td>14.23</td>
<td>87.70</td>
<td>20.41</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>22.23</td>
<td>0.99</td>
<td>0.74</td>
<td>16.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GO/PEDOT:PSS/PANI (1:1:1)</td>
<td>Forward</td>
<td>22.98</td>
<td>1.03</td>
<td>0.7</td>
<td>16.57</td>
<td>92.89</td>
<td>22.20</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>22.89</td>
<td>1.05</td>
<td>0.754</td>
<td>18.12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.3.11 Electrochemical Impedance Spectroscopy (EIS) of Perovskite Solar Cells made of the Different HTMs at GO, PEDOT:PSS, GO/PANI (2:1), PEDOT:PSS/PANI (2:1), GO/PEDOT:PSS/PANI (1:1:1) in the Dark

To understand the charge transfer process at the HTL/perovskite interface, electrochemical impedance spectroscopy (EIS) was used to characterize perovskite solar cells with different HTLs. Figure 4.36a contains Nyquist plots of the cells measured in dark showing semicircles, which are related to the charge transfer resistance (R\(_{CT}\)) at the HTL/perovskite interface. The R\(_{CT}\) values were fitted using a standard equivalent circuit as shown in Figure 4.36b and are summarized in Table 4.18. The results are in agreement with the device performance from J-V characteristics. The perovskite solar cells fabricated using the GO/PEDOT:PSS/PANI (1:1:1) composite HTL have the lowest R\(_{CT}\), indicating the most efficient charge transfer at the HTL/perovskite interface. In
addition, cells with GO/PANI and PEDOT:PSS/PANI have lower $R_{CT}$ compared to individual GO and PEDOT:PSS.

![Nyquist plots of perovskite solar cells with different HTMs](image)

Figure 4.36 (a) Nyquist plots of perovskite solar cells with the different HTMs at GO, PEDOT:PSS, GO/PANI (2:1), PEDOT:PSS/PANI (2:1), GO/PEDOT:PSS/PANI (1:1:1) in the dark, (b) equivalent circuit used for fitting

Table 4.18 Charge transfer resistance ($R_{CT}$) at the HTL/perovskite interface with different HTMs

<table>
<thead>
<tr>
<th>Hole transport material</th>
<th>$R_{CT}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>155.23</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>130.81</td>
</tr>
<tr>
<td>GO/PANI (2:1)</td>
<td>118.22</td>
</tr>
<tr>
<td>PEDOT:PSS/PANI (2:1)</td>
<td>94.04</td>
</tr>
<tr>
<td>GO/PEDOT:PSS/PANI (1:1:1)</td>
<td>35.47</td>
</tr>
</tbody>
</table>
4.3.12 Transient Measurements for the Solar Cells made of the Composites of PEDOT:PSS, GO, and PANI HTMs

Plots of the charge transport time and carrier life time obtained from transient photocurrent and photovoltage measurements of perovskite solar cells fabricated with pristine and composite hole transport materials are shown in Figure 4.37 and Table 4.19, respectively. Charge transport times of 0.92 µs, 0.80 µs and 0.25 µs were obtained for the cells fabricated with GO/PANI (2:1), PEDOT:PSS/PANI (2:1) and GO/PEDOT:PSS/PANI (1:1:1), respectively which were lower compared to charge transport time of 1.22 µs and 1.16 µs for the cells with pristine GO and PEDOT:PSS. Carrier life time of pristine GO was the longest (3.64 µs) while pristine PEDOT:PSS was the shortest (0.18 µs). Adding PANI to PEDOT:PSS led to a device (PANI:PEDOT=2:1) with a longer carrier life time (0.19 µs). Further addition of GO to PANI/PEDOT composite results in a device (PANI:PEDOT:GO=1:1:1) with a longer carrier life time (2.13 µs) compared to those made of pristine PEDOT:PSS and PEDOT:PSS/PANI (2:1). These results are not highly significant; however, they are in good agreement with CS-AFM, KFM, JV and EQE characteristics confirming that positive PANI has a large positive impact on accelerating charge transport thus increasing surface current, short circuit current (Jsc) and Incident photon-to-current conversion efficiency (IPCE).

Figure 4.37 (a) TPC and (b) Normalized TPV of pin PSCs fabricated with different pristine and composite HTMs.
Table 4.19 Fitted charge transport lifetime and carrier life time of perovskite solar cells fabricated with pristine PEDOT:PSS, pristine GO and their composites with PANI as HTMs.

<table>
<thead>
<tr>
<th>HTM</th>
<th>Charge transport time (µs)</th>
<th>Carrier life time (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>1.22</td>
<td>3.64</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>1.16</td>
<td>0.18</td>
</tr>
<tr>
<td>GO/PANI (2:1)</td>
<td>0.92</td>
<td>0.89</td>
</tr>
<tr>
<td>PEDOT:PSS/PANI (2:1)</td>
<td>0.80</td>
<td>0.19</td>
</tr>
<tr>
<td>GO/PEDOT:PSS/PANI (1:1:1)</td>
<td>0.25</td>
<td>2.13</td>
</tr>
</tbody>
</table>

4.3.13 The Stabilized Photocurrent Density and PCE Obtained while Holding the Solar Cell near the Maximum Power Point voltage of 0.86 V

To figure out the reliability of this device, the stabilized photocurrent was measured (Figure 4.38). The device delivered almost a steady photocurrent with an average value of 20.5 mAcm\(^{-2}\), corresponding to almost a steady PCE with an average value of 16.0%, measured at a constant bias of 0.86 V near the maximum power point for a period of 120 s.

