INVESTIGATION OF ZINC OXIDE QUANTUM DOTS BASED THIN FILMS ON FLEXIBLE SUBSTRATE FOR PEROVSKITE SOLAR CELLS

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INVESTIGATION OF ZINC OXIDE QUANTUM DOTS BASED THIN FILMS ON FLEXIBLE SUBSTRATE FOR PEROVSKITE SOLAR CELLS

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LIST OF SYMBOLS

α	Absorption coefficient
θ	Bragg diffraction angle
n	Carrier concentration
Cs	Cesium
L	Crystallite size
δ	Dislocation density
ρ	Electrical resistivity
K	Extinction coefficient
NH_2CHNH_2	Formamidinium
β	Full width at half maximum
t	Goldschmidt tolerance factor
d	Interplanar spacing between the planes in the atomic lattice
R_A, R_B & R_X	Ionic radii of A, B cation and X anion respectively
a and b	Lattice constant
CH_3NH_3	Methyl ammonium
$MAPbI_3$	Methylammonium lead triiodide
NiO_x	Nickel oxide
V_{OC}	Open-circuit voltage
n	Refractive index
Ag	Silver
J_{SC}	Short-circuit current
ε	Strain
TiO_2	Titanium dioxide
λ	Wavelength

LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
CB	Conduction band
CTM	Charge transport material
DSCs	Dye sensitized solar cells
EDX	Energy dispersive X-ray spectroscopy
ETM	Electron transport materials
FA	Formamidinium
FESEM	Field emission scanning electron microscopy
FF	Fill factor
FPKSCs	Flexible perovskite solar cells
FTO	Fluorine-doped tin oxide
FWHM	Full width half maximum
HTM	Hole transport materials
ITO	Indium-doped tin oxide
ITO/PET	Indium-doped tin oxide coated Polyethylene naphthalate
LED	Light emitting diode
MA	Methylammonium
NS	Nanostructure
OSC	Organic solar cells
PCBM	Phenyl-C61-butyric acid methyl ester
PCE	Power conversion efficiency
PEN	Polyethylene naphthalate
PET	Polyethylene terephthalate
PKSCs	Perovskite solar cells
PV	Photovoltaic
PVD	Physical vapor deposition
QDs	Quantum dots
QDSCs	Quantum dots solar cells
TCO	Transparent conductive oxide
TEM	Transmission electron microscopy
VB	Valence band

XRD	X-ray diffraction
ZQ_C	ZQDs solution concentration
ZQDs	Zinc oxide quantum dots
ZnO	Zinc oxide

PENYIASATAN FILEM NIPIS BERASASKAN BINTIK KUANTUM ZINK OKSIDA PADA SUBSTRAT FLEKSIBEL UNTUK SEL SURIA PEROVSKIT

ABSTRAK

Sel suria perovskit halida organologam (PKSCs) mendapat perhatian yang luar biasa kebelakangan ini kerana ciri optoelektroniknya yang baik, kebolehprosesan yang mudah, keberkesanan kos dan kecekapan penukaran kuasa yang tinggi. Ini disebabkan oleh spektrum penyerapan cahaya perovskit yang luas, sifat ambipolar dan panjang resapan cas yang panjang menjadikannya calon yang menjanjikan teknologi fotovoltaik (PV) berkos rendah. Walau bagaimanapun, suhu pemprosesan yang tinggi, kos dan kestabilan bahan pengangkutan cas biasa yang rendah menjadi penghalang kepada pencapaian PKSC fleksibel (FPKSC) yang cekap serta pengkomersilan peranti tersebut. Bahan pengangkutan elektron (ETM) konvensional adalah mahal dan/atau memerlukan suhu pemprosesan tinggi yang merumitkan proses. Selain itu, bahan pengangkutan lubang (HTM), terutamanya bahan organik yang biasa digunakan, adalah mahal, mempunyai kekonduksian yang rendah dan kebanyakannya perlu dipertingkatkan dengan pengedopan. Kelemahan-kelemahan pada antara muka, penjajaran tahap tenaga, kestabilan dan kualiti filem serta keseragaman bahan pengangkutan cas (ETM dan HTM) mendegradasi prestasi peranti dan menyebabkan histerisis tinggi ekoran pengumpulan cas antara muka. Dalam penyelidikan ini, bintik kuantum zink oksida (ZQDs) disintesis melalui teknik pemendakan dalam larutan yang kos efektif dan pada suhu yang rendah. Larutan ZQDs koloid yang disediakan telah disalut putar pada substrat PET dan ITO/PET yang fleksibel. Penalaan sifat optik dan elektrik melalui perubahan parameter eksperimen tanpa sebarang pengedopan telah dilaporkan. Pengaruh ketebalan filem

dan kepekatan larutan ZQDs (ZQC) pada sifat struktur, permukaan, komposisi, optik dan elektrik filem nipis yang disalut putar dan kesannya terhadap prestasi sel suria perovskit fleksibel telah disiasat. Selain itu, rintangan mekanikal peranti PKSC yang fleksibel telah diterokai. Pertama, filem nipis ZQDs telah didepositkan melalui pengoptimuman ZQC sebagai ETM yang mana filem terdeposit pada 50 mg/mL memaparkan sifat ETM yang sesuai dan prestasi PV yang lebih tinggi. Tambahan pula, ketebalan filem ZnO dipelbagaikan dengan menukar kitaran salutan putaran dan filem yang dioptimumkan (133 nm) telah mempamerkan prestasi peranti yang lebih baik dengan Jsc tinggi apabila digunakan sebagai ETM dalam PKSC. Akhir sekali, peranti berasaskan struktur nano ZQDs yang dioptimumkan (berdasarkan kepekatan dan ketebalan) telah digunakan untuk menyiasat fleksibiliti mekanikal dan kesan terhadap prestasi fotovoltaik yang direalisasikan. Peranti tersebut mempamerkan fleksibiliti mekanikal yang baik, mengekalkan sehingga 73.2% daripada PCE awal selepas 15 bilangan kitaran lenturan pada jejari kelengkungan lentur 11 mm.

