Hydrophobic Hole Transport Material for Perovskite Solar Cells

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DEDICATION

To,

THE ALMIGHTY

With Gratitude

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Abstract

Over the past few years organic-inorganic halide perovskite solar cells have drawn an extensive attraction due to high solar cell efficiencies, which have gone past 20%. The issue that still prevails is the stability of these perovskite based solar cells. One of the obvious reasons is the fast degradation under high relative humidity due to water-solubility of the organic component of the material. So, aim of the research is to figure out and design a hydrophobic hole transport layer which will prevent the moisture to barge in, hence, saving the integrity of the organic component of the cell and as result improving the stability of the whole cell. PbPc and NiO are considered as the options to encounter the issue of moisture. PbPc has shown good hydrophobic abilities with a contact angle of 86.1°, apart from great hole mobility traits. While, NiO seems to have lower resistance to the moisture as contact angle was hard to calculate, though it can be a good hole transport candidate.

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List of Abbreviations

PSC	Perovskite Solar Cell
DSSC	Dye-Sensitized Solar Cell
HTL	Hole Transport Layer
HTM	Hole Transport Material
ETL	Electron Transport Layer
ETM	Electron Transport Material
PbPc	Lead Phthalocyanine
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
UV-VIS-NIR	Ultravoilet-Visible-Nearinfrared

Chapter 1.

Introduction

In 1991, Micheal Gratzel and Brian O'Regan were able to design a high efficiency dye sensitized solar cell (DSSC) [1]. Methylammonium lead halide perovskite material was used as an inorganic sensitizer in liquid-based DSSC in 2009, showing 3.1% efficiency for bromine and 3.8% efficiency for iodine [2], which was doubled within 2 years via optimization of the coating conditions of perovskite [3]. But the liquid-based perovskite solar cell had stringent stability concerns, especially the rapid dissolution of the perovskite in liquid electrolytes. A durable and stable solar cell with an efficiency of 9.7% was developed in 2012 by using solid hole conducting material instead of liquid electrolyte [4], introducing a whole new dimension of solar cells, termed as Perovskite Solar Cells.

During the year 2013, work was carried soundly upon the performance of these cells yielding in an enormous progress with energy conversion efficiencies reaching a confirmed 16.2%. Values of about 20% efficiencies have been claimed till the date [5]. The issue that still remains is the stability of these perovskite based solar cells. Especially, the rapid degradation of the organic component of the material under high relative humidity due to water-solubility. Using mixed halide perovskite (combination of iodide and bromide) [6] and encapsulating perovskite material with carbon nanotubes have shown better stability and resilience to the moisture but still no rigid solutions are crafted to cater the problem. Another approach to overcome the very problem is replacing the typical HTMs like: spiro-MeoTAD with hydrophobic materials. Recently, Carbon nano structures, Nickel oxide, multiple Thiophene cores and Metal Phthalocyanines (PbPc/CuPc) have been used as HTMs and showed promising results under high humidity conditions over a long period of time.

1.1. Motivation

The very basic reason for the high level of success of Perovskite Solar Cells is that the Perovskites have great solar light absorption capabilities. Energy Band Gap is also 1.5, which is pretty much suitable for solar cell operations. Ultrafast charge generation, high carrier mobilities and slow recombination rates also make them resilient and productive. Only major issue is the stability of these cells and if we can improve this issue by making few changes, we ought to take them. As they are the future of the solar cells industry.

1.2. Objectives

- To develop a hydrophobic hole transport layer for perovskite solar cell to restrict the moisture which deteriorates the organic component of the cell.
- To study the properties of the hydrophobic hole transport material and optimize it for the perovskite solar cell.

1.3. Relevance to National Needs

Solar being one of the promising renewable resource of energy has shown striking upshots over the years. Silicon based solar cells (1st generation) are having a sound impact throughout the world to cater with the energy needs. Pakistan has also shown a solid interest in minute as well as large scale plants. Quaid-e-Azam solar power plant is the most recent venture which is going to add in the national energy grid (1000MW). Moreover, the rates of solar energy per kW are also in the reduction process as we speak.

The world is improvising in an upward manner and a wide range of newer solar cells are being introduced. So, perovskite solar cells being the 3rd generation of the solar cells and the latest of all are the future of solar cell industry and my research is surely going to add a sound part in their progression.

1.4. Break Down of Work

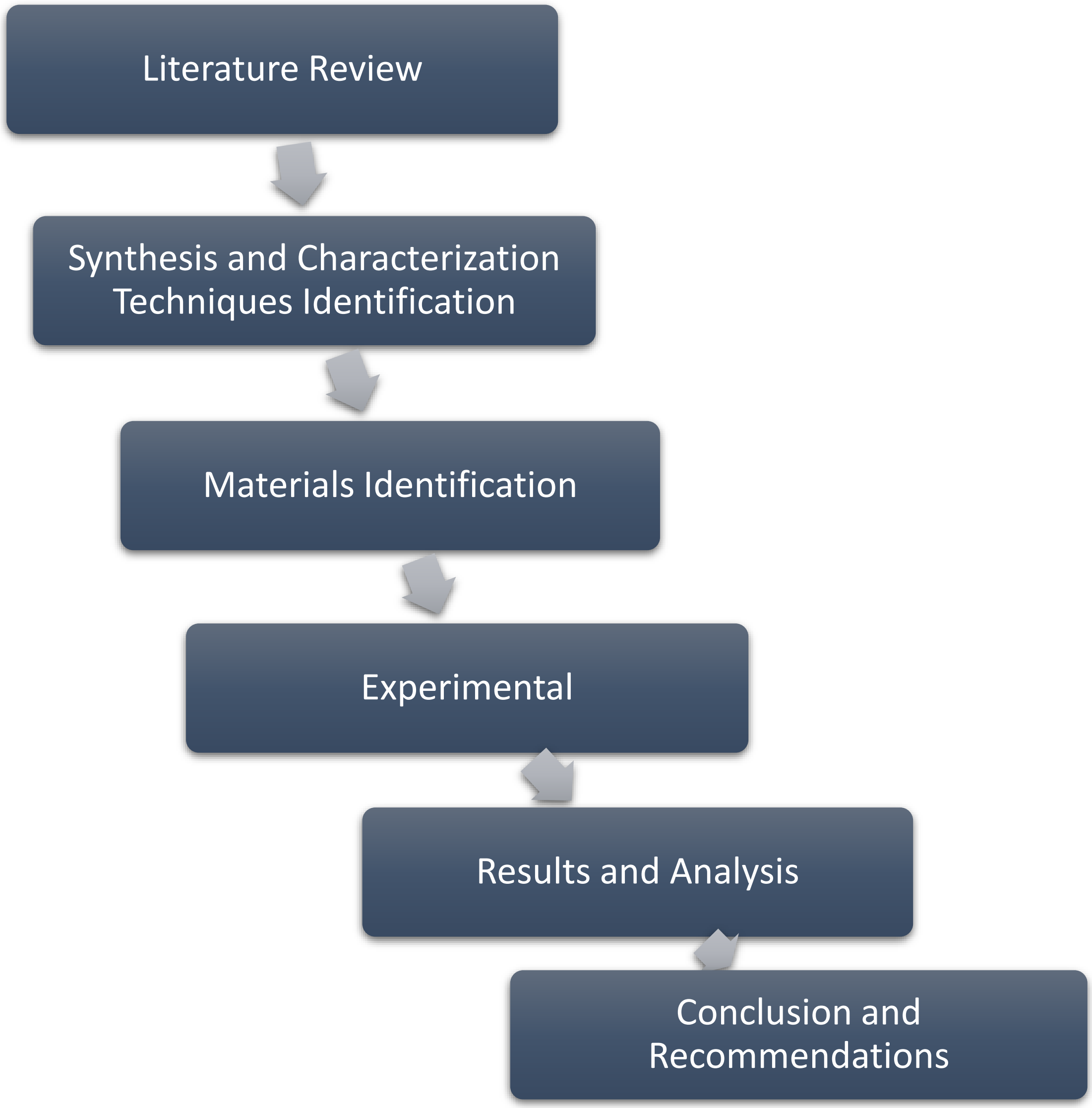

Figure 1.1 Breakdown of research work

1.5. Summary

Over the past few years organic-inorganic halide perovskite solar cells have drawn an extensive attraction due to high solar cell efficiencies, which have gone past 20%. The issue that still prevails is the stability of these perovskite based solar cells. One of the obvious reasons is the fast degradation under high relative humidity due to water-solubility of the organic component of the material. So, aim of the research is to figure out and design a hydrophobic hole transport layer which will prevent the moisture to barge in, hence, saving the integrity of the organic component of the cell and as result improving the stability of the whole cell.

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Chapter 2.
Literature Review

This chapter engulfs the historical development from the solar cells from the first illumination detection under sunlight and the timeline of how they swamped the generations towards the modern sophistication. In the light of literature perovskite solar cells are deeply discussed and the purview where our study is meant has been explained in detail.

2.1. History of Solar Cells

In 1839, Edmond Becquerel- a French Physicist found that two different brass plates immersed in a liquid produced a continuous current when illuminated with sunlight [1]. Later in 1873, Willoughby Smith and in 1877, W.G. Adams and R.E. Day respectively discovered PV effects in Selenium [2]. In 1883, Charles Fritz developed a solar cell based on Selenium over a thin layer of Gold, yielding an efficiency of less than 1% [2]. Over 7 decades, work continued to be done using copper oxide and cadmium selenide, but it was Chapin, who in 1954, designed first silicon based single crystal solar cell at Bell Labs with 6% efficiency [3]. By the year 1959, they had gained an efficiency of over 10%, but due to the rigid usage of fossil fuels, they couldn’t gain much of attention. Solar cells drew attention during 1970s Arab Oil Embargo. After that solar industry was properly developed by the various nations. Today countries like Germany are self-sufficient in the solar cell industry, and the efficiencies up to the order of 25% have been achieved.

2.2. Evolution

2.2.1. First Generation and Second-Generation Solar Cells

The silicon solar cells being pioneer are referred to as the First Generation of Solar Cells. 1954, Photovoltaic technology was fostered as a diverse and distinctive form, when Daryl Chapin, Calvin Fuller and Gerald Pearson developed the silicon photovoltaic (PV) cell at Bell Labs—the first solar cell able to convert sufficient solar energy into electrical power with an efficiency of 4-6% [3]. This turned out to be a hallmark towards a whole new dimension of energy generation. In view with that, Hoffman Electronics developed an 8% efficient solar cell by the year 1957 [3]. In 1958, T. Mandelkorn, U.S. Signal Corps Laboratories, fabricated n-on-p silicon solar cells [4], which appeared to be more resistant to radiation damage and were better suited for space. Hoffman Electronics thus developed 9% efficient solar cells used in Vanguard I, the first solar powered satellite, which was launched with a 0.1W, 100 cm^2 solar panel [5]. In 1959, Hoffman Electronics created a 10% efficient commercial solar cell, and introduced the use of a grid contact, reducing the cell's resistance [5]. In 1960, Hoffman electronics managed to devise a 14% efficient solar cell [6]. By the year 1972, Woodall and Hovel designed high efficiency GaAlAs-GaAs solar cells, with which they were able to achieve more than 16% [7].

Thin film solar cells are the Second Generation of Solar Cells after crystal-based Silicon Solar Cells. The aim was to have a higher production yield, higher efficiencies and cost-effectiveness. It has been seen that material cost is low due to lower wastages and lesser material required. Processes are comparatively low cost and faster with enhanced yield and cheaper base materials. There is a long list of materials used on lab scale but only few came up promising which are used on commercial level for solar cell fabrication namely:

- Amorphous Silicon
- Polycrystalline Silicon Thin Film
- GaAs
- CdTe
- $CuInSe_2$
- $CuInGaSe_2$ (CIGS)
- Cu_2ZnSnS_4 (CZTS)

Materials used for Thin film Solar Cells purposes should be low cost, highly stable and non-toxic with high absorption co-efficient, readily-dopped and easily be metalized. Second generations are more often referred to as thin film solar cells, as they are comprised of films of semiconductor materials up to few micron thicknesses.

Mass production of amorphous silicon cells is cheaper as processes are less energy intensive. But they have failed to provide higher efficiencies. CdTe is a poisonous compound and has been a concern in the regard but having ideal energy band gap makes it suitable for solar cells applications [8]. Companies like First Solar have been working on them for long. CIGS have shown efficiencies up to 20% but their commercialization has been the issue over the years [9].