![Figure 4.38](chart.png)

Figure 4.38 The stabilized photocurrent density (black) and PCE (blue) obtained while holding the solar cell near the maximum power point voltage 0.86 V.
4.4 Substituting Conventional High Cost PEDOT:PSS by Facile Synthesis of Polyaniline

4.4.1 Cyclic Voltammetry Analysis for Measuring HOMO and LUMO of the Electrochemically Synthesized HNO₃-PANI and HNO₃-LiTFSI-PANI

The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the electrochemically synthesized Polyaniline (HNO₃-PANI) were measured using cyclic voltammetry (CV) experiment, carried out on a potentiostat/galvanostat (Ametek VERSASTAT3-200). A solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu4NPF6) in acetonitrile as electrolyte, platinum wire (Sigma Aldrich) as counter electrode, thin film of HNO₃-PANI deposited on ITO substrates as working electrode, and Ag/AgCl as the reference electrode were used for the measurements. Voltage was swept at a scan rate of 25 mVs⁻¹ at room temperature and in a nitrogen gas environment. Ferrocene was used as an external reference. Figure 4.39a shows one oxidation peak of ferrocene at the potential 0.3V while the electrochemically synthesized HNO₃-PANI has one oxidation peak at the potential 0.9V (Figure 4.39b) and one reduction peak at the potential -0.9V (Figure 4.39c). Two oxidation peaks of electrochemically synthesized HNO₃-LiTFSI-PANI in the positive scan at the potentials 0.9V and 1.0V are shown in Figure 4.39d and two reduction peaks in the negative scan at the potentials -0.9V and -1.2V are shown in Figure 4.39e. HOMO and LUMO values were calculated using the following equations:

\[
E_{\text{HOMO(Polymer)}} = E_{\text{HOMO(Ferrocene)}} - E_{\text{OX(Polymer)}} + E_{\text{OX(Ferrocene)}}
\]

\[
E_{\text{LUMO(Polymer)}} = E_{\text{HOMO(Ferrocene)}} - E_{\text{RED(Polymer)}} + E_{\text{OX(Polymer)}}
\]

Table 4.20 shows the HOMO and LUMO of HNO₃-PANI with the values -5.4 eV and -3.0 eV, respectively, thus the bandgap is 2.4 eV. This large bandgap of HNO₃-PANI makes it transparent to light, thus suitable as an HTM for the p-i-n perovskite solar cell. Doping the electrolyte solution with LiTFSI results in two HOMO values for HNO₃-LiTFSI-PANI (-5.4 eV and -5.5 eV), as well as two
LUMO values (-2.6 eV and -3.0 eV). Figure 4.40 is a schematic diagram showing energy levels of CH$_3$NH$_3$PbI$_3$, HNO$_3$-PANI, and LiTFSI-HNO$_3$-PANI. These results project an increase in the work function of PANI as a result of LiTFSI doping, thus expecting improvement in $V_{OC}$ of the fabricated device.

Figure 4.39 Cyclic voltammetry (CV) analysis for measuring (a) oxidation potential of ferrocene, (b) HOMO and (c) LUMO of the electrochemically synthesized HNO$_3$-PANI. (d) HOMO and (e) LUMO of the electrochemically synthesized HNO$_3$-LiTFSI-PANI
Table 4.20 Cyclic voltammetry measurements for Ferrocene and electrochemically synthesized HNO$_3$-PANI

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{OX}$ (V)</th>
<th>$E_{RED}$ (V)</th>
<th>$E_{HOMO}$</th>
<th>$E_{LUMO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrocene</td>
<td>0.3</td>
<td>---</td>
<td>-4.8</td>
<td>----</td>
</tr>
<tr>
<td>HNO$_3$-PANI</td>
<td>0.9</td>
<td>-0.9</td>
<td>-5.4</td>
<td>-3.0</td>
</tr>
<tr>
<td>LiTFSI-HNO$_3$-PANI</td>
<td>1.0</td>
<td>-1.2</td>
<td>-5.5</td>
<td>-2.6</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>-0.9</td>
<td>-5.4</td>
<td>-3.0</td>
</tr>
</tbody>
</table>

Figure 4.40 Schematic diagram showing energy levels of CH$_3$NH$_3$PbI$_3$, HNO$_3$-PANI, and LiTFSI-HNO$_3$-PANI