INVESTIGATION OF ZINC OXIDE QUANTUM DOTS BASED THIN FILMS ON FLEXIBLE SUBSTRATE FOR PEROVSKITE SOLAR CELLS

ABSTRACT

Organometallic halide perovskite solar cells (PKSCs) have recently garnered tremendous attention because of their good optoelectronic features, easy processability, cost-effectiveness and high power-conversion efficiency. This is attributed to the perovskite broad light absorption spectrum, ambipolar nature and long charge diffusion length which make it a promising candidate as a low-cost photovoltaic (PV) technology. However, the high processing temperature, cost and low stability of the typical charge transport materials have hindered the achievement of efficient flexible PKSC (FPKSC) and commercialization of the device. Conventional electron transport materials (ETM) are either expensive and/or required high processing temperature, which complicates the process. Moreover, the hole transport materials (HTM), especially commonly used organics are expensive and have low conductivity mostly enhanced by doping. Weakness in the interface, energy band alignment with perovskite absorber, stability, film quality and uniformity of charge transport materials (ETM and HTM) degrade device performance and cause high hysteresis owing to interfacial charge accumulation. Zinc oxide (ZnO) is studied as low-cost and low temperature processed ETM suitable for FPKSC with good electron mobility, but ZnO compact thin film ETM suffered severe hysteresis. ZnO quantum dots (ZQDs) nanostructures have the advantage of improving carrier extraction efficiency due to its large specific surface area. Furthermore, nanostructures can also work as scattering centers and increase the light harvesting in PKSC. In this research, ZQDs is synthesized via a cost-effective and solution-

processed precipitation technique at low temperature (60-150 ^{o} C). The as-prepared colloidal ZQDs solution was spin-coated onto flexible Polyethelene terephthalate (PET) and indium-doped tin oxide coated Polyethelene terephthalate (ITO/PET) substrates. Tuning the optical and electrical properties of ZQDs films through changing experimental parameters without any doping has been reported. The influence of film thickness and ZQDs solution concentration (ZQ_C) on the structural, surface, compositional, optical and electrical properties of the spin-coated thin films and their effects on the FPKSCs performance were investigated. Moreover, the mechanical bending resistance of the FPKSC device is studied. Firstly, ZQDs films were deposited through the optimization of ZQ_C as ETM wherein 50 mg/mL deposited film displayed suitable ETM properties. Furthermore, the ZQDs films thickness was varied by changing the spin-coating cycles and optimized film (133 nm) demonstrated good optoelectronic features. Current density-voltage (J-V) characterization of PKSC is performed using LED-based solar simulator (46 mW/cm^2, 25 ^{o}C). The illuminated J-V characteristic curve of the PKSC with structure PET/ITO/ZQDs/$MAPbI_3$/NiO/Ag prepared at 50mg/mL ZQ_C shows the highest power conversion efficiency (PCE) of 4.74% with short-circuit (J_{sc}) of 5.53 mA/cm^2, open-circuit voltage (V_{oc}) of 0.90 V and fill factor (FF) of 43.8%. For the ZQDs film thickness, best PCE, J_{sc}, V_{oc}, and FF of 4.86%, 6.29 mA/cm^2, 0.73 V and 48.2% respectively are achieved for device with 133 nm thickness ZQDs film ETM. These outweigh the performance of the reference PET/ITO/$MAPbI_3$/NiO/Ag PKSC which demonstrates PCE, J_{sc}, V_{oc}, and FF of 0.22%, 1.48 mA/cm^2, 0.28 V and 24.1% respectively. Finally, the optimized (concentration and thickness wise) ZQDs nanostructure-based device was used to investigate the mechanical flexibility and its effect on the realized photovoltaic performance. The device exhibited relatively good

mechanical flexibility and retained up to 73.2 % of the initial PCE after 15 of bending cycles at 11 mm bending curvature radius. The overall low response of the PKSC and fast performance degradation recorded are attributed to the weak PKSC sensitivity owing to the irradiation from the LED-based solar simulator system, poor ITO layer adhesion and exposure to oxygen and moisture.

CHAPTER 1

INTRODUCTION

1.1 Background

The ever-increasing global energy demands coupled with the environmental challenges (global warming due to CO_2 emissions) and depletion threat posed by the traditional energy sources such as fossil fuels call for diversification of energy sources. The world energy consumption is believed to upsurge by ~28 % in 2040 (Figure 1.1) [1] due to rapid economic development, population increase and electrification. An efficient, clean and cost-effective renewable energy sources become the alternative for the human society development. Amongst all the different new energy technologies emerging to replace the traditional fossil fuels, the solar photovoltaic (PV) is undeniably one of the most promising technologies which rekindled scientists and researchers' interest alike. Solar cell is a device that convert solar radiation (light energy) directly into electrical energy through PV effect or photochemical reactions. Conventionally, silicon wafers (such as monocrystalline and polycrystalline) and thin film based solar cells (such as Cadmium Telluride, amorphous silicon, copper-indium-gallium-selenium (CIGS) and Gallium Arsenide), the so called first and second generation solar cells respectively, have been evolved as the solar cells for electrical energy generation from solar energy [2]. However, high cost of production, complicated preparation process and relatively low conversion efficiency (compared with theoretical maximum of 33%) are among the major shortcomings of some first and second generation PV devices. These geared scientific research community towards exploring alternative solar cells materials that will encourage harnessing solar energy at lower cost, simple production process and high power conversion efficiency (PCE). These give birth to third generation (3G)

solar cells including dye-sensitize solar cells (DSCs), quantum dots solar cells (QDSCs), organic solar cells (OSCs) and perovskite solar cells (PKSCs) [3]. Mostly, it composed of inorganic, organic and hybrid composites semiconductors and facile solution-processed based technique. Nevertheless, PCE is among other factors that hindered commercialization for DSCs, QDSCs and organic solar cells. Thus, a need for a PV technology that produces cost effective, sturdy and high efficiency solar cells.

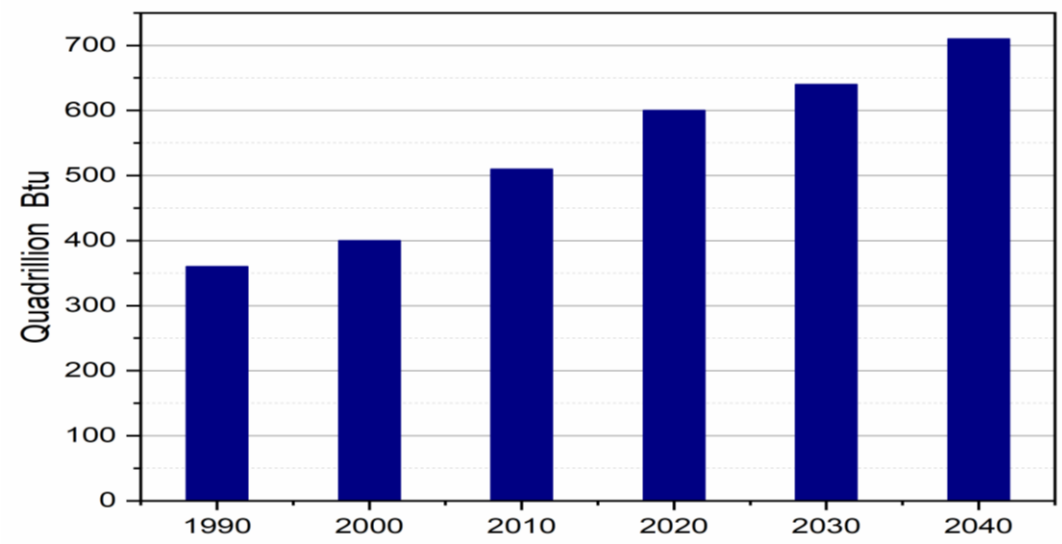

Figure 1.1 World energy consumption projection up to year 2040. Data adopted from Ref [1].