2.2.2. Third Generation Solar Cells

In 1988, Micheal Gratzel and Brian O’Regan designed first dye sensitized solar (Gratzel Cell) which laid the foundation of the Third Generation Solar Cells [10]. In 1991, the aforementioned were able to design a high efficiency dye sensitized solar cell (DSSC) [11]. A typical DSSC device comprises a semiconductor photoanode, generally titanium dioxide (TiO_2), covered with a thin layer of dye sensitizer, a counter electrode and electrolyte [12]. The dye sensitizer under light illumination generates photoelectrons which inject into the conduction band of the TiO_2 [13]. The electrons flow out through the back contact and external load to reach the counter electrode, where they are involved in the reduction of the redox mediator which is oxidized by the sensitizer [14].

Regardless of the significant enhancement, DSSCs is still lower in energy efficiency compared with silicon solar cells. So, there is a great deal of research in optimization of the various components of DSSC is going on as we speak to enhance the efficiencies. In view with that, methylammonium lead halide perovskite material was used as an inorganic sensitizer in liquid-based DSSC in 2009, owing 3-4% efficiency [15], which was doubled within 2 years via optimization of the coating conditions of perovskite [16]. But the liquid-based perovskite solar cell had stringent stability concerns, especially the rapid dissolution of the perovskite in liquid electrolytes [17].

2.2.3. Perovskite Solar Cells

A durable and stable solar cell with an efficiency of 9.7% was developed in 2012 by using solid hole conductor material instead of liquid electrolyte, introducing a whole new dimension of solar cells, termed as Perovskite Solar Cells [18]. During the year 2013, work was carried soundly upon the performance of these cells yielding in an enormous progress with energy conversion efficiencies reaching a confirmed 16.2% and values of about 22% efficiencies have been claimed till the date [19]. Several approaches have been catered with to optimize the cell conditions, but still a huge margin of improvement prevails.

Keeping in view the thin film formation of Solar Cells, the materials incorporated ought to have certain characteristics. They should have a high absorption coefficient and long diffusion lengths, so that enough absorption can be mined from few microns of coated material. Besides, the band gap of the employed material should be within the range of 1 to 1.6 EV, to achieve the near best efficiencies.

Organic-inorganic methylammonium lead halide perovskites ($CH_3NH_3PbI_3$) have thus, acquired a prodigious lure as a photovoltaic material due to their immense power conversion efficiencies, low cost, extraordinary optical and electronic properties i.e. optimal band gap of 1.5, impressive carrier mobility, high absorption coefficients and long diffusion lengths [20].

To be precise, the absorption coefficient of methylammonium lead iodide perovskite ($CH_3NH_3PbI_3$) is about $10^4 cm^{-1}$ in the visible light spectrum [21], which is almost ideal for solar cell applications. Energy Band Gap is also pretty much suitable for solar cell operations. Ultrafast charge generation, high carrier mobilities and slow recombination rates also make them resilient and productive.

2.2.3.1. Issues and Remedies

Practically, solar cells ought to have a sound long-term stability. Unfortunately, perovskite solar cells show unstable behavior upon exposure to the irradiation under UV-light [22]. This failure relates to deterioration of TiO_2 layer [22]. So, a more suitable material is needed to be used as electron transport material (ETM) which can sustain UV-light or more enhanced protection measures should be taken to prevent the cell against UV-irradiation. Another issue regarding the stability of the perovskite solar cells is the fast degradation at high relative humidity because of the water-solubility of the organic component of the material [23].

Using mixed halide perovskite (combination of iodide and bromide) [24] and encapsulating perovskite material with carbon nanotubes have shown better stability and resilience to the moisture but still no rigid solutions are crafted to cater the problem. Another approach to overcome the very problem is replacing the typical HTMs like: spiro-MeoTAD with hydrophobic materials. Recently, Metal Phthalocyanines (PbPc/ZnPc) have been used as HTMs and showed promising results under high humidity conditions over a long period of time. This tends to be a doorway for more firm and stable perovskite cells.

2.2.3.2. Design Structure

Organic-inorganic Perovskite Solar Cells have been constructed with various designs. The approaches which have been mostly followed are:

2.2.3.2.1. Mesoporous Device Structures / Planar Device Structures

Perovskite solar cells typically are comprised of a glass substrate and a combination of Flourine dopped tin oxide (FTO) with compact TiO2 layer is used as ETM, typically deposited via spin coating[21]. An optional mesoporous TiO2 layer is also prepared sometimes [25]. Perovskite layer is deposited by depositing the mixture of methyl ammonium iodide (CH3NH3I) and lead iodide (PbI2). HTM layer (PbPc) can be deposited via evaporation and Gold (Au) electrode is then thermally evaporated. These cells are just like n-i-p solar cells.

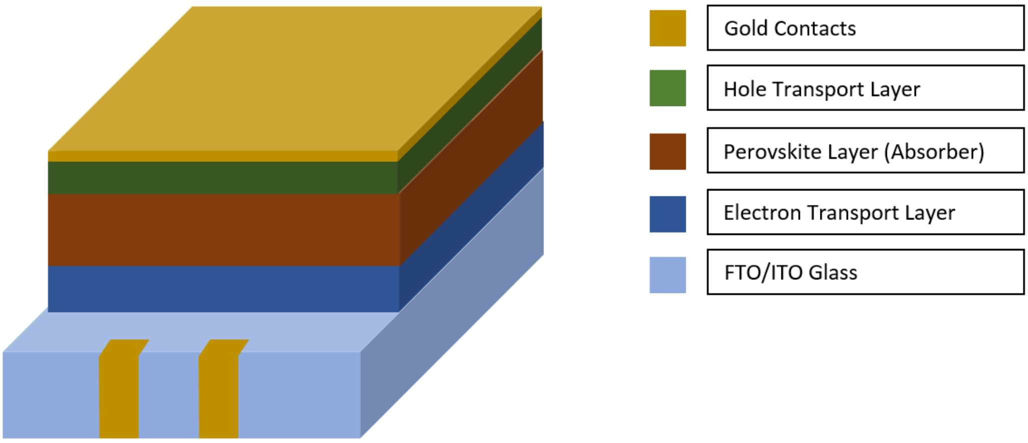

Figure 2.1 A typical Perovskite Solar Cell with proposed layers

In view the long-term stability of PSCs high reported PCEs, they are snatching a lot of eyes. Mesoporous TiO_2 based PSCs show instabilities when subjected to UV light, as oxygen adsorbed on surface is desorbed, thus revealing deeper electron trap sites. Such trap sites work as recombination cores for photo-emitted electrons, ensuing a great reduction in the charge collection efficiencies.

Sum et al. and Snaith et al. independently reported that the organic-inorganic hybrid PSCs comprehend stretched charge/carrier diffusion lengths (~100 nm for $CH_3NH_3PbI_3$ and ~1000 nm for $CH_3NH_3PbI_{3-x}Cl_x$)[26]. Other works show that, single crystals of $CH_3NH_3PbI_3$ were optimized to generate diffusion lengths larger than even 175 μm [21]. Additional studies established that perovskites display ambipolar behavior, suggesting that the perovskite materials can transport both the charge carriers solely by themselves across the terminals of cell [27]. So, using a planar structure instead of mesoporous structure sounds more viable option. The first successful demonstration of the planar structure can be traced back to The perovskite/fullerene structure reported by Guo et al., was the first piece of work where planar structure was used, showing an efficiency around 4% [28]. Mediocre film quality and insufficient absorption of the perovskite layer were the reason behind such low efficiency.

The breakthrough of the planar perovskite structure was obtained by using a dual source vapor deposition, providing dense and high-quality perovskite films that achieved 15.4% efficiency [29]. Recently, the efficiency of the planar structure was pushed over 19% through interface engineering [30].

The planar structure can be separated into two classes depending on which discerning contact is used on the bottom-side, i.e.

- Regular (n-i-p)
- Inverted (p-i-n)

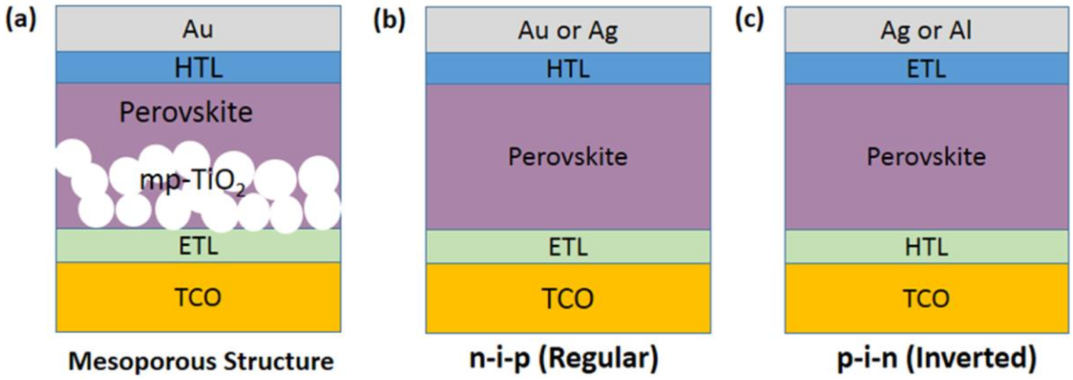

Figure 2.2 showing (a) mesoporous PSCs (b) n-i-p or regular PSCs (c) p-i-n or inverted PSCs [25]

The p-i-n structure is a derivative of the organic solar cell, and typically, numerous charge transport layers used in organic solar cells were successfully relocated into solid state PSCs.

2.2.3.3. Working Principle

Perovskite Solar Cells (PSCs) work on the basic photovoltaic principle i.e. conversion of light (solar) energy into electrical energy. So, the very first step in the process is the absorption of light. Perovskite material thence, is used as a light absorber in PSCs. So, When the light falls on the active layer of PSC, sensitizer absorbs the incident sunlight excite the electrons from the ground state i.e. highest occupied molecular orbital (HOMO) of valance band to excited state i.e. lowest unoccupied molecular orbital (LUMO) of conduction band.

When the light strikes a semiconductor material, formation of excitons (electron-hole pair) may occur with respect to the band gap and absorption coefficient of the material. These excitons can get diffused into the material, decreasing the number of excitons reaching the acceptor/donor junction. Thus, short diffusion lengths can reduce the solar cell efficiency.

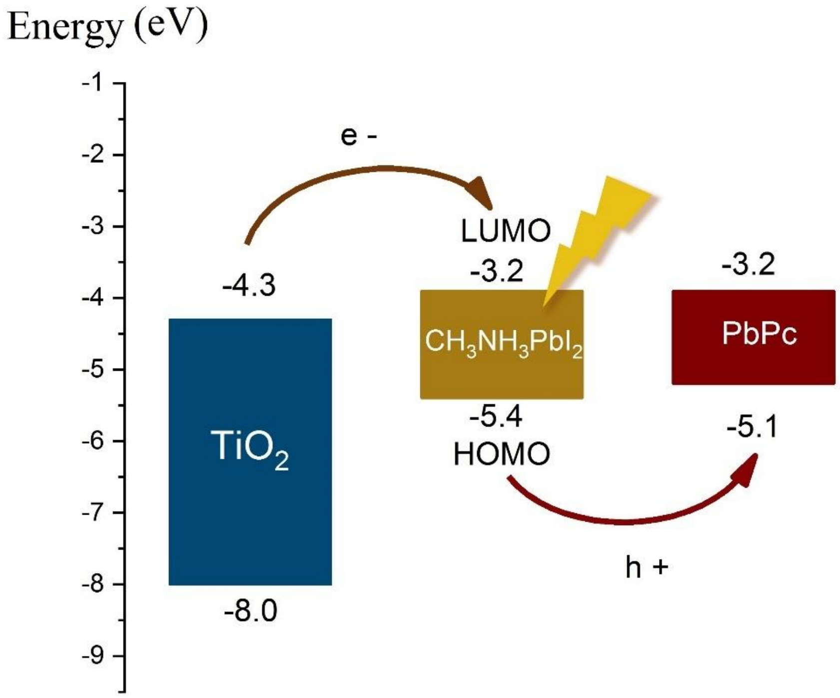

Figure 2.3 conduction of electrons and transport of holes in accordance with HOMO and LUMO of atoms

The excitons are supposed to be broken, with electron and hole getting separated. It is hard to remove charges from each other. Hence, it may cause recombination, drifting the exciton to ground state. Recombination can be a lethal hindrance in the efficiency of solar cells.

After the separation, electron from LUMO of conduction band jumps to conduction band of electron transport layer (ETL) while, electron from HOMO of the Hole Transfer Layer (HTL) jumps to HOMO of valance band of the material.