4.4.2 AFM Topography Images of PEDOT:PSS and the Electrochemically Synthesized HNO$_3$-PANI

AFM measurements of PANI doped with different concentrations of HNO$_3$ (0.8, 0.9, 1.0M) were carried out and their topographical images are shown in Figure 4.41. The PANI film doped with 0.8M HNO$_3$ has a root mean square (Rms) value 3.82 nm. Increasing HNO$_3$ concentration to 0.9M HNO$_3$ decreases the Rms value to 3.35 nm. Beyond 0.9M HNO$_3$, the Rms value increases up to 21.50 nm. These Rms values are indications of the roughness of the prepared films. This means the PANI doped with 0.9M HNO$_3$ is the smoothest film. The increase in roughness beyond 0.9M HNO$_3$ is attributed to the enhancement in polymerization rate as HNO$_3$ acts as a dopant as well as a catalyst for
polymerization. This increase in polymerization rate results in an agglomeration of PANI, thus increasing film roughness, leading to PANI film with gaps that trap charge carriers and form solar cells with lower Jsc and FF values.

(a) Rms=8.00 nm  (b) Rms=3.35 nm  (c) Rms=21.5 nm

Figure 4.41 AFM topography images of electrochemically synthesized HNO₃-PANI doped with (a) 0.8M HNO₃, (b) 0.9M HNO₃, (c) 1.0M HNO₃

AFM measurements of HNO₃-PANI doped with different concentrations of LiTFSI (6.25, 15, 50mM) were carried out, and their topographical images are shown in Figure 4.42. The HNO₃-PANI film doped with 6.25mM LiTFSI has a root mean square (Rms) value of 2.35nm. Beyond 6.25mM LiTFSI, Rms values increase gradually, which means roughness increases resulting in devices with lower Jsc values. This increase in roughness may be due to too much of LiTFSI, blocking PANI from proper polymerization in addition to its agglomeration in large amounts on the PANI surface and between its chains, thus increasing its roughness.

6.25mM LiTFSI (Rms=2.35)  15mM LiTFSI (Rms=3.98)  50mM LiTFSI (Rms=5.52)

Figure 4.42 AFM measurements of HNO₃-PANI doped with different concentrations of LiTFSI (6.25, 15, 50mM)
AFM measurements of PEDOT:PSS and electrochemically synthesized PANI were carried out and their topographical images are shown in Figure 4.43. PEDOT:PSS film is the smoothest with a root mean square (Rms) value 1.89 nm. The PANI film doped with 0.8M HNO₃ has a high Rms value of 8.00 nm. Increasing HNO₃ concentration to 0.9M HNO₃ decreases the Rms value to 3.35 nm, and adding 6.25mM LiTFSI in the electrolyte solution leads to a PANI film with an Rms value 2.35 nm. These Rms values are indications of the roughness of the prepared films, this means increasing HNO₃ concentration to 0.9M HNO₃ decreased roughness, and adding 6.25mM LiTFSI resulted in smoother PANI films. One would expect better charge extraction and collection, thus improved Jsc for the fabricated device. This is because HNO₃ and LiTFSI not only act as dopants, but also as catalysts, increasing the polymerization rate of aniline, resulting in full coverage of the substrate surface and thus a smoother and more compact PANI film.

Figure 4.43 Tapping mode AFM topography images of (a) PEDOT:PSS and the electrochemically synthesized HNO₃-PANI doped with, (b) 0.8M HNO₃, (c) 0.9M HNO₃, (d) 0.9M HNO₃, 6.25mM LiTFSI
4.4.3 KPFM Measurements of Perovskite, PEDOT:PSS, and PANI Doped with HNO₃ and LiTFSI.

KPFM images of perovskite film, PEDOT:PSS film, and the different electrochemically synthesized PANI film doped with 0.9M HNO₃ and 6.25mM LiTFSI and their surface potential distribution acquired from KPFM images are shown in Figure 4.44. Results show that PEDOT:PSS has more negative surface potential (-180mV) than PANI films, indicating why PEDOT:PSS-based solar cells achieved the highest Voc. Solar cells based on PANI doped with LiTFSI have more negative surface potential (-78.1mV) compared to those which contain PANI without LiTFSI (-50.1mV) confirming that adding LiTFSI results in enhancement in Voc. This is may be attributed to LiTFSI increasing the work function of PANI due to the generation of new HOMO energy as shown by HOMO-LUMO measurements (Figure 4.39).
Figure 4.44 KPFM images of (a) Perovskite, (b) PEDOT:PSS, (c) PANI doped with 0.9M HNO₃ (d) PANI doped with 0.9M HNO₃ and 6.25mM LiTFSI, and (e) their surface potential distribution.
4.4.4 CS-AFM Images of PEDOT:PSS and the Electrochemically Synthesized PANI Doped with Different Concentrations of HNO$_3$ and LiTFSI