In a decade of its emergence, the perovskite solar cells proved to be unique among other counterpart technologies in terms of cost effectiveness and rapid increase in PCE as depicted in Figure 1.2. as well as simple fabrication process route. Perovskite semiconductor materials attract wide attention in solar cell research due to its fascinating features such as high dual electron and hole mobility, tunable bandgap (1.55-2.3 eV) from ultraviolet to infrared through varying constituents [4]–[6], room temperature dissociation of exciton due to weak binding energy, high absorption coefficient, longer carrier diffusion length, high diffusion velocity, high dielectric constant, large Bohr radius [7, 8], among others. These myriad optoelectronic

properties of organic-inorganic hybrid perovskite materials make them a good choice for solar PV application in contrast with the traditional organic and inorganic counterparts.

From the introduction of organometallic halide perovskite PV device by Kojima's research team in 2009, tremendous improvement have been recorded in the architecture, composition and optimization of PKSCs [9]. PKSCs can be fabricated via simple processing techniques with high PCE at low cost. In a decade of its emergence, PCE as high as 25.7 % is achieved as depicted in Figure 1.2 [10–12]. Due to the exceptional light absorption feature of perovskite semiconducting material, a thin layer (~200 to 600 nm) is required cutting down production cost [13], [14]. Besides, incorporating low-temperature processed inorganic metal oxide layer engineer the chemical composition of semiconducting perovskite material altering its properties like optical and electronic which invariably enhanced the performance efficiency and stability of the PV devices.

Typically, PKSC employed p-type and n-type materials as holes and electrons transport layers, respectively with the perovskite light absorber sandwich in between the two layers. Electron transport material (ETM) primarily extract and transport electron charge carriers from perovskite light absorber to electrode as well block holes from reaching the electrode for high PKSC performance. Traditionally, TiO_2 is the ETM used in PKSCs but suffer from high cost and high temperature processing (~500 ^{o}C). Zinc oxide (ZnO) is identified as a cost-effective and low temperature processing material with a good charge mobility than TiO_2 for excellent electron extraction and suitable for use on flexible substrates [8,15]. ZnO compact thin film (usually deposited by sputtering) is previously studied as ETM in PKSC [16]–[18].

However, PKSC based on compact ZnO thin film ETM suffered serious hysteresis which lead to underestimation of the real PKSC performance [19]. ZnO nanostructures are proved to improved carrier extraction efficiency due to its large specific surface area compared to compact thin film. Furthermore, nanostructures can also work as scattering centers and increase the light harvesting in PKSC [8]. Mostly, transparent flexible substrates are plastics which cannot withstand high temperature processing (>150 ^{o}C) but has the advantages of low-cost, favorable bendability, high optical transparency, and chemical stability [20]. Moreover, solution-processable ZQDs nanostructures allow manipulation of quantum confinement and energy band alignment to improve charge extraction and PKSC performance. Therefore, for widespread use of this emerging solar cells, cost effective ETM with low processing temperature and solution based is needed for flexible PKSC (FPKSC) devices that will be cost-effective compared with leading crystalline-silicon.