2.2.3.4. Absorber Layer (Perovskite Layer)

Though methylammonium ($CH_3NH_3PbI_3$ or $MAPbI_3$) perovskite (Organic-Inorganic) as the light absorber material in perovskite solar cells (PSCs) by Kojima et al. in 2009 appeared to be promising with high power conversion efficiency (PCE) [17] and these efficiencies have been improving as much as 23% over the past few years. Unfortunately, organic-inorganic PSCs regardless of their high efficiencies and performances still suffer from certain degradations because of the weak level of the hydrogen-bonding between monovalent organic cation and octahedral PbI_2 [31]. Such a PSC break downs to PbI_2 under common external stresses, like: electric charge, moisture, photo-oxidation and UV irradiation.

Using CsX (Cesium Halide) instead of $MAPbI_3$ along with PbI_2 (all inorganic PSCs) has revealed improved stabilities due to stronger inter-molecular bonding and adherence. All Inorganic CsPbX PSCs have also made known excellent optical and electrical properties, like: high absorption coefficient, low exciton binding energy, ultra-large charge carrier diffusion length and superhigh defect tolerance with low trap state density [32], [33]. $CsPbI_3$ was used earlier as perovskite absorber layer but the phase responsible to absorb light was quite hard to control. $CsPbI_2Br$ is recently been under work due to rather ease in phase control with promising light absorption capabilities and high stabilities [34]. $CsPbI_3$ films require a high-temperature annealing process (>260°C) to acquire a light absorbing cubic phase and large crystalline structures with superlative charge transport [35]. But drop in temperatures may root to phase shifts. To sustain the thermal stability low temperature processing is favorable. For that matter, addition of Hydriodic Acid (HI) to PbI_2 prior to the solution processing of PbI_2 and CsBr is valuable which reduces the annealing temperature less than 150°C, providing healthy chance for the required cubic phase to stay intact [36], [37].

Another promising way to keep the organic-inorganic perovskite solar cells intact is by using a mix of DMSO (Dimethyl sulfoxide) and DMF (Dimethylformamide) in solution processing of MAI with PbI_2 [38]. DMF is a polar solvent and have extensively been used in solution processing of various organic-inorganic PSCs. But using DMSO in appropriate proportion alongside DMF can not only enhance the solubility of PbI_2 in DMF which typically is no more than 0.4 Molar, but also enhance the thickness and stability of absorber layer. Excess usage of DMSO though is not advisable as it may result in recombination. Apart from DMSO, Caffeine is also reported to be used in the mix, which has shown good results in recent past [39].

2.2.3.5. Electron Transport Layer (ETL)

ETL is responsible for extracting the electrons from absorber layer. Since the inception of PSCs many materials like graphene, PCBM, CNTs and Titania have been used as ETL [40], [41], [35]. Titania has extensively been used as ETL since the emergence of PSCs. Titania have been used as compact as well as mesoporous layer and sometimes as a combination of both with compact working as transport and mesoporous supporting the absorber layer. There were reports on mesoporous layer to be helpful in overcoming UV-Irradiation, though conformity of the solution stands a question. So, Still singular compact layer has shown good results in PSCs application [35].

2.2.3.6. Hole Transport Layer

HTL is essential to complete the flow of electric current. HTL must possess:

- Efficient electron blocking
- Efficient hole extraction

Diverse kinds of materials have been deliberated and used as HTLs consequently, including inorganic, polymeric, and small organic molecules. Spiro-OMeTAD [2,20,7,70-tetrakis(N,N-di-p-methoxyphenyl-amine)9,90-spirobifluorene] has extensively been used as a HTM over the last six years and has shown great efficiencies [42]. Other molecules like ZnO, CuI, Cu_2O, CuSCN, GO, MoO_3, VO_x, WO_x, PTAA and thiphene cores have been used as HTL[43].

The rudimentary degradation mechanism in PSCs is the breakdown of perovskite material under moisture, which consequences into breakage of $MAPbI_3$ into its components. Its occurrence is as following:

$$CH_3NH_3PbI_3 \longrightarrow PbI_2 + CH_3NH_2 + HI$$

Equation 2.1

The $CH_3NH_3PbI_3$ thin films are found to undergo decomposition under thermal stress at a temperature amid 100°C and 140°C [44].

To overcome the degradation of perovskite material due to moisture, the HTL should be composed of hydrophobic material. Various hydrophobic materials can be utilized as HTL bearing the basic hole transport properties along with their hydrophobic capabilities. CuO, NiO and various Metal Phthalocyanines have shown fair results when incorporated in PSCs.

2.2.3.6.1. NiO

NiOx is one of the most prevalent inorganic material due to its exceptional potentials, for instance deep-lying valence band, sophisticated optical transmittance and pertinent work function [45], [46]. Jeng et al. originally fabricated NiOx films as HTL in the p-i-n-type devices and attained a PCE of 7.8% [47]. The devices based on vapor-deposited NiO films are supposed to attain decent performance, though, vapor deposition consumes energy for high vacuum and deems expensive. NiO also has a fair resistance to moisture and may as well keep the perovskite layer intact under moisture.

NiOx layer may comprise great deal of surface defects, which in turn can perform as probable trap states [48]. These traps in NiOx layer are prone to absorb hydroxyl group [49], which potentially the deforms the perovskite structure [50].

2.2.3.6.2. PbPc

Metal phthalocyanines are aromatic molecules comprised of a macrocyclic ring with a large π-conjugated system which stack through π−π supramolecular interactions [51], [52], [53]. In general, they possess highly symmetrical square planar D4h structures with high thermal and chemical stabilities. Their lower costs, exceptional stability, flexibility, decent electrical reaction and comfortable manufacture have presented them as diverse ingredients. These prevailing materials deem potent in the fields of molecular electronics and optoelectronics [54], [55].

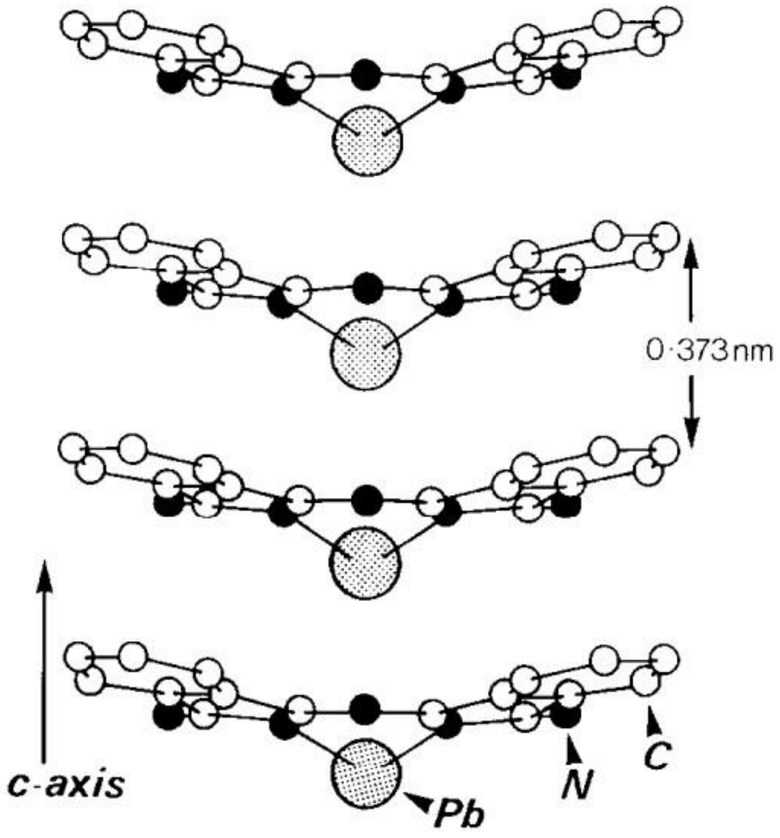

Figure 2.4 Structure of PbPc

Among many Metal phthalocyanines' compounds, lead (II) phthalocyanine (PbPc) has an unusual structure with C4v symmetry like a shuttlecock [56]. Studies certify that there are two polymorphs of PbPc crystals, the monoclinic (α-phase) and the triclinic (β-phase) [52], [57]. Both these crystalline polymorphs have shown varied responses to air, nitrogen oxide and water vapours [52].

Aim of our study is to check NiOx and Lead Phthalocyanines as Hydrophobic Hole Transport Materials in PSCs and to study their transport and hydrophobic properties.

Summary

Since the fabrication of first solar cell in 1946, a lot have been put forth in the field. Silicon was the first successful material extensively used in the regard with different formations. In early years they were tested mostly by the massive companies in space expeditions. There was a slow growth in the early years but in the 70's, especially during Arab Oil Embargo, a dynamic shift was seen towards mass production and research development of Solar Cells. A new thin films generation came into research which brought a high promise. But there were a lot of issues regarding performance and stabilities to cater with. With the intervention of liquid based dye-sensitized solar cell, new dimension of solar cells emerged in the early 90's. But they seemed to have a constant performance and quality issues over the years. It was when perovskite material was used as dye in such cells that acquired the attention of researchers. A new rise in performance was seen with the fabrication of first solid based perovskite solar cells. With the adjustments, researchers were able to device more than 20% efficient solar cells, best the history seen. Though they come with a promise of higher performances but issues regarding their stabilities remain prevailing. ETL and HTL both are responsible in the degradation issues. Our purview is to device such a hydrophobic HTL which can save the perovskite layer under high moisture conditions.

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Chapter 3.

An Introduction to Synthesis and Characterization Techniques

This chapters gives a detailed account of all the manufacturing and synthesis techniques along with the characterizations techniques which we acquired to complete our study.

3.1. Manufacturing Techniques

Since the inception of PSCs, various techniques have been used to manufacture the cells. As PSCs belong to Thin Films and Nano Sciences so, most of the techniques involved are the ones used in Nano or Thin Films fabrication. Few common practices are:

3.1.1. Spin Coating

The precursors are prepared in accordance with proper stoichiometry and then spin coated on the desired surface. A motor is used to generate a centrifugal force to spin the desired substrate/wafer at high rpm as much as 6000 for a defined time [1]. It can be done in steps defined via console. Objectively a solution of the desired material is prepared. DMF, DMSO and 2-propanol have been used as solvents in case of PSCs [2].

Once the solution is prepared, the substrate is then spun at a high speed whereas, the thickness of the film is controlled via spinning speed, surface tension and the viscosity of the solution. The solvents used are often volatile or with low boiling points. So, a consequent heating/annealing helps to remove them and provide the desired film. Main positive aspect of spin coating is that it’s cheaper than most of the alternate existing techniques, yet it provides good quality films if optimized properly. PCE of over 20% has been achieved using such methodology [3].

Figure 3.1 Spin Coater available at USPCASE, NUST for deposition of various layers

3.1.2. Dip Coating

Dip coating is a simple and old-fashioned technique that can be used for deposition of thin films on substrates, cylinders and blocks. The film thickness depends on the viscosity of solution, surface tension and gravity. It also depends upon the immersion time of substrate into coating solution, the more rapid substrate withdrawal causes the thicker film [3]. The dip-coating process involves following stages:

3.1.2.1. Immersion:

The first stage of the process is the dipping of substrate in the solution of desired coating material at a constant speed.

3.1.2.2. Time duration:

The substrate should be dipped in to the solution for a known time duration. Time duration of immersion of substrate effect the thickness and then drawn up with constant speed.

3.1.2.3. Deposition:

When the substrate is drawn up thin layer deposits itself on the substrate. The withdrawal of substrates should be carried out at a constant speed for getting uniform film. The speed of pulling up a substrate defines the thickness of the film. [4]

3.1.2.4. Drainage:

After pulling up the substrate the excess liquid will drain from the substrate surface.

3.1.2.5. Evaporation:

Finally, substrate is annealed on the suitable temperature for evaporating the solvents forming thin film.

3.1.2.6. Thermal Evaporation / Vacuum Deposition

Thermal evaporation is a common physical vapor deposition (PVD) technique. In thermal evaporation resistive heating is characteristically used as a source to evaporate a solid material in a vacuum atmosphere to deposit a thin film. A high vacuum is created in the chamber to heat the material until the desired vapor pressure is generated. The evaporated material thence travels through the vacuum and coats the substrate situated across the right locale.

Various components of vacuum thermal evaporator are:

3.1.2.7. Crucible

Current passes through that and melts the charge. Crucible can sublimate on very high temperatures, so it can contaminate our film.

3.1.2.8. Charge

Is placed in the crucible, which is deposited on the substrate. Normally metals and dielectrics are used as charge in thermal evaporation.

3.1.2.9. Substrate (wafers)

At which the film is deposited. Normally glass (can be FTO or ITO).