CSAFM images of PEDOT:PSS (Figure 4.45a) and the electrochemically synthesized PANI doped with 0.8M HNO$_3$ (Figure 4.45b), 0.9M HNO$_3$ (Figure 4.45c), and 6.25mM LiTFSI in addition to 0.9M HNO$_3$ (Figure 4.45d) with surface current values 0.226, 0.147, 0.379, and 0.369 nA are shown. This means conductivity increases by increasing doping degree or by increasing HNO$_3$ concentration in the electrolyte solution. Polyaniline conductivity depends on its oxidation state and protonation degree. This is because during the polymerization of aniline monomer into PANI, aniline is oxidized into an anilinium cation radical at the N-position, which delocalizes by conjugation into O- and P- positions. Then coupling happens between radicals at N- and P- positions, so the N atom is involved in the polymer chain, and its oxidation state greatly affects PANI conductivity. If all N atoms are oxidized into imine groups, PANI is called Pernigraniline Base (Violet) and if all N atoms are reduced into amine groups, PANI is called Leucoemeraldine Base (Yellow). If PANI is half oxidized, it is called emeraldine base, which is the only form that could be conductive via protonation of imine groups giving the conducting emeraldine salt (Green). That could be achieved by doping the electrolyte solution with a strong acid such as HNO$_3$. Decreasing HNO$_3$ concentration leads to some un-protonated imine groups, decreasing conductivity. This is why PANI film doped with 0.9M HNO$_3$ has higher surface current than the film doped with 0.8M HNO$_3$. Adding LiTFSI in the electrolyte solution concentration results in protonation of amine groups, thus decrease in surface current.
(a) CS = 0.226 nA

(b) CS = 0.147 nA

(c) CS = 0.379 nA

(d) CS = 0.369 nA

Figure 4.45 CS-AFM images of (a) PEDOT:PSS film and the electrochemically synthesized HNO₃-PANI doped with (b) 0.8M HNO₃, (c) 0.9M HNO₃, (d) 0.9M HNO₃, 6.25mM LiTFSI

4.4.5 JV Characteristics and Transient Measurements of PSCs made from PEDOT:PSS, and PANI Doped with Different Concentrations of HNO₃

J-V characteristics of perovskite solar cells (PSCs) made of PANI doped with different concentrations of HNO₃ as a HTM compared with PSC fabricated using PEDOT:PSS as an HTM are shown in Figures 4.46a and b. Table 4.21 indicates that the photovoltaic parameter of fabricated perovskite solar cells using PANI as an HTM is comparable with that which is fabricated using PEDOT:PSS. Results show that the device made of PANI doped with 0.8M HNO₃ achieved power conversion efficiency (PCE) up to 7.60%. Increasing the doping degree to 0.9M HNO₃ enhances the PCE to 16.19% which is comparable to that of a PEDOT:PSS based cell with 15.11% PCE. Beyond 0.9M HNO₃, efficiency starts to decrease. Solar cells containing PANI doped with 1.0M HNO₃ achieved 10.46% PCE. The enhanced efficiency is attributed to the improved J_sc and FF as
a result of increasing the doping degree. This is because the protonation degree of imine groups increases by increasing the doping degree, so conductivity increases. The enhanced $J_{SC}$ is also attributed to the decrease in PANI roughness as shown by AFM results. The decrease in $J_{SC}$ beyond 0.9M HNO$_3$ is because of the increase in roughness which results from the high polymerization rate. This roughness leads to HTM films with gaps that trap charge carriers, thus depressing charge transport and decreasing $J_{SC}$.

Charge transport time and carrier life time obtained from transient photocurrent and photovoltage measurements of perovskite solar cells based on PEDOT:PSS and the PANI films doped with different HNO$_3$ concentrations as hole transport materials for PSC are shown in Figure 4.46c and d, and Table 4.21. Charge transport times of 1.08 µs, 0.86 µs and 1.34 µs were obtained for the cells fabricated with PANI doped with 0.8M HNO$_3$, 0.9M HNO$_3$ and 1.0M HNO$_3$, respectively, compared to a charge transport time of 0.99 µs for the cells with pristine PEDOT:PSS. These results match with JV characteristics (Figure 4.46a,b) as they confirm the great effect of doping degree of the hole transporting PANI on charge extraction, thus on $J_{SC}$ in the p-i-n perovskite solar cell. Transient photovoltage (TPV) results are in good agreement with $V_{OC}$ from JV characteristics. The carrier lifetime of PEDOT:PSS, which has the highest $V_{OC}$ (0.97 V), is longest (1.02 µs) compared to 0.72 µs for PANI doped with 0.8M HNO$_3$. Increasing the doping degree to 0.9M HNO$_3$ decreased carrier lifetime to 0.53 µs. Further increasing HNO$_3$ concentration to 1.0M results in a decrease in carrier lifetime to 0.3 µs, thus decreasing $V_{OC}$ from 0.87V to 0.85V (Table 4.21). These increases in carrier lifetime may be because of the positive shift of the polaron band as a result of increasing doping degree of PANI (emeraldine salt) with HNO$_3$, thus decreasing its work function and Voc. Also, the decrease in work function increases the driving force of hole extraction and collection in the hole transport layer, resulting in shorter transport time and better $J_{SC}$. 
Figure 4.46 (a) Forward and (b) reverse J-V characteristics, (c) TPC, and (d) TPV of PSCs made from PEDOT:PSS, and PANI doped with different concentrations of HNO₃.