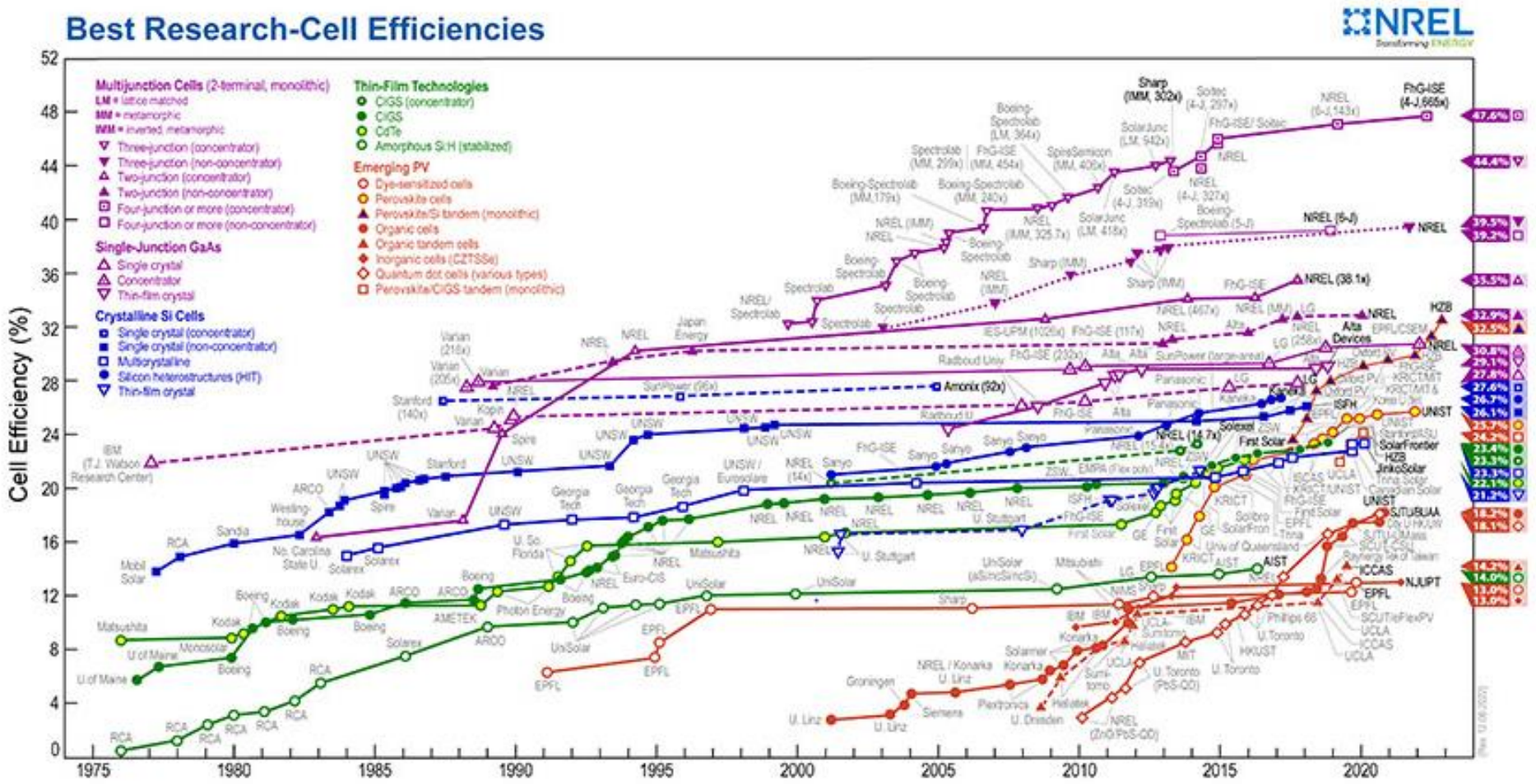

Figure 1.2 NREL PV research solar cell record efficiencies chart 2023 [11].

1.2 Perovskite solar cells

1.2.1 Device structure

PKSC is a new promising type of solar cell based on hybrid organic-inorganic halide perovskite material. The generic molecular structure of the halide perovskite material is ABX_3 with A stands for CH_3NH_3 (methyl ammonium, MA), NH_2CHNH_2 (formamidinium, FA) or Cesium (Cs), B = Pb or Sn, X = Cl, Br or I halides [21] and the crystal structure as depicted in Figure 1.3 [6].

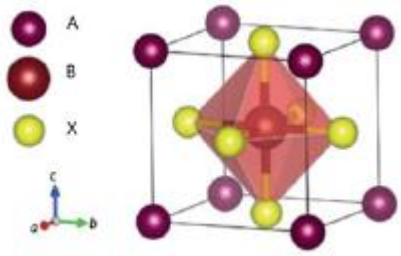

Figure 1.3 The crystal structure of perovskite material [6].

One of the most critical factors for determining PKSCs performance is the device structure. Configuration wise, PKSCs is broadly categorized into regular n-i-p and inverted p-i-n depending on which transport material (ETM/HTM) is encountered by the incident light first. These two structures can be called mesoscopic when mesoporous layer is incorporated or planar otherwise. These make the total number of different PKSC configurations to four as shown in Figure 1.4: the mesoscopic (n-i-p) structure, the planar (n-i-p) structure, the planar p-i-n structure, and the mesoscopic p-i-n structure configurations.

However, in FPKSCs hardly mesoscopic structure is used due to the high temperature processing requirement of some ETMs such as TiO_2 (~500^oC) which flexible substrates cannot withstand and complexity of the fabrication methods. Therefore, planar structure is widely employed in FPKSCs than mesoscopic [22].

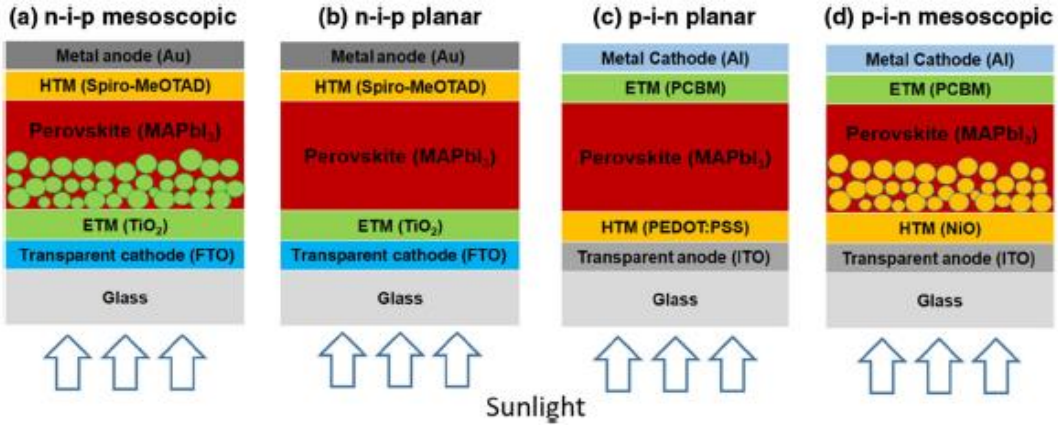

Figure 1.4 The schematic diagram for the different structures of perovskite solar cells (a) mesoscopic n-i-p, (b) planar n-i-p, (c) planar p-i-n, (d) mesoscopic p-i-n, configuration [23], [24].

The operational mechanism of PKSCs is illustrated schematically in Figure 1.5. Incident photons is absorbed by the perovskite light absorber layer through the transparent electrode, resulting in the formation of excitons. Free charge carriers (electrons and holes) are generated upon exciton dissociation due to its weak binding energy at the perovskite/charge-transporting layer interface [25]. When these free charge carriers (electrons and holes) are effectively injected into the ETM and HTM respectively, due to their long diffusion length. The HTM and ETM ensure selective charge collection at the anode (FTO (fluorine-doped tin oxide)/ITO (indium-doped tin oxide)) and the cathode (mostly metal), while minimizing carrier recombination [26].

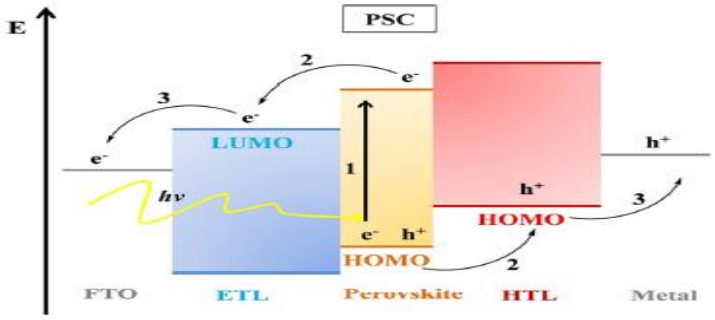

Figure 1.5 PKSC energy band diagram and operation principle [27].