3.1.2.10. Roughing and turbo molecular pump

The range creating 10^{-2} torr and 10^{-8} torr pressures respectively.

Thermally evaporated films were also prepared giving films of uniform thickness, resulting in PCE of 15% [4].

3.1.3. Mix Coating and Evaporation

In mix coating and evaporation few layers of PSCs are deposited via spin coating and few through thermal evaporation. Hybrid approach of using both spin coating and vacuum deposition to engineer PSCs has also been established with the efficiency of 12% [5].

3.2. Characterization Techniques

Characterization techniques are used to understand the device structures, chemical compositions and their optical and electrical behavior. Various techniques used for PSCs and specifically for our study are mentioned below:

3.2.1.1. Scanning Electron Microscopy (SEM):

SEM is objectively used to determine the surface morphology of the materials or films. A simple compound microscope uses visible light with a good capacity to magnify any material surface for analysis. Whereas, SEM uses electron beam about 1000-time shorter wavelength than visible light so, SEM tends to magnify the material surface much higher than simple microscope.

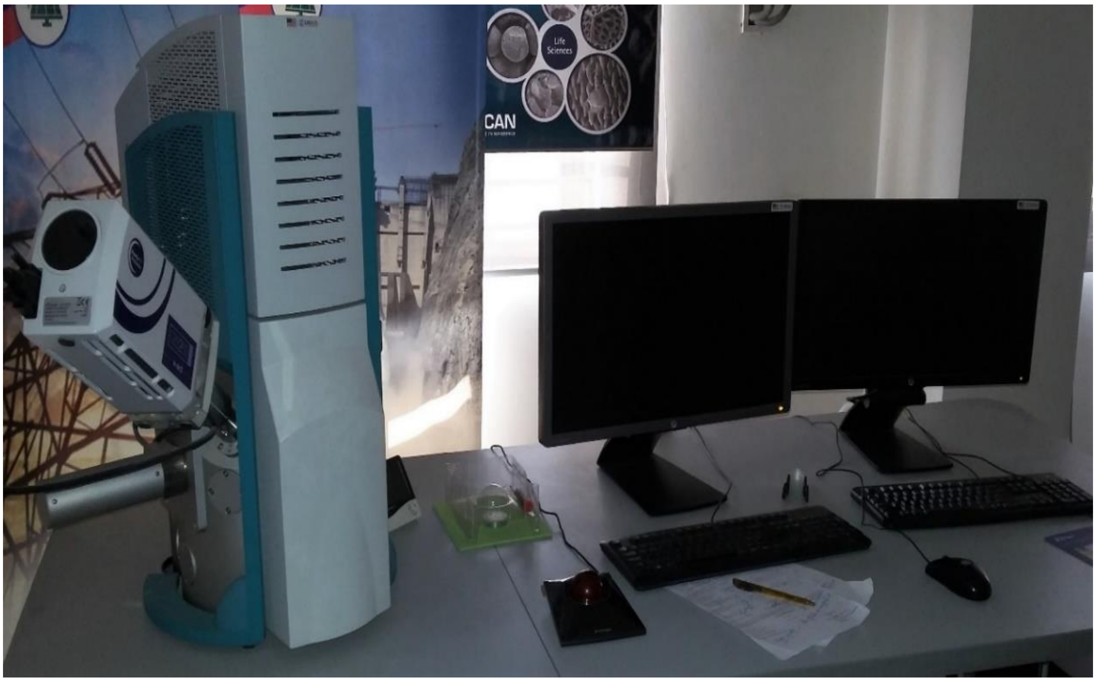

Figure 3.2 SEM available at USPCASE, NUST

3.2.1.2. Working Principle:

The electron beam is produced thermionically by means of electron gun fixed on a tungsten filament cathode. The tungsten tends to have the uppermost melting point and least vapor pressure; therefore, it is precisely suitable for electron beam generation via heating thermionic electron guns. The condenser lenses of diameter ~4–50 Å are used for focusing of electron beams and deflection coils whilst, controlling of electron beam is achieved by using deflection coils. The schematic diagram of SEM shows the comprehensive flow of process from the start i.e. generation of electron beam to end i.e. the beam strikes the sample. Lastly, the generated signals i.e. secondary electrons are analyzed with the help of detector and the output is exhibited [8].

When the electron beam strikes the surface of sample, diverse sorts of signals are generated carrying information about film or surface morphology. These signals comprise secondary electrons, back scattered electrons and X-rays. Finally, these signals are detected by detectors and analyzed for various results. Surface morphology is determined by the information provided by secondary electrons whereas, the chemical composition of material is evaluated by the information provided by back scattered electrons [8].

3.2.2. X-Ray Diffraction (XRD)

XRD is a characterization technique used to understand the crystal structures, phase changes and lattice parameters of the desired samples.

3.2.2.1. Working Principle

When X-rays are incident upon crystalline materials, they interact with atoms of the material and refract X-rays of characteristic energy [9]. Each material exhibits a discrete pattern even in a mixture of materials. XRD basically uses the principal of constructive interference of refracted X-rays [10].

When X-rays interact with matter at atomic level, they may cause diffraction, fluorescence or ionization. In XRD, when X-rays strike atoms, they make the electrons in atoms to vibrate with frequency same as their own frequency which results in the constructive interference due to high scattering angles and is given by Bragg's law [11].

$$2d\sin\theta = \lambda$$

Where, θ = The angle between the incident beam and plane

λ= X-rays wavelength

d= Spacing between the planes

Figure 3.3 XRD machine available at USPCASE, NUST

When a focused X-ray beam interacts with the planes of atoms, part of the beam becomes scattered radiation, which in turn forms diffraction patterns related to the crystal structure of the material. Both directions of the scattered rays and their intensities provide important knowledge of the PSCs.

The model D8 Advance with Da-Vinci design by BRUKER as shown in the figure has more advanced capabilities like:

- It can switch betwixt Bragg-Brentano and parallel-beam geometries with a single push button.
- Contains a modern day Diffraction Suite with an integrated virtual diffractometer.
- An advanced and sophisticated DaVinci Mode which enables the machine to recognize and configure the components in real time.
- An easy and swift switch of focus from line to point via a Twist-Tube.

3.2.3. Ultraviolet-Visible Spectroscopy (UV-Vis)

UV-Vis spectroscopy is a vital optical technique in which visible (400nm - 700nm) and ultraviolet (190nm - 400nm) regions of the electromagnetic spectra are utilized to attain evidence about the light absorption and transmittance of molecules[12]. Other than that, this technique is also handy for determining impurities, saturation, unsaturation and existence of hetero-atoms in the material. A qualitative analysis can also be performed to determine the type of compounds present in the sample. The spectrum obtained is thence compared to spectra of known compounds.

3.2.3.1. Working Principle

When a sample is placed in front of the UV-Vis spectra the electrons get excited to higher anti-bonding orbitals. Smaller the energy gap between HOMO and LUMO of a material, easier is the excitation of electrons by longer wavelength radiations. When a molecule with an energy equal to gap between HOMO-LUMO is exposed to radiation with a wavelength corresponding to that energy, the electron is jumped from HOMO to LUMO. This is referred to as electronic transition bonding to anti-bonding and denoted by σ - σ^*. The graph between absorption or transmittance of light on X-axis and different wavelengths on Y-axis is obtained and analyzed [12].

3.2.4. Hall Effect

Hall Effect is used to measure resistivity, conductivity and mobility across the surface. In Hall Effect a magnetic field is applied perpendicular to the flow of current generated via creating a potential difference across a conductive surface. This effect was discovered by Edwin H. Hall in 1879- an American Physicist.

When potential difference is applied across a conductor, current starts to flow which is a combination of electrons, holes or ions. When a perpendicular magnetic field is applied, these charge carriers experience a force, called Lorentz Force, which make these charges to bend from their path making equal and opposite charges on contrasting faces. This parting of charges creates an electric field which hinders the movement of more charges, so a stable electric potential is built till the charges are flowing.

3.2.5. Current Voltage Characterization (I-V)

I-V curves are used to characterize the electrical properties of a solar cell depends on electrodes active regions to benefit carrier injection, charge transport and exciton dissociation etc [13]. Current-Voltage (I-V) characteristic curve states Solar Cell’s electrical performance, to better understand the properties of the device and material incorporated [14]. Current-voltage characteristics or I-V curve is basically a graphical representation of the electric current generated across the device and the voltage stipulated. I-V curve gives the Information about the open circuit voltage (Voc), short circuit current (Isc) and Fill factor (FF) of the device which is enough information for calculating solar cell efficiency. Generally, device or junction I-V characteristics are determined using Keithley source meter under dark and illuminated vacuum environment. The Keithley source measure Unit (SMU) model 2004 is available at NUST, that can provide voltage or current and at the same time measure voltage or current. It is integrated unit of digital multimeter, current/voltage source and a load.

It can be used for multiple applications like testing of batteries, solar cells, thin films, thermistors, low and high-power diodes.

Figure 3.4 Solar Simulator available at USPCASE, NUST

Summary

Many methods are utilized by the researchers in the synthesis and fabrication of PSCs like: spin coating, dip coating, thermal evaporation, sputtering and mix coating. The best process for available materials is chosen in accordance with their chemical and physical behaviors. Once the layers are deposited using certain technique, these layers are tested with the help of various characterization techniques to understand their surface morphology, crystal structure, optical and electrical behavior. Various characterization techniques being used in our course of study like: SEM, XRD, UV-VIS-NIR, Contact Angle Measurement, J-V Curve determination and Hall Effect are explained.

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Chapter 4.

Experimental

This chapter provides information about the precise quantities of materials used under different techniques along with various characterizations done to better understand their behaviors.

4.1. Fabrication of ETL

ETL used in our case study was Titania (TiO_2). A compact Titania layer was deposited on FTO glass using spin coater. Titania Paste: Ti-Nanoxide BL/SC was acquired from Solaronix which deems to be an organotitanate formulation to deposit a compact blocking layer of TiO_2. The compact layers formed as such also work as a blocking layer.

4.1.1. Spin Coating of ETL

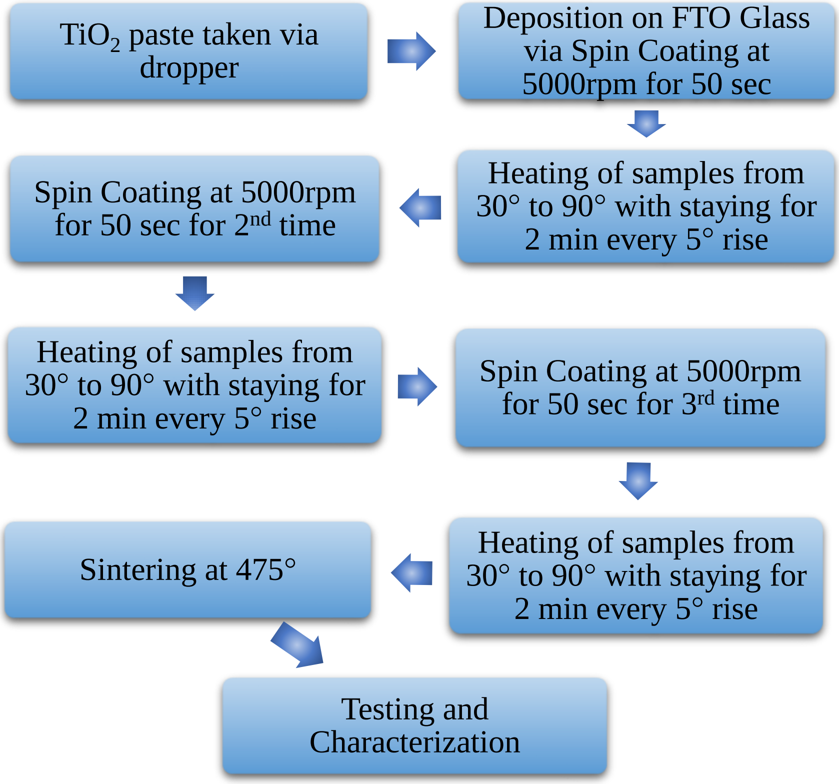

Figure 4.1 Step by step preparation of TiO_2 ETL

Titania was deposited on FTO via spin coating with using single step of 5000rpm for 50 sec. After single coat films were step-annealed from 40°C to 90°C with keeping them stay for two minutes every 5°C rise. Three coats and consequent step-annealing were taken out to achieve the desired thickness. Finally, Titania deposited FTO films were annealed at 475°C to acquire the ideal compact Titania layer for electron transport purposes.

Sintering at High temperature should be gradual to avoid any damages to the film. It is highly recommended for more compact film generations.