Table 4.21 Photovoltaic parameters of perovskite solar cells made with PEDOT:PSS and PANI doped with different concentrations of HNO₃ as HTMs.

<table>
<thead>
<tr>
<th>HTM</th>
<th>Scan</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mAcm⁻²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>η (%)</th>
<th>TPC (µs)</th>
<th>TPV (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>Forward</td>
<td>18.31</td>
<td>0.92</td>
<td>0.65</td>
<td>11.02</td>
<td>0.99</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>20.08</td>
<td>0.97</td>
<td>0.78</td>
<td>15.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PANI (0.8M HNO₃)</td>
<td>Forward</td>
<td>12.97</td>
<td>0.87</td>
<td>0.57</td>
<td>6.39</td>
<td>1.08</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>13.11</td>
<td>0.88</td>
<td>0.66</td>
<td>7.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PANI (0.9M HNO₃)</td>
<td>Forward</td>
<td>21.30</td>
<td>0.86</td>
<td>0.71</td>
<td>13.05</td>
<td>0.86</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>22.10</td>
<td>0.87</td>
<td>0.78</td>
<td>16.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PANI (1.0M HNO₃)</td>
<td>Forward</td>
<td>14.27</td>
<td>0.85</td>
<td>0.64</td>
<td>7.71</td>
<td>1.34</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>15.35</td>
<td>0.85</td>
<td>0.8</td>
<td>10.46</td>
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</tr>
</tbody>
</table>
4.4.6 J-V Characteristics and Transient Measurements of PSCs made from PANI Doped with Different Concentrations of LiTFSI.

J-V characteristics of perovskite solar cells (PSCs) made of PANI doped with different concentrations of LiTFSI in addition to 0.9M HNO₃ as a HTM are shown in Figures 4.47a,b and Table 4.22 indicates photovoltaic parameters. Results show that the device made of PANI un-doped with LiTFSI salt achieved a PCE of 16.19%. Adding a small amount (6.25mM) LiTFSI into the electrolyte solution enhanced efficiency up to 16.94% as a result of the improved $J_{SC}$ and $V_{OC}$. This is because doping with LiTFSI increased the work function of PANI (Figure 4.44), thus increasing $V_{OC}$. Adding a new energy level in between perovskite and the HTL (PANI) by doping with LiTFSI improved charge extraction at the perovskite/PANI interface, thus enhancing $J_{SC}$. Also, the improved $J_{SC}$ is because LiTFSI doping decreased the roughness of PANI film as shown by AFM (Figure 4.42), resulting in PANI film with less trapping gaps. Therefore, there is better charge transport across the film and improved $J_{SC}$.

Charge transport time and carrier lifetime obtained from transient photocurrent and photovoltage measurements of perovskite solar cells based on PANI films doped with different LiTFSI concentrations in addition to 0.9M HNO₃ as hole transport materials for PSC are shown in Figure 4.47c,d and Table 4.22. Charge transport times of 86 µs, 81 µs, 1.36 µs and 1.49 µs were obtained for the cells fabricated with PANI doped with 0mM, 6.25mM, 15mM and 50mM LiTFSI, respectively. These results match with $J_{SC}$ results from JV characteristics (Figure 4.47a,b). Carrier lifetime of the device made of PANI doped with 0mM < 6.25mM < 15mM < 50mM LiTFSI had values of 0.53 µs < 0.75 µs < 0.82 µs < 1.25 µs, respectively. These results are in good agreement with the $V_{OC}$ from JV characteristics which showed that $V_{OC}$ of the device made of PANI doped with 0mM < 6.25mM < 15mM < 50mM LiTFSI had values of 0.87V < 0.93V < 0.95V < 0.96V.
Figure 4.47 (a) Forward and (b) reverse J-V characteristics, (c) TPC, and (d) TPV of PSCs made from PANI doped with different concentrations of LiTFSI.

Table 4.22 PV parameters and transient data for PSCs made from PANI doped with different concentrations of LiTFSI.

<table>
<thead>
<tr>
<th>LiTFSI</th>
<th>Scan</th>
<th>J_{sc} (mAcm^{-2})</th>
<th>V_{oc} (V)</th>
<th>FF</th>
<th>\eta (%)</th>
<th>TPC (\mu s)</th>
<th>TPV (\mu s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No LiTFSI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forward</td>
<td>23.88</td>
<td>0.87</td>
<td>0.70</td>
<td>14.54</td>
<td>0.86</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>Reverse</td>
<td>23.86</td>
<td>0.87</td>
<td>0.78</td>
<td>16.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.25 mM LiTFSI</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forward</td>
<td>24.28</td>
<td>0.93</td>
<td>0.63</td>
<td>14.23</td>
<td>0.81</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>Reverse</td>
<td>24.28</td>
<td>0.93</td>
<td>0.75</td>
<td>16.94</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.5 mM LiTFSI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forward</td>
<td>20.68</td>
<td>0.94</td>
<td>0.65</td>
<td>12.62</td>
<td>1.36</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>Reverse</td>
<td>21.08</td>
<td>0.95</td>
<td>0.71</td>
<td>14.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 mM LiTFSI</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Forward</td>
<td>17.85</td>
<td>0.95</td>
<td>0.61</td>
<td>10.36</td>
<td>1.49</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>Reverse</td>
<td>17.87</td>
<td>0.96</td>
<td>0.76</td>
<td>12.95</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.4.7 J-V Characteristics and IPCE Spectra of PSCs made from PEDOT:PSS, and PANI Doped with Different Concentrations of HNO₃ and LiTFSI as HTMs