1.2.2 ZnO nanostructure-based electron transport material

As electron transport layer continue to have critical impact on the perovskite PV device performance and stability, many materials were explored to replace the mesoporous high temperature sintering of TiO_2 [17], [28]–[31] translating to reduced cell material and fabrication cost as well as processing time. ETM as crucial part of PKSC should have good interfacing feature, excellent transport property, high quality and easy fabrication processes for optimum device performance, especially for fast extraction and transport of photogenerated electrons in addition to blocking holes to mitigate charge recombination [32]. Zinc oxide emerged as a direct wide bandgap (3.2-3.3 eV), intrinsically n-type semiconductor material among others to substitute TiO_2. Recently, ZnO nanostructures received considerable attention and significant progress has been made in the synthesis and characterization of its various types including nanowalls, nanorods, nanowires, nanoflowers, nanotubes and quantum dots for optoelectronic applications especially PKSC [33]–[36][37]. These are attributed to their low-temperature processing compatibility and huge electron mobility (205-300 cm^2/Vs) which reduced production cost and enhanced PV device performance. ZQDs nanostructure have attracted considerable attention as a potential ETM material for PKSCs due to their unique size-dependent properties and excellent electron transport characteristics. In particular, the small size of ZQDs (typically <

10 nm) leads to quantum confinement effects, which can significantly enhance the electron mobility and reduce charge recombination losses in PKSC device.

However, ZnO nanostructures ETM demonstrate high influence in PV performance. Therefore, it is crucial and necessary to optimize parameters such as solution concentration and film thickness and elaborate their impacts on the performance of PKSCs based on flexible substrate.

1.3 Problem statement

Organic-inorganic hybrid perovskite materials are the most promising candidates for highly effective, inexpensive solar cells (used in combating the world energy crisis) with distinctive electrical and optical properties [38]. Due to its matched bandgap with perovskite absorber and high transmittance, which ensure the high performance of solar cells, TiO_2 is the most commonly used ETM for PKSCs. However, under most conditions, high-temperature annealing is required to produce a high-quality compact or mesoporous TiO_2 film, which limits its applications in flexible devices and raises the cost of production. Further, the degradation of solar cell performance is reported to be associated with the TiO_2's lower electron mobility, which is in the range of 0.1 - 4 $cm^2\ V^{-1}\ s^{-1}$, as opposed to 7.5 $cm^2\ V^{-1}\ s^{-1}$ for perovskite materials [8], [39].

Organic conducting materials, such as fullerene and its derivatives, have also been widely used as the ETM in PKSCs in addition to TiO_2 ETM. A low-temperature solution processing can be used to fabricate them, which is advantageous for lowering the cost. However, the electron mobility of C_{60} (fullerene) film is about 1 $cm^2\ V^{-1}\ s^{-1}$, and that of PCBM (a fullerene derivative) is $2.6 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$, both of which are lower than that of TiO_2 [40], [41]. On the other hand, the valence band

of fullerene and its derivatives (−6.3 eV for C_{60}, −6.0 eV for PCBM, compared with vacuum energy level) is higher than that of TiO_2 (−8.0 eV, compared with vacuum energy level), which result in weaker hole blocking ability. Furthermore, it has been reported that fullerene derivatives, such as PCBM molecules, interact with oxygen and water, resulting in device degradation [8], [42].

As an alternative to TiO_2 and organic conducting materials, ZnO ETM-based PKSCs have recently received much attention. ZnO is considered an effective and promising alternative to TiO_2 in PKSCs despite having a lower power conversion efficiency (PCE) than TiO_2-based PKSCs (about 17%) [8]. This is because ZnO has much higher electron mobility (205-300 $cm^2\ V^{-1}\ s^{-1}$) than TiO_2, which has the potential to increase electron transport efficiency and decrease recombination loss as an ETM. ZnO can easily be crystallized and doped. Its nanostructures can be fabricated at low annealing temperatures (60-150 ^{o}C), resulting in lower costs and thermal budget and thus being potentially valuable for flexible devices [43], [44]. This ZnO low processing temperature make it compatible with flexible substrate like PET which have ~150 ^{o}C temperature tolerance [45]. ZnO also has a higher transmittance in the visible spectra compared with TiO_2 [46]. These properties make ZnO a promising ETM for PKSCs. Thus, investigating ZnO quantum dots-based thin films on a flexible substrate for efficient PKSCs will provide information on optimizing the material quality of ZQDs ETMs, thereby reducing the carrier recombination, and improving charge collections.

1.4 Objectives

The research objectives are:

1. To characterize the synthesized ZQDs nanostructure through low temperature solution-based processing method.
2. To determine the influence of ZQDs concentration and film thickness on physical properties of ZQDs thin films for PV application.
3. To evaluate the performance of FPKSC based on ZQDs nanostructure ETM and the mechanical bending tolerance of the fabricated FPKSC device.

1.5 Thesis originalities

The originalities of this research work are as follows:

1. Investigation of the ZQDs NS based thin films on bare and ITO coated PET synthesized via low temperature precipitation route. The ZQDs particle size and the structural, morphological, optical and electrical characteristics of the ZQDs thin films on the two substrates were demonstrated and compared.
2. Elucidating the effects of ZQDs solution concentration and thin film thickness on its physical properties. Revealing the optimum solution concentration and film thickness of 50 mg/mL and 133 nm respectively.
3. Investigate the impacts of the ZQDs parameters on the PV performance of FPKSC and its mechanical bending flexibility. Achieving high V_{oc} (730 mV) and enhanced J_{sc} in comparison to reference device.

1.6 Thesis organization

This thesis comprises of five chapters and structured as:

Chapter 1 presents a brief introduction of world energy challenge, PV as the solution, the champion PKSCs technology and ZQDs NS role in improving PKSC

performance. Furthermore, problem statement, objectives of the research, and thesis originalities, were further described.

Chapter 2 discusses perovskite materials, solar cell principle of operation, and configuration. This chapter also reviews related literature on the charge transport materials in PKSC and FPKSC, ZnO ETM based on compact films and nanostructures. Besides, the NiO_x HTM and substrates for FPKSC were reviewed.

Chapter 3 explains the methodology employed for the study from substrates preparation, ZQDs synthesis, $MAPbI_3$ preparation, NiO_x film deposition, techniques and apparatus utilized to characterize the prepared materials and the fabricated PKSC devices.

Chapter 4 presents and discusses the results of the spin-coated ZQDs nanostructure thin films on bare PET and ITO/PET and compared, effect of ZQDs concentration and film thickness on its physical properties. $MAPbI_3$ perovskite films based on varying ZQDs film (concentration and thickness) are characterized. PKSCs featuring ZQDs as ETM are fabricated and influence of ZQ_C and thickness on PV performance are studied. Finally, mechanical bending resistance of the flexible PKSC best device are assessed.

Chapter 5 concludes and summarizes findings of this research work. Recommendations for future research were also outlined in the chapter.

CHAPTER 2

LITERATURE REVIEW AND RESEARCH BACKGROUND

2.1 Overview

This chapter discusses perovskite materials, solar cell principle of operation, and configuration. Related literature on the charge transport materials in PKSC and FPKSC, ZnO ETM based on compact films and nanostructures were also reviewed. Besides, the NiOx HTM and substrates for FPKSC reviews were presented.