4.2. Fabrication of Absorber Layer

Absorber layer or Perovskite Layer is typically prepared using solution processing with DMF as solvent to the PbI_2, the solution is then spin coated on to the ETL and obtained films are dipped in $MAPbI_3$ solution to form the perovskite layer. The layer thence formed seem to have degradation issues with moisture on a consistent basis. Therefore, alternate approaches are also been put forth to hinder the issue. One of them is the addition of DMSO in a one-step solution processing of the perovskite layer formation, which not only improves the stability but also provides better solubility of PbI_2 in DMF[1]. Apart from that Caffeine also showed better stabilities as its molecules tend to generate a molecular lock with Pb^{++}[2]. We are going to consider both the possibilities to device our absorber layer.

4.2.1. Experimental

Experimental procedure for absorber layer was taken out in Argon environment in a glove box to keep the moisture levels at bay.

4.2.1.1. $CH_3NH_3I.PbI_2.DMSO$ as Hybrid Perovskite Layer (Case 1)

In first case we used PbI_2, CH_3NH_3I and DMSO in 1:1:1 i.e. 9.22g, 3.18g and 1.42ml, respectively. All of them were dissolved in 12.66ml of DMF and stirred at room temperature on a magnetic stirrer in the glove box for 1 hr. Once the solution was achieved, the FTO glasses with Titania ETL were dipped in the solution to dip coat the absorber layer.

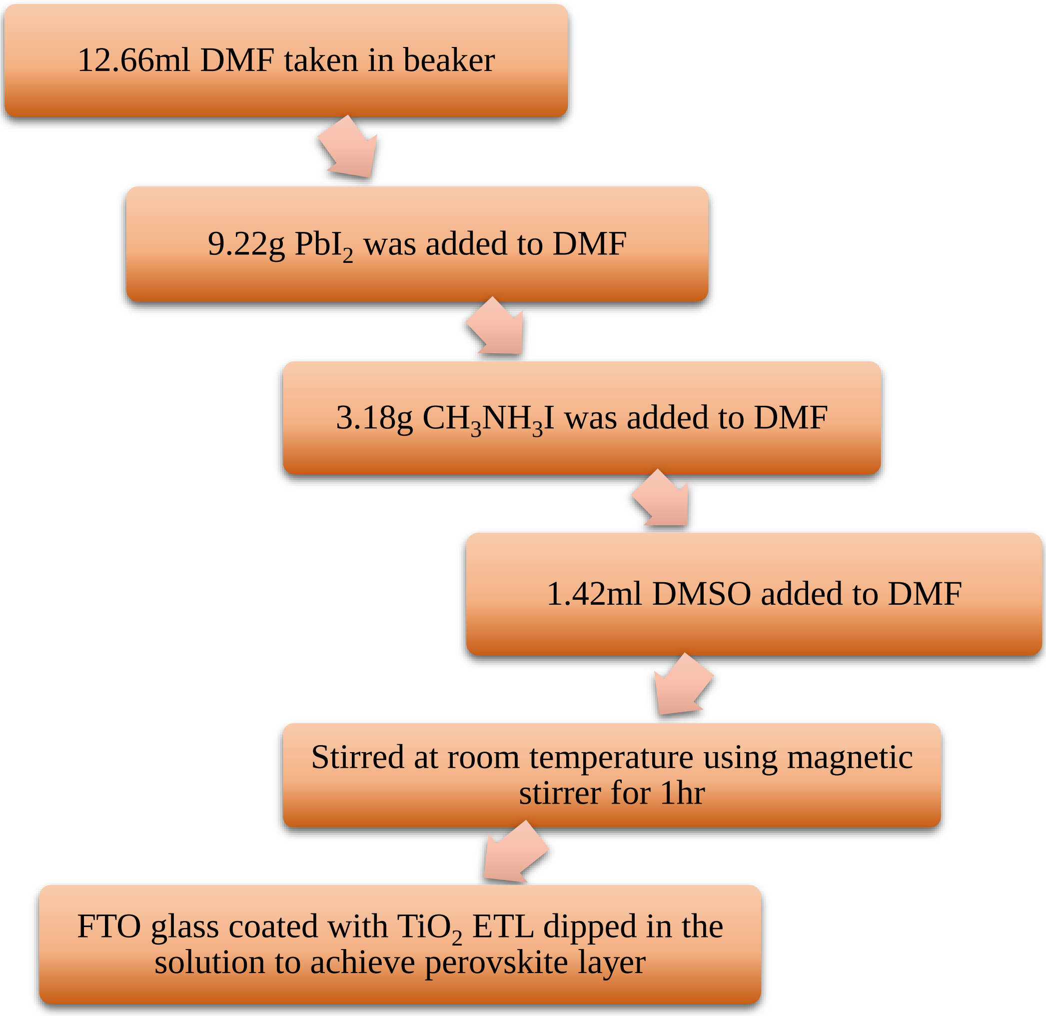

Figure 4.2 Step by step preparation of Perovskite layer without Caffeine

4.2.1.2. $CH_3NH_3I.PbI_2$.DMSO.Caffeine as Hybrid Perovskite Layer (Case 2)

In second case along with the same amount of ingredients mentioned above, 0.12g of Caffeine was also added to provide further stability. The solution was stirred on a magnetic stirrer in the glove box at room temperature for 1 hr. The FTO glasses with coated Titania ETL were dipped in the solution to dip coat the prepared solution.

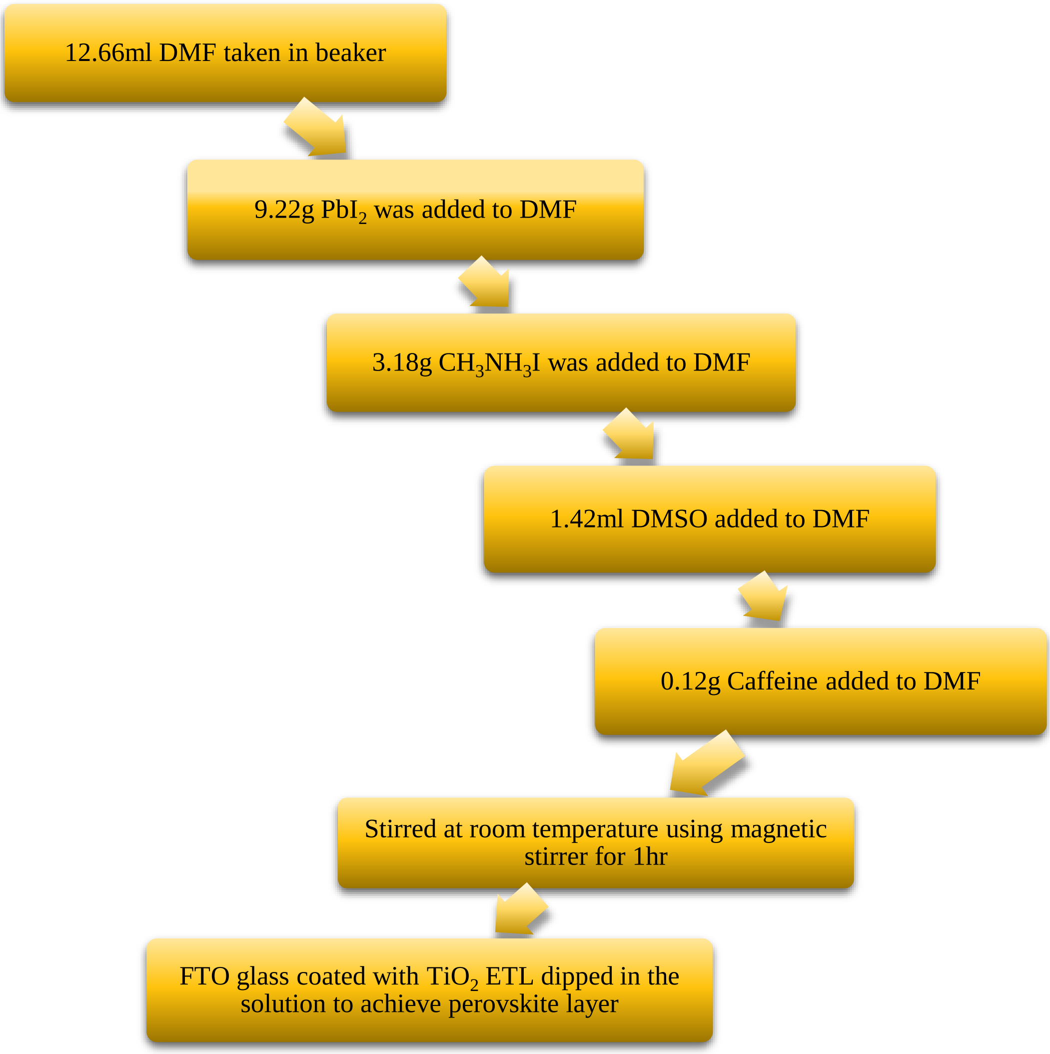

Figure 4.3 Step by step preparation of Perovskite layer with addition of Caffeine

4.3. Fabrication of HTL

NiO and PbPc were used to fabricate a couple of HTLs to better understand the behaviors. Lets take them one by one.

4.3.1. NiO preparation as HTL

NiO was prepared using coprecipitation method.

4.3.1.1. Materials:

- $NiCl_2.6H_20$ Solution (7.1 gm dissolved in 300 ml DW)
- NaOH Solution (0.8 gm dissolved in 200 ml DW)
- Ethylene Glycol 10 ml.

4.3.1.2. Preparation of NiO:

Co-Precipitation Technique used.

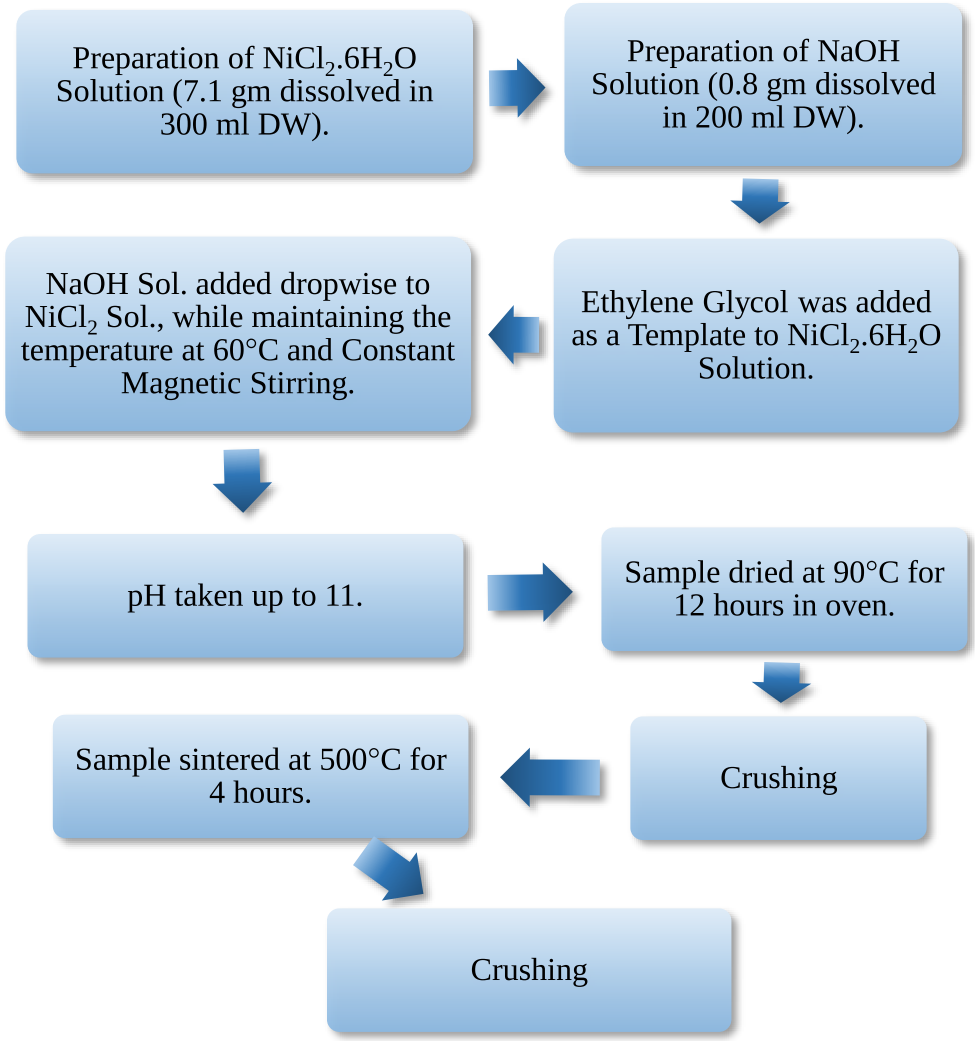

Figure 4.4 Step by step preparation of NiO

4.3.1.3. Deposition of NiO

Once prepared 0.5g of NiO was taken in 3ml ethanol and were subjected to grinding with the help of a morter and pastel. A honey like gel was obtained which was taken in a syringe to spin coat on the glass surface with following ramps (R) and time (t):

Table 4.1 Spin Coating parameters for NiO

rpm	time
R_1 = 500 rpm	t_1 = 30 sec
R_2 = 3000 rpm	t_2 = 30 sec

4.3.2. PbPc as HTL

Various hydrophobic HTLs (PbPc) were fabricated by depositing upon FTO glass. Thermal evaporation under high vacuum of $1.2*10^{-3}$ or 10^{-7} Torr is used to deposit a layer of metal phthalocyanine of about 40-60 nm. After the deposition various characterizations were undertaken.