J-V characteristics of perovskite solar cells made of PANI doped with different concentrations of HNO₃ and LiTFSI as HTMs compared to the PEDOT:PSS based cell are shown in Figure 4.48a and b. Table 4.23 shows the photovoltaic parameters of the fabricated devices. Results show that the device made of PANI doped with 0.8M HNO₃ achieved power conversion efficiency (PCE) up to 7.60%. Increasing the doping degree to 0.9M HNO₃ enhances PCE to 16.19% which is higher compared to the PEDOT:PSS based cell with 15.11% PCE. The enhanced efficiency is attributed to the improved J_{SC} and FF as a result of increasing doping degree, which is in good agreement with AFM and CS-AFM measurements. This because protonation degree of imine groups increases by increasing the doping degree, so conductivity increases. The enhanced J_{SC} is also attributed to the decrease in PANI roughness as shown by AFM results (Figure 4.43). Adding 6.25 mM LiTFSI in the electrolyte solution results in further enhancement in solar cell efficiency, up to 16.94%, which is attributed to the improved V_{OC} and J_{SC}. The enhanced V_{OC} is in good agreement with KFM results (Figure 4.44) which confirmed that doping PANI with LiTFSI increased its work function of the hole transporting PANI, thus increasing V_{OC}. LiTFSI enhanced the J_{SC} of the solar cell; however, CSAFM images showed it decreased the surface current of PANI as a result of doping amine groups. The enhanced J_{SC} of the device is because LiTFSI generated a new hole transporting energy level between the HOMO of perovskite and HOMO of PANI, thus facilitating and enhancing charge extraction and collection, resulting in better J_{SC}.

The IPCE spectra (Figure 4.48c) are in good agreement with the J_{SC} values obtained from the J-V characteristics. IPCE of a 0.8M HNO₃-PANI based solar cell is 62.23% compared to 76.97% for the PEDOT:PSS based device. Increasing doping degree of PANI to 0.9M HNO₃ increased IPCE to 89.90% as a result of increasing protonation of imine groups (higher conductivity). Also, doping with 6.25 mM LiTFSI improved IPCE up to 93.56% because of the enhanced charge
extraction as a result of generation of new HOMO energy level between those of perovskite and PANI.

Figure 4.48 (a) Forward and (b) reverse J-V characteristics, and (c) IPCE spectra of perovskite solar cells made from PEDOT:PSS, and PANI doped with different concentrations of HNO₃ and LiTFSI as HTMs
Table 4.23 PV parameters of perovskite solar cells made from PEDOT:PSS, and PANI doped with different concentrations of HNO₃ and LiTFSI as HTMs for perovskite solar cell.

<table>
<thead>
<tr>
<th>HTM</th>
<th>Scan</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>IPCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>Forward</td>
<td>18.31</td>
<td>0.92</td>
<td>0.65</td>
<td>11.0</td>
<td>76.97</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>20.08</td>
<td>0.97</td>
<td>0.78</td>
<td>15.1</td>
<td></td>
</tr>
<tr>
<td>PANI (0.8M HNO₃)</td>
<td>Forward</td>
<td>12.97</td>
<td>0.87</td>
<td>0.57</td>
<td>6.39</td>
<td>62.23</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>13.11</td>
<td>0.88</td>
<td>0.66</td>
<td>7.60</td>
<td></td>
</tr>
<tr>
<td>PANI (0.9M HNO₃)</td>
<td>Forward</td>
<td>23.88</td>
<td>0.87</td>
<td>0.70</td>
<td>14.5</td>
<td>89.90</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>23.86</td>
<td>0.87</td>
<td>0.78</td>
<td>16.1</td>
<td></td>
</tr>
<tr>
<td>PANI (0.9M HNO₃, 6.25mM)</td>
<td>Forward</td>
<td>24.28</td>
<td>0.93</td>
<td>0.63</td>
<td>14.2</td>
<td>93.56</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>24.28</td>
<td>0.93</td>
<td>0.75</td>
<td>16.9</td>
<td></td>
</tr>
</tbody>
</table>

4.4.8 Transient Measurements of Perovskite Solar Cells based on PEDOT:PSS and the Different PANI Films as HTMs

Charge transport time and carrier lifetime obtained from transient photocurrent and photovoltage measurements of perovskite solar cells based on PEDOT:PSS and the different PANI films as hole transport materials are shown in Figure 4.49 and Table 4.24. Charge transport times of 1.08 µs, 0.86 µs and 0.81 µs were obtained for the cells fabricated with PANI HTMs doped with 0.8M HNO₃, 0.9M HNO₃ and 6.25mM LiTFSI in addition to 0.9M HNO₃, respectively, compared to charge transport time of 0.99 µs for the cells with pristine PEDOT:PSS. These results match with JV characteristics as they confirm the great effect of doping degree and dopant type of the hole transporting PANI on charge extraction, thus on $J_{SC}$ in the p-i-n perovskite solar cell. Transient photovoltage (TPV) results are in good agreement with the $V_{OC}$ from JV characteristics.