2.2 Perovskite materials

Perovskite materials are known to possessed the crystal structure of calcium titanate ($CaTiO_3$). The formula ABX_3 is used to represent perovskite crystal structure as displayed in Figure 2.1. A = inorganic or organic cation (Cs, CH_3NH_3, or NH_2CHNH_2); B = metallic cation (Pb, Sn or Ge); and X = Cl, Br or I anion. Each component of the organometallic halides perovskites contributes enormously to their remarkable properties which make it the best suitable material for PV applications. The use of organic cation influence dielectric constant of the material resulting in long carrier lifetime (200 ns) [47]. The metal ion plays vital role in defect tolerance and low electron effective mass while halides allow tuneable bandgap (1.55-2.3 eV) [4] when mixed in different ratios [47], [48].

Goldschmidt tolerance factor (t) (Equation 2.1) determined the formation tendency of perovskite and ranges from 0.80 to 1.10 for a stable structure.

$$t = \frac{R_A + R_X}{\sqrt{2}(B + R_X)} \tag{2.1}$$

where R_A, R_B and R_X are ionic radii of A, B cation and X anion respectively.

Methylammonium lead trihalide ($MAPbX_3$, halide X can be Cl, Br or I) is the most employed absorber material for PKSC attributed to its low temperature crystallization (60-100 ^oC) and excellent PV performance. The unit cell parameters increased from 5.68-6.27Å with the halide (Cl, Br and I) atomic number increase. However, large size and aspheric shape of MA causes distortion in the matrix resulting in phase transition from orthorhombic, tetragonal to cubic with increasing temperature in the range -113 - 57 ^oC [49]. The energy bandgap of methylammonium lead trihalide perovskite is tunable with anion and cation compositional change in the range of 1.5–2.3 eV. The $MAPbI_3$ perovskite material have a direct bandgap of ~1.55 eV. Replacing I with Br increases bandgap to 2.3 eV. The crystallographic properties of $MAPbX_3$ also varies with halogen atom employed. This is evident on changing the I anion with Br leading to tetragonal and cubic crystallization of $MAPbI_3$ and $MAPbBr_3$ respectively and reduced lattice constant [50].

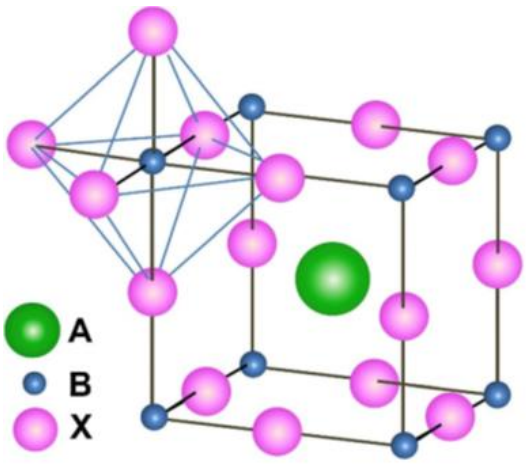

Figure 2.1 ABX_3 perovskite crystal structure [49].

2.3 Perovskite solar cell principle of operation

As presented in the introductory chapter, Section 1.2.1, there exist various kinds of PKSCs. Fundamentally, the photoactive absorbing perovskite layer is inserted

between ETM and HTM of the PKSC. Upon exposing the solar cell to sunlight, perovskite active layer absorbs photons producing paired electron-holes called excitons as depicted in Figure 2.2. These photogenerated excitons will generate free electrons and holes (charge carriers) and subsequent current to the external circuit. The electrons are extracted, transported through ETM and then collected by the TCO electrode whereas the HTM does the same to holes but collected by the back contact.

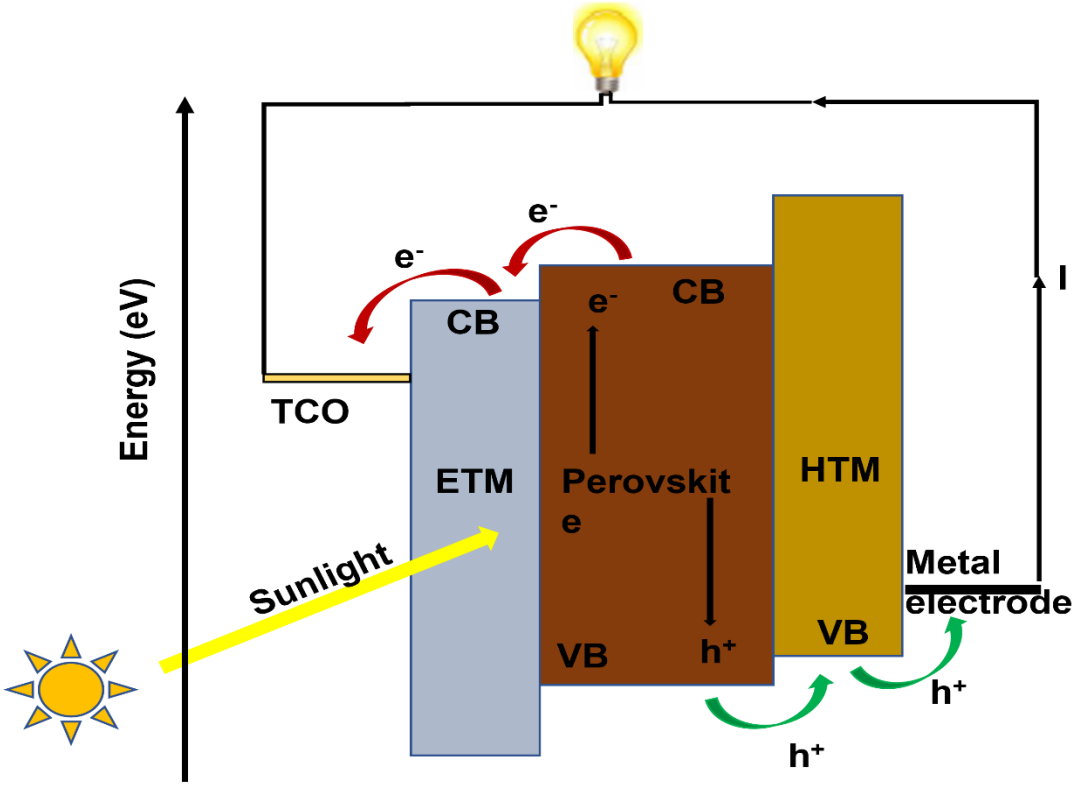

Figure 2.2 Illustration diagram of operating principle of perovskite solar cells.