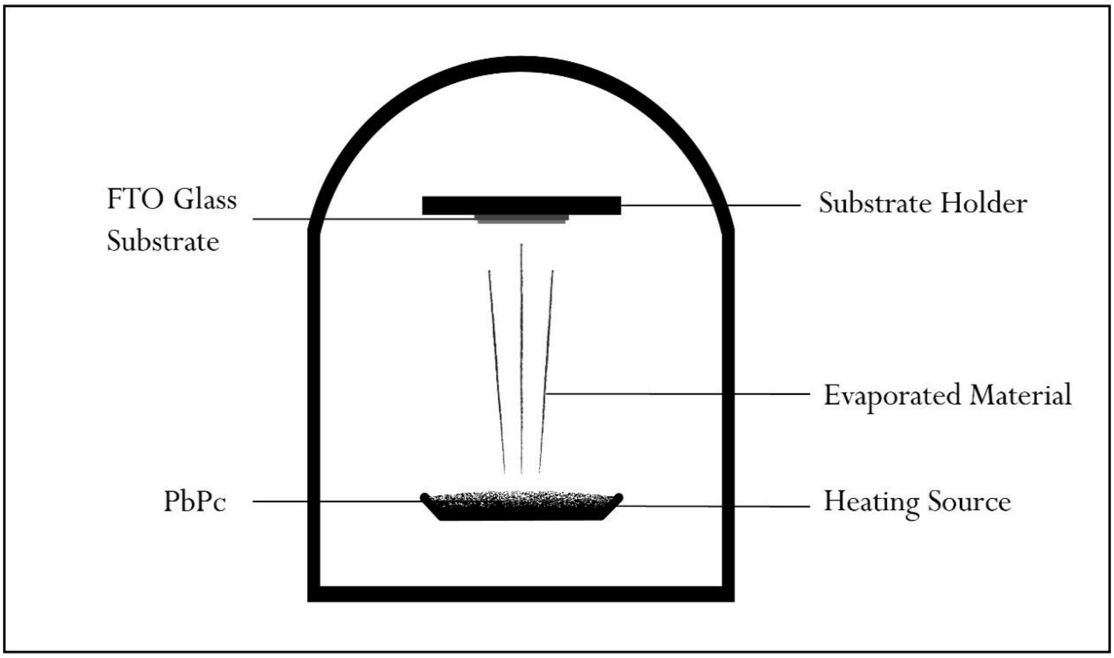

Figure 4.5 Thermal Evaporation of PbPc of FTO Glass

4.4. Contact Growth via Thermal Evaporation

A silver top layer of 100 nm, covering the top layer of cell is grown using thermal evaporation of silver.

4.5. Characterization of Fabricated Layers

Layers fabricated via different methodologies are characterized for their optical, morphological, structural and electrical properties.

4.5.1. Optical Characterization

For optical fabrication UV-VIS-NIR Spectrophotometer (UV-3600 Plus, SHIMADZU) is used to understand the absorbance and percent transmittance of the layers. A set of data is obtained when the light pass through the surface. The data generated by the Spectrophotometer is arranged in the form of graphical representation using MS Excel.

4.5.2. Morphological Characterization

To understand the surface morphology and surface quality, SEM (VEGA 3 LMU, TESCAN) was used. Studies have been done using SEM, at a magnification of up to 500 nm with an accelerating voltage of about 20 kV and a magnification of about 50 kX.

4.5.3. Structural Characterization

For crystal structures XRD (D8 Advance, BRUKER) was incorporated. 2Ө angle is used for both PbPc and NiO, from 10° to 70°. Jade is used to analyze the obtained peaks to understand the crystal structures. To better understand the crystallography, peaks are compared against the previously conducted studies.

4.5.4. Contact Angle Measurement

Contact angle was measured using Goniometer. A water droplet of 3-µm size was used to pour upon the surface of fabricated layers to calculate the contact angle of the droplet with the surface. Contact angle thence gives the information about hydrophobicity of the surface i.e. if the angle of contact is lower than 90° it suggests that the surface is hydrophilic but if it is greater than 90°, the surface is hydrophobic.

4.5.5. I-V Characterization

IV measurements of cell under stimulated light were done using SLB-150A, Sciencetech. The fabricated cells were subjected to simulated sunlight and IV-Curves were generated via collecting the current with the help of silver contacts.

Summary

Titania ETL was deposited on FTO Glass using spin coating methodology and then perovskite layer was deposited using dip coating. Finally, NiO HTL was deposited using coprecipitation method and PbPc HTL was deposited using Thermal Evaporation. Separate samples of NiO and PbPc on FTO Glass were also prepared for a comparative analysis to understand their hole transport characteristics.

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Chapter 5.

Results and Discussion

This chapter discusses results obtained by characterizations of the films prepared using various techniques shown in the previous chapters.

5.1. HTL Characterization

We are going to discuss various HTLs one by one deposited as discussed in the experimental section.

5.1.1. PbPc deposited on FTO Glass as HTL

5.1.1.1. Morphological Characterization

In SEM a focused beam of high energy electrons is incident upon the surface of the specimen to attain information about the surface morphology.

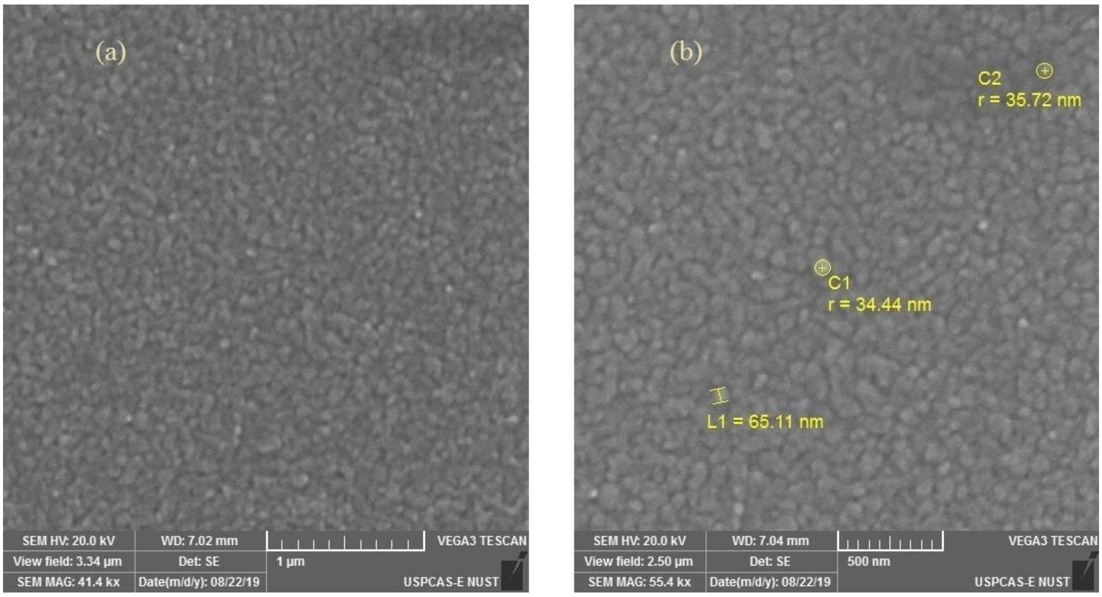

Figure 5.1 SEM of PbPc on FTO Glass at (a)1um and (b) 500nm

SEM was done at 5 um and 500 nm. The results show that films were smooth and evenly distributed even at the higher resolutions. The formation of such smooth and compact layers is due to high vacuum conditions, higher melting point of PbPc of around 230°C and the fact that it sublimes.

5.1.1.2. Structural Characterization

XRD peaks of the samples used relate to the peaks available for PbPc in literature. The peaks were found coherent to the α-phase of PbPc which objectively is responsible for hole transport purposes. The characteristic peaks at 12.61° and 16.51° correspond to the (320) and (420) monoclinic diffraction planes, respectively[1]. It suggests that thermal evaporation is the right tool to deposit PbPc on any surface.

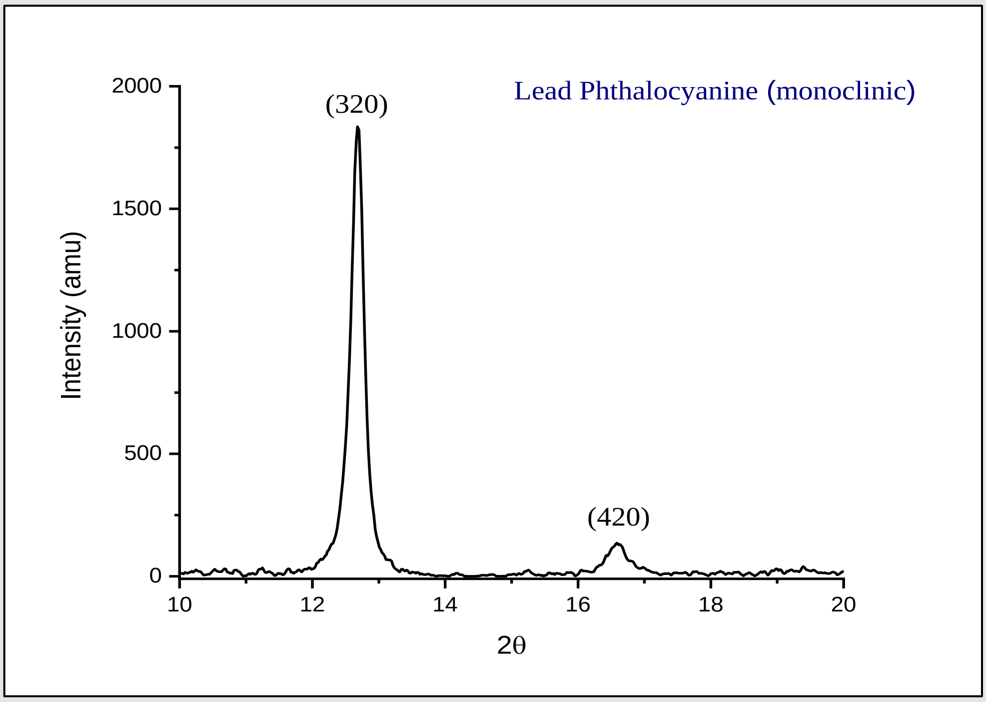

Figure 5.2 XRD of PbPc on FTO glass suggesting the peaks at α-phase

5.1.1.3. Optical Characterization

UV-Vis yields a spectrum of absorption and transmittance of light which provides knowledge about the amount of light passing through various wavelengths. The visible light lies between the wavelengths of 400-800 nm. In view with that the graph in the figure shows that the around 35% of light for PbPc is passing within the visible region. As solar light which is harnessed for solar cell purposes lie within visible range, so, PbPc provides good transmittance for such light.