Carrier lifetime of PEDOT:PSS, which has the highest $V_{OC}$ (0.97 V), is the longest (1.02 µs) compared to 0.72 µs for PANI doped with 0.8M HNO₃.
Increasing doping degree to 0.9M HNO$_3$ decreased carrier lifetime to 0.53 µs. Further doping HNO$_3$-PANI with LiTFSI results in an increase in carrier lifetime to 0.75 µs, thus improving $V_{OC}$ from 0.87V to 0.93V (Table 4.24). These enhancements in PV parameters occur because LiTFSI generated a new energy level between the HOMO of perovskite and HOMO of PANI, thus increasing the work function of the hole transporting and improving $V_{OC}$ and carrier lifetime. Also, the new energy level facilitates and enhances charge extraction and collection in the hole transport layer resulting in shorter transport time and better $J_{SC}$.

![Figure 4.50](image.png)

Figure 4.50 (a) TPC and (b) Normalized TPV of p-i-n perovskite solar cells based on PEDOT:PSS and the different PANI films as HTMs.

Table 4.24 Fitted charge transport lifetime and carrier life time of perovskite solar cells based on PEDOT:PSS and the different PANI films as HTMs.

<table>
<thead>
<tr>
<th>HTM</th>
<th>TPC (µs)</th>
<th>TPV (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>0.99</td>
<td>1.02</td>
</tr>
<tr>
<td>PANI (0.8M HNO$_3$)</td>
<td>1.08</td>
<td>0.72</td>
</tr>
<tr>
<td>PANI (0.9M HNO$_3$)</td>
<td>0.86</td>
<td>0.53</td>
</tr>
<tr>
<td>PANI (0.9M HNO$_3$, 6.25mM LiTFSI)</td>
<td>0.81</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Chapter 5: Conclusions

5.1 Summary

Today’s world is energy driven, and a clean renewable source of energy such as sunlight is important to meet the growing energy demand for a sustainable future. Conversion of solar energy into electricity by photovoltaics is one of the most promising approaches to solve global energy issues. Crystalline silicon solar cells dominate the photovoltaic industry with a relatively expensive manufacturing process; thus, modern research focuses on manufacturing devices from low cost materials and simple solution processing. Perovskite solar cells (PSCs) offer tremendous potential for simple and low-cost solution-based fabrication with high power conversion efficiency, making them a promising renewable energy source alternative to the most common non-renewable energy sources (fossil fuels). PSCs can compete with the dominant silicon solar cells in terms of power conversion efficiency, cost, and ease of processing. There has been great progress in PCEs of PSCs within the last 10 years, with 6.5% in 2011 [13], more than 20% in 2015 [14], 22.1% in 2016 [15], and 23.3% in 2018 [16].

Organometal halide perovskite materials demonstrate several advantages including excellent optical properties, low exciton binding energy (∼45 meV), ambipolar charge transport, long charge carrier lifetimes, and long electron–hole diffusion lengths. They have a tetragonal structure with a band gap of 1.5 eV, thus allowing absorption of broader band wavelengths of light. These properties make perovskite an excellent light harvesting material for use in thin-film photovoltaic applications. The most widely used perovskite for solar cell applications is methylammonium lead triiodide (CH$_3$NH$_3$PbI$_3$). There are two structures for PSC, the regular n-i-p device typically fabricated using Spiro-OMeTAD as a hole transport material (HTM), and the inverted p-i-n device fabricated using PEDOT:PSS as an HTM.

Regarding the n-i-p perovskite solar cell, to fully crystallize an individual precursor component into a perovskite phase, several strategies have been adopted such as one-step deposition, sequential two-step deposition and vapor-phase deposition. The two-step deposition has been widely used for achieving high
efficiency perovskite solar cells. However, it suffers from forming a rough perovskite film and the uncontrollable surface morphology of CH$_3$NH$_3$PbI$_3$ causing poor reproducibility as well as the residual PbI$_2$ in CH$_3$NH$_3$PbI$_3$ thin films that deteriorates device performance. Another issue for n-i-p PSCs is spiro-OMeTAD which is a state-of-the-art hole transport material. The challenging synthesis routes and exorbitant cost of the spirobifluorene central core make it a relatively expensive material.