Generally, ETM/perovskite and HTM/perovskite interfaces act as the electrons and holes separation centers in PKSC, transported by ETM and HTM and collected by TCO and back electrode respectively [51]. Then the photocurrent is tapped via TCO and metal electrodes to the external circuit. The recorded high PV performance (25.7% PCE) of PKSC is ascribed to perovskite materials high carrier mobility (800 V^{-1} s^{-1}) and longer diffusion length (100 nm) [12]. As shown in Figure

2.3, other carrier transport processes also affect the performance of perovskite solar cells which include exciton annihilation (a), charge carrier recombination at the ETM/HTM interface (b), reverse transmission of electrons and holes and non-radiative carrier recombination (c, d).

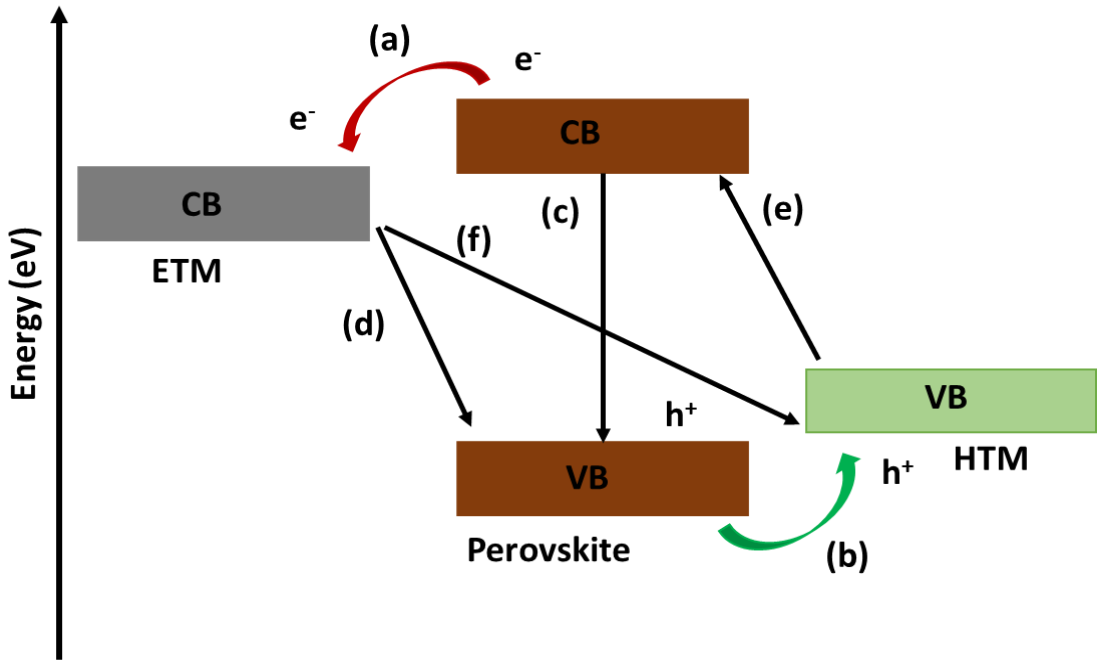

Figure 2.3 PKSC schematic illustration of charge transfer and recombination process.

2.4 Perovskite solar cell configuration

From the emerging of perovskite solar cells in 2009 employing traditional dye-sensitized solar cell configuration, several configurations have been developed due to the ambipolar nature of perovskite material. As introduced in Section 1.2.1, initially normal mesoporous architecture and mesoporous inverted architecture prevailed as demonstrated in Figure 2.4 (a) and (b). Device configuration is among the performance deciding factors in PKSC, improving charge separation at the charge transport material (CTM)/perovskite interface, efficient transport and collection by CTM and electrodes respectively.

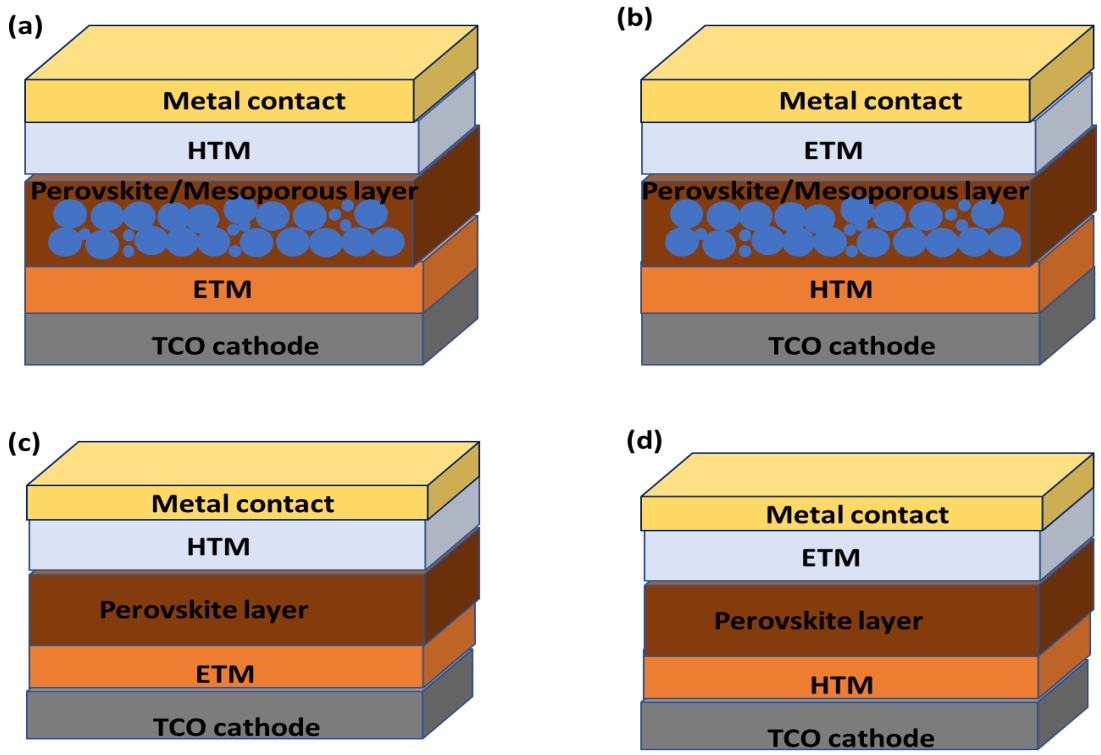

Figure 2.4 PKSC Schematic illustration of charge transfer and recombination process.