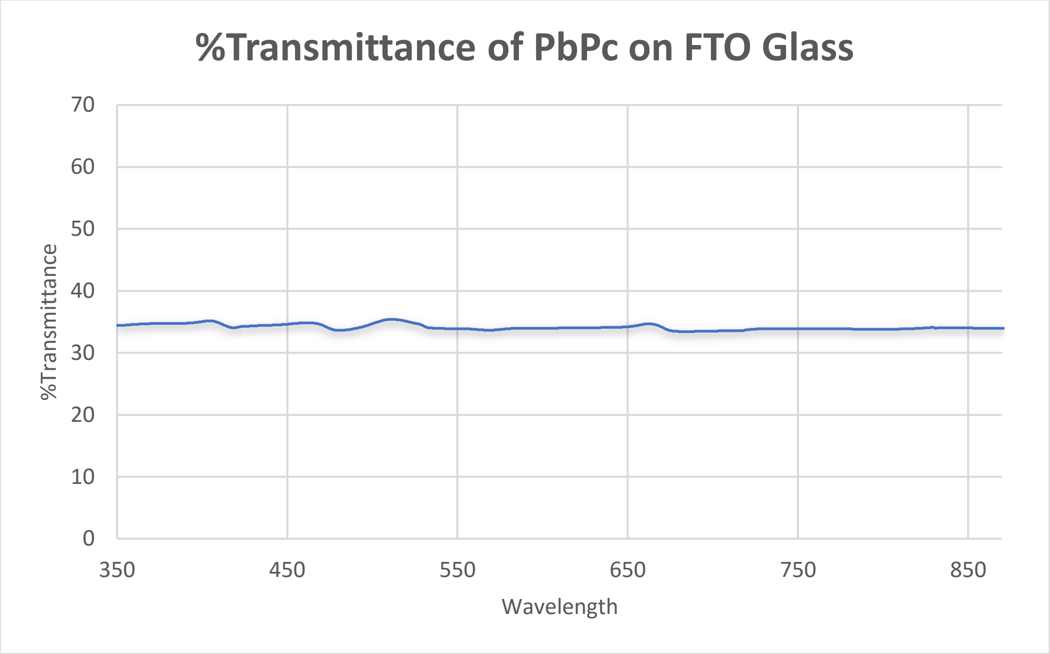

Figure 5.3 %transmittance of PbPc coated on FTO Glass using UV-VIS-NIR

5.1.1.4. Hydrophobicity Measurement

Contact angle for the fabricated PbPc films was observed using a goniometer. A 3-µm sized water droplet was poured upon the surface of slide. The contact angle of about 86.1° was observed which suffice the hydrophobic characteristics of the film. In general, the surfaces generating an angle of more than 90° are referred to as hydrophobic but with keeping view the viscosity of water, any angle closer to 90° is highly hydrophobic.

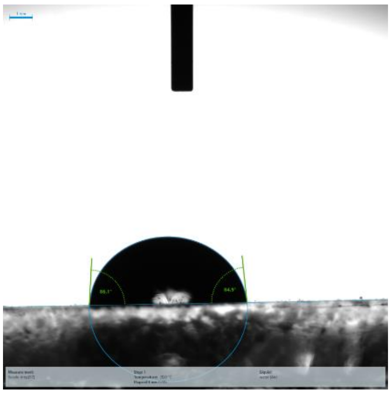

Figure 5.4 Contact Angle Measurement of PbPc on FTO Glass via Goniometer

5.1.2. NiO deposited on glass as HTL

5.1.2.1. Morphological Characterization

Grain Like Nano structures observed by SEM Imaging. Grain size of r= 27.28 nm, 28.50 nm, 25.53 nm was observed at 500 nm scale. They can be seen in the figure attached.

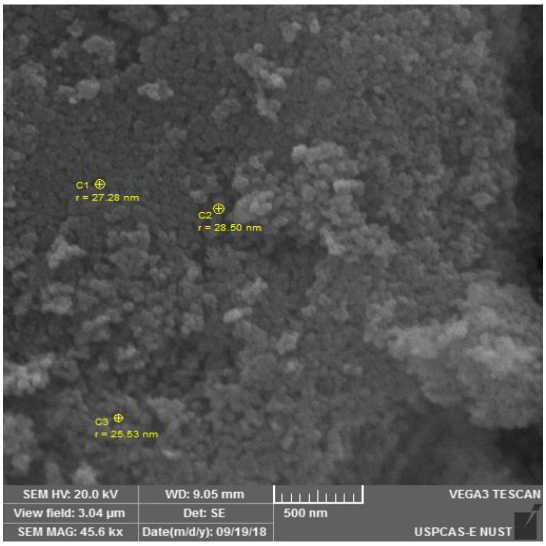

Figure 5.5 SEM image of NiO at 500nm

5.1.2.2. Optical Characterization

The figure shows that the around 50% of light for NiO is passing within the visible region. As solar light which is harnessed for solar cell purposes lie within visible range, so, NiO provides high transmittance for such light.

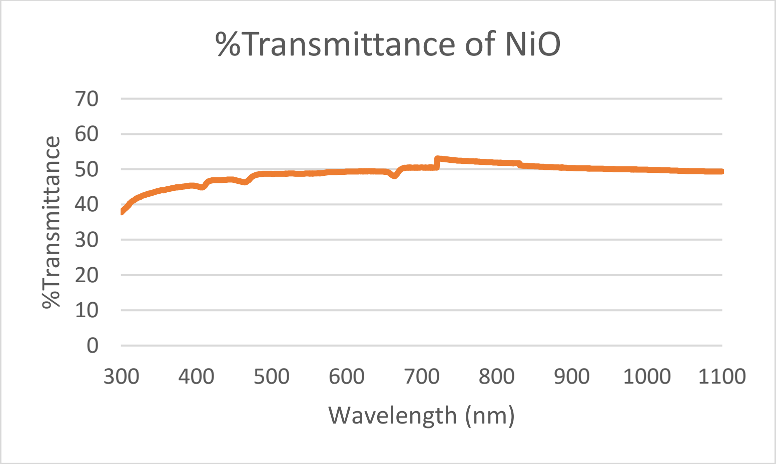

Figure 5.6 %Transmittance of NiO film

5.1.2.3. Structural Characterization

NiO peaks observed in the XRD characterization well match to JCPDS Card No. #47-1049 indicating the face-centered cubic phase of NiO, which affirms the fact that the crystals formed during the process are of NiO.

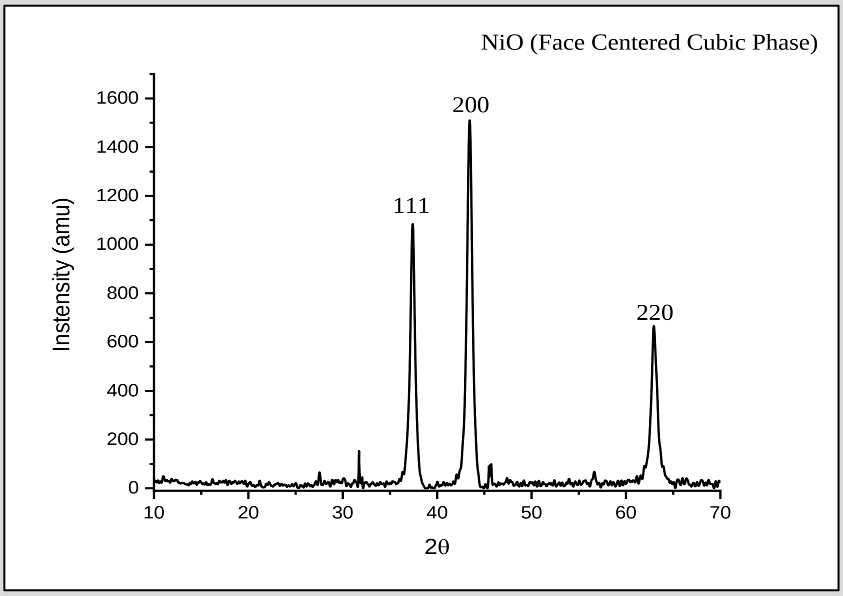

Figure 5.7 XRD characteristic peaks of NiO

The spectrum shows three characteristic peaks at 37°, 43° and 63° showing the diffraction plane of (111), (200) and (220), respectively[2]. Absence of other peaks are testifying that NiO film is in its pure crystalline form.

5.1.3. Electrical Characterization

Hall Effect measurements of NiO and PbPc yielded the following results:

Table 5.1Hall Effect Measurements of NiO and PbPc

	NiO	PbPc
Resistivity	6.481 E+4 Ω	5.830 E+3 Ω
Conductivity	1.543 E-5 $(\Omega\text{-cm})^{-1}$	1.715 E-4 $(\Omega\text{-cm})^{-1}$
Mobility	2.299 E+1 cm^2/Vs	3.284 E-1 cm^2/Vs

5.1.4. I-V Characterization

NiO cells could not indulge any I-V curves, in fact the cells were short circuited and showed a linear ohmic curve. While, PbPc based cells showed I-V character but with poor efficiency. There were some issues regarding perovskite layer deposition. So, I-V Curve generated showed very little Current and Voltage value. Input power was taken as 0.1W/cm^2.

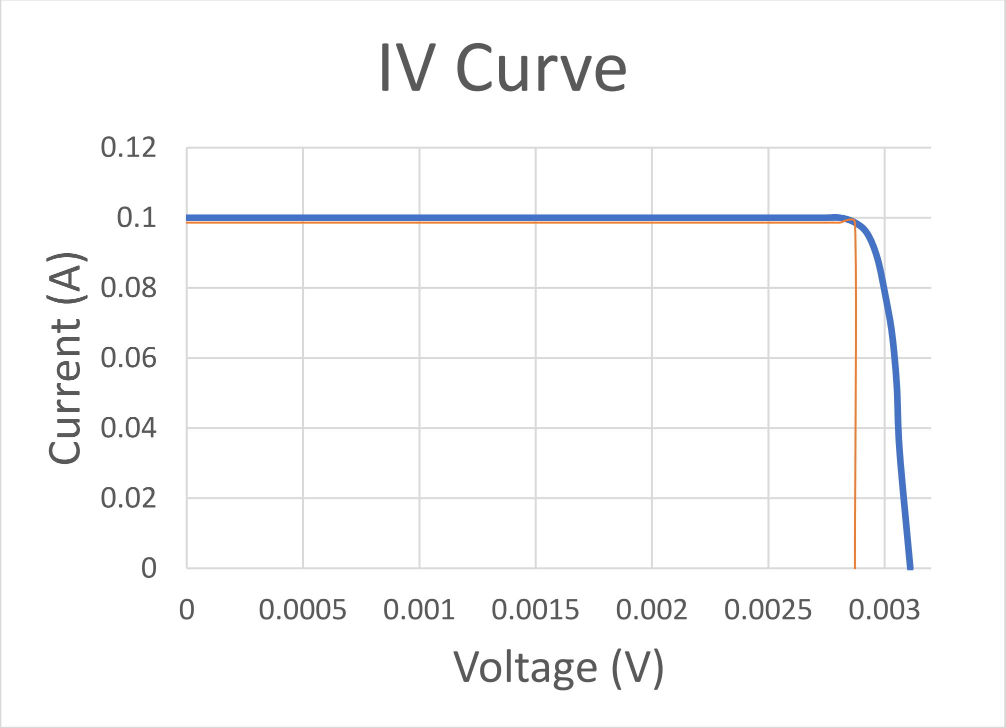

Figure 5.8 I-V Curve for PSC without caffeine

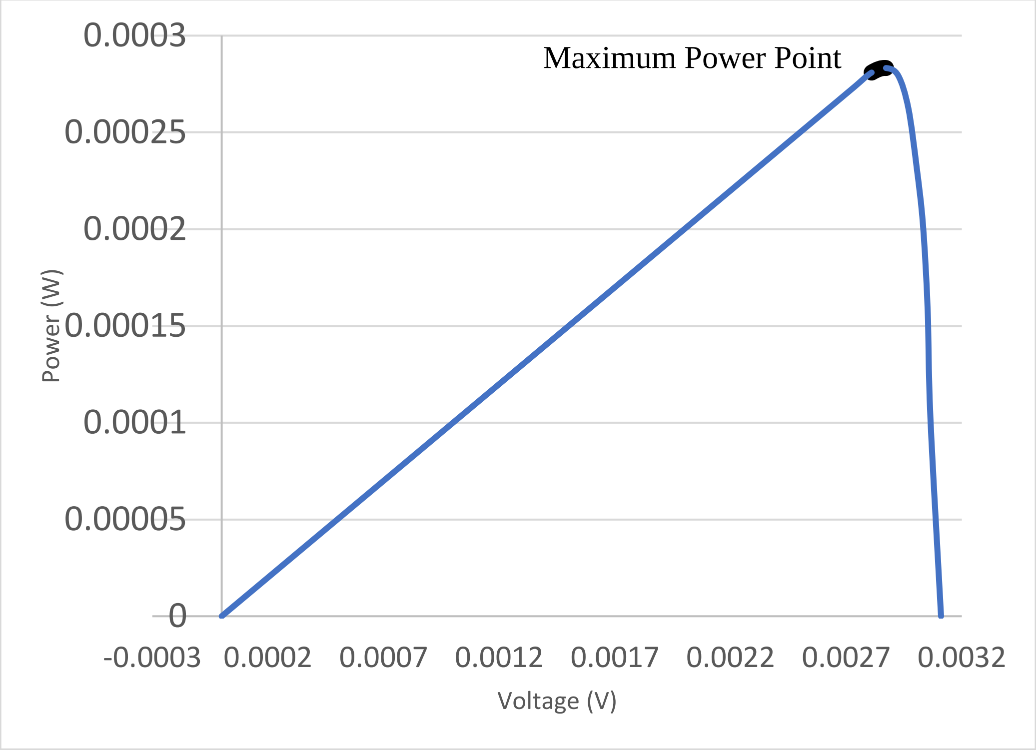

Figure 5.9 Power and Voltage curve for MPP

Table 5.2 Results drawn from IV Curve

Open Circuit Voltage	V_{oc} (V)	0.00311
Short Circuit Current	I_{sc} (A)	0.09999
Max. Power Point	M_{pp} (W)	0.00031
Voltage at M_{pp}	V_{mp} (V)	0.00287
Current at M_{pp}	I_{mp} (A)	0.09863
Fill Factor	F.F.	0.91091
Efficiency	η	0.28%

The reason behind such low efficiency is incomplete formation and degradation of perovskite layer. As dip coating was used for the absorber layer formation and a single solution of $CH_3NH_3PbI.PbI_2.DMSO$ in DMF was used, which seems to be an unadvised option for further studies.