PCE of the p-i-n device is lower than that of the n-i-p device. However, it is more preferred as it can be fabricated at a lower temperature (<100 °C) compared to 450 °C for the regular n-i-p structure. This enables the use of flexible substrates and the roll to roll production of perovskite solar cells. PEDOT:PSS is the most commonly used hole-transport layer (HTL) in p-i-n perovskite solar cells. However, use of PEDOT:PSS has several limitations such as (1) its large particle size inducing degradation of the device because of the aggregation of particles causes defects, (2) high costs and low electrical conductivity limiting its use as an HTL, and (3) its acidic property affecting device stability. Carbon-based materials and conducting polymers can help alleviate these limitations because of their high conductivity and excellent electrocatalytic activity.

Transparent conducting polymers have high-conductivity and good stability which makes them promising candidates as alternate hole transport materials to PEDOT:PSS. Polyaniline is one of the most promising potential electronic conducting polymers that can be used as an HTM in perovskite solar cells due to high conductivity, environmental stability, low cost, easy synthesis, and high degree of processability. In addition, it can be synthesized with high purity and transparency. Polymerization of aniline into PANI can be done chemically, electrochemically, photochemically or enzyme-catalytically. Chemically prepared polyaniline:poly (styrenesulfonate) (PANI:PSS) has been used as an efficient hole transport material (HTM) in inverted planar perovskite solar cells (PSCs) achieving PCEs up to 11.67%. PANI:PSS is a cheaper alternative to PEDOT:PSS; however, efficiency is low, the chemical synthesis of
PANI is long, uses many materials, and the produced PANI contain many impurities which affect device performance and may need purification.

One big challenge for PSCs is the aspect of short-term and long-term stability. The instability of PSCs is mainly related to environmental influence such as moisture, oxygen, heat, and light. The moisture degrades the perovskite material into its reactants, while heat, light, and oxygen oxidize it into free radicals that propagate, resulting into its complete breakage.

It is clear that PSCs are not reproducible or stable and HTMs are expensive, hindering its commercialization. It is important to find out ways to achieve high quality, defect free solution processed perovskite film, simple and scalable synthesis of cheap hole transport material, and efficient charge extraction from perovskite absorbers to enable high efficiency and stability of perovskite photovoltaics. The goal of this dissertation was to obtain cheap PSCs with high performance via engineering hole transport and perovskite absorber layers by (1) the doping of perovskite precursor solution using additives, (2) substituting conventional high cost spiro-OMeTAD by the facile synthesized thiophene-based materials, (3) synergistic combination of PEDOT:PSS with graphene oxide and polyaniline, and (4) substituting the high cost PEDOT:PSS with the facile synthesis of polyaniline electrochemically, targeting stable perovskite solar cells with high efficiency

5.2 Conclusion

New approaches aimed towards commercialization of perovskite solar cells have been implemented via engineering of hole transport and perovskite absorber layers to achieve higher efficiency, cheaper, and more stable perovskite solar cells. Perovskite precursor solutions for n-i-p PSCs were doped by adding optimized amounts of TBAI₃, LiI, LiTFSI and BMImI resulting in a perovskite film with higher crystallinity and lower roughness, thus achieving better charge transport in the cell. The adsorbed heteroatom on the TiO₂ surface improved electron injection into its conduction band, enhancing J_SC, while positive shifting of the TiO₂ Fermi level (E_f) enhanced V_OC, thus improving device efficiency.
Heteroatoms of dopants can act as heat and light stabilizers as they can bind to the generated free radicals generated during heat and light exposure, thus blocking their propagation. Thiophene based materials with better $\pi$-conjugation across the fused thiophene rings were used as HTMs for the n-i-p PSC. PSC fabricated with H16 with a MPDTP core exhibited efficiency of 18.16%, which is comparable to the device with the state-of-the-art-HTM spiro-OMeTAD (18.27%). Furthermore, the H16 based device has good stability after two months of aging in controlled (20%) humidity in the dark. In addition, the synthetic cost of H16 is roughly 1/5 of that of spiro-OMeTAD. Nanocomposites of PEDOT:PSS, GO, and PANI were prepared and used as an HTM for the p-i-n PSC. The synergistic engineering between them introduced additional energy levels between perovskite and PEDOT:PSS, and further increased the conductivity of PEDOT:PSS. PANI/PEDOT:PSS/GO (1:1:1) film achieved the highest PV performance (18.12% PCE). PANI nanoparticles fill the gaps among GO microparticles and GO improves adhesion of PANI, while PEDOT:PSS increases the compactness in the films, thus achieving the highest $J_{SC}$. PANI and GO increased the work function of PEDOT:PSS, thus increasing the $V_{OC}$ up to 1.05 V compared to 0.95 V for the device based on pristine PEDOT:PSS. PANI thin film was synthesized by the simple and scalable electrochemical method and used as an HTM for the p-i-n PSC, as an alternative to PEDOT:PSS. Results showed that efficiency of PANI-PSC was 16.94% compared to 15.11% for the PEDOT:PSS-PSC. This approach is an important step towards commercialization of the p-i-n PSC with the roll-to-roll manufacturing.

5.3 Future work

Further work on understanding the effect of doping perovskite precursor solution on the performance of the inverted perovskite solar cell can be studied. Also, PANI can be used for doping the HTL of the n-i-p perovskite solar cell.
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