5.2. Comparison of PbPc and NiO as HTL

From the characterization of PbPc it is known that thermal evaporation of PbPc yields smooth and better films. Keeping the substrate temperature on lower side also provide α-phase which is good for solar cell purposes. Considerable transmittance of light (35%) also suggests its greater candidacy as hole transport material especially for inverted type of perovskite solar cells. High contact angle also supports the hydrophobic behavior required to keep the absorber layer from the deterioration due to moisture.

NiO on the hand though gives characteristic NiO peaks but the grain formations deem to hinder the transmittance which way better in case of PbPc. It showed higher transmittance (50%), non-uniformity of the film may have contributed in that. The hydrophobicity also could not be measured as the droplets tend to spread on the surface of NiO.

So, the results imply that PbPc shows far better hydrophobicity than NiO and thus can be used as moisture reluctant HTM. Besides, reasonable light transmittance also deems it to be a better candidate as HTM.

Summary

SEM results of PbPc addresses to the fact that thermal evaporation yields high quality films and XRD peaks affirms the fact that at low temperature the desired phase, which is suitable for Solar Cell purposes is achieved. UV-VIS-NIR results suggest that PbPc comprehends good light transmittance when prepared via thermal evaporation. High contact angle found using Goniometer also confirms the fact PbPc is hydrophobic in nature and can resist the moisture, if subjected to any. While, NiO deposited via coprecipitation seems to be on hydrophilic side and does possess the power to hinder the moisture. Though XRD confirms its structure to be the right one. SEM results of NiO relate to the fact that there may be small sized grains and can be effective in hole mobility.

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Chapter 6.
Conclusions and Recommendations

This chapter sheds light on the conclusions drawn from the undertaken studies and what could possibly be recommended on their basis.

6.1. Conclusions

Following conclusions can be drawn from the results mentioned in precious chapter:

- Thermal Evaporation of PbPc yields smooth and compact films with the required α-phase structures, which are essential for hole mobility.
- PbPc films bear good hydrophobic properties due to smooth and compact distribution of films.
- NiO showed more transmittance as it may have been because of non-uniformity of the films than for PbPc films.
- NiO prepared via coprecipitation do not depict hydrophobic behavior as films are mesoporous and hence cannot be considered as a hydrophobic HTL.
- I-V Curve of PbPc based cell showed poor efficiency as perovskite layer was degraded due to the fabrication technique employed.
- NiO when incorporated in cell was short circuited due to non-uniformity of film giving ohmic curves.

6.2. Recommendations

- PbPc deposited via thermal evaporation can be used as a hydrophobic HTL in Perovskite Solar Cells.
- NiO can be used as a good HTL by improving the uniformity and thickness of the film.

Annex 1

MSNANO-2019

Hydrophobic Hole Transport Material For Perovskite Solar Cells

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ABSTRACT

Over the past few years organic-inorganic halide perovskite solar cells have drawn an extensive attraction due to high solar cell efficiencies, which have gone past 20%. The issue that still prevails is the stability of these perovskite based solar cells. Obvious reasons for these instabilities relate to deterioration of electron transport media under UV-irradiation, hysteresis losses within the cell and fast degradation under high relative humidity due to water-solubility of the organic component of the material. Using mixed halide perovskite (combination of iodide and bromide) and encapsulating perovskite material with carbon nanotubes have shown better stability and resilience to the moisture but still no rigid solutions are crafted to cater the problem. Another approach to overcome the very problem is replacing the typical Hole Transport Materials (HTMs) like: spiro-MeoTAD with hydrophobic materials. Recently, Metal Phthalocyanines (PbPc/CuPc) have been used as HTMs and showed promising results under high humidity conditions over a long period of time. This tends to be a doorway for more firm and stable perovskite cells. We thence have studied various properties of PbPc to comprehend its behavior as hydrophobic hole transport material using various characterization techniques like: X-Ray Diffraction, Contact Angle Measurement, Scanning Electron Microscopy and UV-VIS-NIR. The results have affirmed that PbPc stands not only as an exceptional HTM but also serves as a hydrophobic layer against the moisture.

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1. Introduction

In 1991, Micheal Gratzel and Brian O'Regan were able to design a high efficiency dye sensitized solar cell (DSSC)[1]. Methylammonium lead halide perovskite material was used as an inorganic sensitizer in liquid-based DSSC in 2009, showing 3.1% efficiency for bromine and 3.8% efficiency for iodine[2], which was doubled within 2 years via optimization of the coating conditions of perovskite[3]. But the liquid-based perovskite solar cell had stringent stability concerns, especially the rapid dissolution of the perovskite in liquid electrolytes[4]. A durable and stable solar cell with an efficiency of 9.7% was developed in 2012 by using solid hole conducting material instead of liquid electrolyte[5], introducing a whole new dimension of solar cells, termed as Perovskite Solar Cells.

During the year 2013, work was carried soundly upon the performance of these cells yielding in an enormous progress with energy conversion efficiencies reaching a confirmed 16.2%[6]. Values of about 20% efficiencies have been claimed till the date[7]. The very basic reason for the high level of success of Perovskite Solar Cells is that the Perovskites have great solar light absorption capabilities. Energy Band Gap is also 1.5, which is pretty much suitable for solar cell operations. Ultrafast charge generation, high carrier mobilities and slow recombination rates also make them resilient and productive. Only major issue is the stability of these cells and if we can improve this issue by making few changes, we ought to take them. As they are the future of the solar cells industry.

Organic-inorganic methylammonium lead halide perovskites ($CH_3NH_3PbI_3$) have thus have acquired a prodigious lure as a photovoltaic material due to their immense power conversion efficiencies, low cost, extraordinary optical and electronic properties i.e. optimal band gap, impressive carrier mobility, high absorption coefficients and long diffusion lengths[8].

To be precise, the absorption coefficient of methylammonium lead iodide perovskite ($CH_3NH_3PbI_3$) is about $10^4 cm^{-1}$ in the visible light spectrum[9], which is almost ideal for solar cell applications. Energy Band Gap is also pretty much suitable for solar cell operations. Ultrafast charge generation, high carrier mobilities and slow recombination rates also make them resilient and productive.

Practically, solar cells ought to have a sound long-term stability. Unfortunately, the stability of the perovskite solar cells is incapacitated due to fast degradation at high relative humidity because of the water-solubility of the organic component of the material[10]. Using mixed halide perovskite (combination of iodide and bromide)[11] and encapsulating perovskite material with carbon nanotubes[12], have shown better stability and resilience to the moisture but still no rigid solutions are crafted to cater the problem. Another approach to overcome the very problem is replacing the typical HTMs like: spiro-MeoTAD with hydrophobic materials. Recently, Metal Phthalocyanines (PbPc/ZnPc) have been used as HTMs and showed promising results under high humidity conditions over a long period of time[13]. This tends to be a doorway for more firm and stable perovskite cells.

To overcome the degradation of perovskite material due to moisture, the HTL should be composed of hydrophobic material. Various hydrophobic materials can be utilized as HTL bearing the basic hole transport properties along with their hydrophobic capabilities. Objective of our research is to develop a hydrophobic hole transport layer -lead phthalocyanine (PbPc) for perovskite solar cell which may restrict the moisture which deteriorates the organic component of the cell along with a study the properties of the hydrophobic hole transport material and optimize it for the perovskite solar cell.

2. Methodology and Experimental

Pallets of PbPc bought from Sigma/Aldrich, were prepared and thermally evaporated on the surface of FTO glass at a vacuum pressure of around 10^{-7} Pa. Structural analysis was performed using XRD (X-ray Diffraction). Morphology of the films was revealed using SEM (Scanning Electron Microscopy). UV-VIS-NIR (Ultraviolet-Visible-Near Infrared) machine was used to understand the spectrum of the light passing through the films. Films were then subjected to a contact angle measurement test to determine their hydrophobicity with the help of a Goniometer.

3. Results and Discussions

SEM results as shown in the Figure 1 at various depths narrate that the films generated via thermal evaporation are smooth and uniform in their morphology.

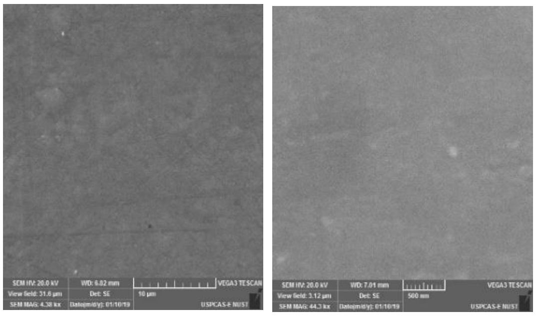

Figure 1 SEM results at 10um and 500nm, respectively

Figure 2 depicts the XRD results of the PbPc film Coated on FTO Glass. The peaks tend to match with the previous studies of PbPc.

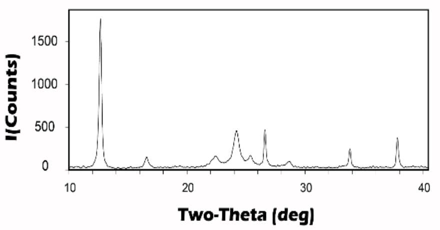

Figure 2 XRD Results of PbPc Coated on FTO Glass

Absorption spectra obtained using UV-VIS-NIR machine as shown in the Figure 3 suggest that the peak absorption is occurring in visible range for PbPc, which makes it an extensive candidate for Solar Cell purposes.

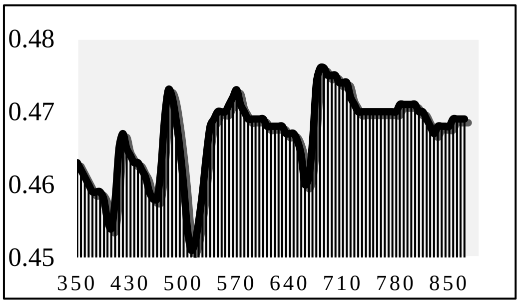

Figure 6.1 Absorption Spectra of PbPc Coated on FTO Glass

Contact Angle Measurement shown in the Figure 4 appears to be around 90 degree, where adhesive forces between the water molecules and the solid surface tend to be on the lower side than the cohesive forces between the liquid molecules, which advocates the surface to be a hydrophobic surface.

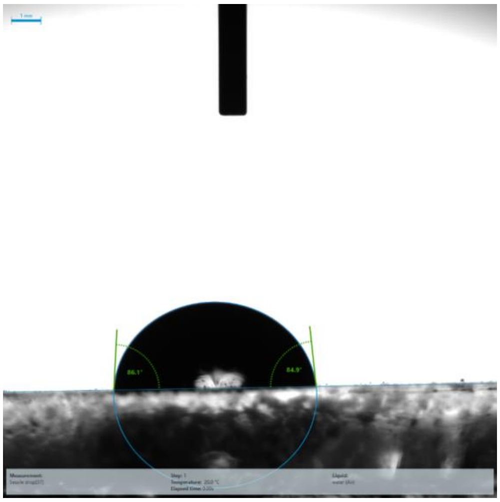

Figure 4 Absorption Spectra of PbPc Coated on FTO Glass

4. Conclusion

PbPc has good absorption capacity with maximum absorbance within visible light range. PbPc has good hydrophobic properties and can enhance the life of perovskite solar cells. Thermal evaporation provides more sophisticated films, hence, a better option for depositing PbPc as hole transport layer.

Acknowledgements

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