Mesoporous PKSC architecture is the most widely used due to its large specific surface area and porosity. These established better adhesion and large area contact with perovskite light absorber via allowing efficient penetration leading to improved carrier generation and mobility. Thus, enhancing the overall PV performance of the PKSCs. TiO_2 is the most employed mesoporous material for PKSC allowing perovskite infiltration into the porous structure and forming interconnected layer. Kim et al., reported the first solid state PKSC based on mesoporous TiO_2 with improved PCE of 9.8% [52]. The efficiency of PKSC using mesoporous transport layer soars rapidly to ~23% in 2019. Mesoporous structure based PKSCs have achieved PCE of 25.7% recently [53]. Although PKSCs based on mesoporous electron transport material have shown excellent performance efficiency,

TiO_2 fabrication involved high annealing temperature (~500 ^oC) which hindered PKSC production on flexible substrates as well as commercialization [16], [17], [54]–[56]. Fabrication time, cost and complexity are adversely affected by this high sintering temperature which prompted testing sapphire (insulator) scaffold as mesoporous structure for perovskite loading [57] which confirmed the ambipolar characteristic of perovskite material: acting as both light absorber and ETM. This and other exceptional features of perovskite semiconductor material draw more attention to PKSC and paved way for planar heterojunction architecture development in PKSCs devices substituting high temperature processed mesoporous architecture [41], [58]–[62]. This planar architecture is also categorized into two based on which CTM is confronted by the incident light first: namely, the normal planar heterojunction n-i-p and inverted planar heterojunction p-i-n structure as demonstrated in Figure 2.4. The five basic components of PKSCs are deposited in the order; TCO cathode, ETM, intrinsic perovskite absorber, HTM and a metal electrode in normal n-i-p architecture whereas in inverted structure ETM and HTM position are interchange as presented in Figure 2.4 (c) and (d) respectively. The planar architecture can be traced back to DSC and is extensively explored in PKSC because of its excellent performance, simple architecture and facile fabrication as compared to inverted configuration. These are beneficial for PKSC on flexible substrates.

Light absorption by intrinsic perovskite absorber layer and charge extraction and transport by ETM/HTMs are among the several factors determining PKSCs performance. Good interfacing and electronic band alignment between perovskite light absorber and charge transport materials is essential and necessary in obtaining high PV parameters such as Jsc and Voc. Therefore, a need for high-quality electron transport material fabrication through controlling various parameters particularly

ZQDs concentration, thickness and other physical properties as described in results and discussion (Chapter 4).

2.5 Charge transport materials in perovskite solar cell and flexible perovskite solar cell

2.5.1 Electron transport material

Typically, in PKSCs, photogenerated electrons are extracted and transported from perovskite light absorber to the FTO/ITO electrode by the layer called ETM. Concurrently, the ETM act as a layer that block holes from reaching the electrode. The characteristics of an efficient ETM for high performance PKSCs includes high visible region optical transmittance, decent electron mobility, suitable energy levels, good chemical and thermal stability and low film surface states. Mostly, ETMs are either inorganic or organic. The inorganic ETM are mostly n-type metal oxides semiconductor materials (such as TiO_2, SnO_2, ZnO and Zn_2SnO_4) whereas perylene diimides (PDI), C70 and C60 fullerenes and its derivatives such as phenyl-C61-butyric acid methyl ester (PCBM) are among the widespread used organic ETMs. Inorganic metal oxides ETM are commonly used due to their low cost and thermal stability as compared to organic ETMs [55], [63]. Typically, mesoporous TiO_2 is used as ETM in PKSCs due to its good visible range optical transmittance (70.4%) and suitable band gap. However, the high temperature (~500^oC) treatment in the fabrication process limits its usage on flexible substrates and raises cost of production. Hence, the need for low-temperature processing materials for PKSCs.

2.5.2 ZnO electron transport material

Moreover, the disparity in the electron mobility of TiO_2 (0.1-4 $cm^2\ V^{-1}\ s^{-1}$) as compared with the lead-based perovskite materials (10-100 $cm^2\ V^{-1}\ s^{-1}$) is critical and

that causes efficiency degradation in PKSCs [64], [65]. ZnO is identified as the promising candidate that will replace TiO_2 as ETM in PKSCs due to its higher electron mobility (200-300 $cm^2 V^{-1} s^{-1}$) [66], [67] and electron diffusion coefficient (1.7×10^{-4} cm^2 s^{-1}). More importantly, ZnO high quality crystal can be synthesized via low temperature (60-150^oC) solution-based process which scales down production cost while enabling use of flexible substrates for roll-to-roll production in PKSC. The ZnO ease of crystallization allow different nanostructures prepared using various methods and employed as ETM in PKSCs as indicated in the literature [8].

2.5.2(a) PKSC and FPKSC based on compact ZnO films ETM

In PKSC, high quality film ETM is critical in improving device efficiency. There are many works reported on the compact ZnO film used as ETM in PKSCs by variety of deposition methods. The ZnO film quality for high PKSC performance may depend on deposition techniques, growth parameters or film thickness. ZnO films grown using magnetron sputtering and sol-gel spin-coating technique were used as ETM by Zhao's group [68] to investigate the growth method effect on the thermal and chemical stability of ZnO ETM based PKSC. In this research, they found that ZnO film based on sputtering exhibits superior quality, with bigger grain size, higher optical transmittance, higher conductivity, and good matched energy-level, than the spin-coated ZnO film. The PKSC based on sputtered ZnO ETM showed improved stability owing to the insignificant OH^- groups contain at ZnO/perovskite interface attributed to the ZnO film deposition environment that is hydrogen-free. Besides, the PCE of the device based on the sputtered ZnO film is 17.22% which is higher than the spin- coated device PCE (14.24%). Tseng et al., [69] investigated the effect of sputtering method growth parameters on the ZnO film quality as well as PKSC

performance. They deposited ZnO film with varied working gas mixture Ar/O_2 (Ar/0% or pure argon, Ar/10%, Ar/20%) based on sputtering technique and reported that the ZnO film grown under pure argon (ZnO-Ar) had the least sheet resistance thereby decreasing device series resistance and hence increasing short circuit-current and fill factor. The ZnO-Ar film produced PKSC with the highest PCE of 15.9% while the mixture ($ZnO-O_2$) yielded PCE of ~12%. The higher PCE in the former is related to the lower shift of the conduction band and valence band of ZnO-Ar film deposited on perovskite layer which improved extraction of electrons from the perovskite.

Using atomic layer deposition (ALD) technique, Lee et al., [70] prepared ZnO films with various thicknesses (5-40 nm) to study their influence on PKSC performance. They found that the ZnO film with 5 nm thickness performed poorly with PCE of ~ 2% because of its incomplete coverage of ITO which resulted in the shunting path between the $MAPbI_3$ absorber layer and the ITO. Subsequently, the performance increases with thickness up to 30 nm which is attributed to exciton dissociation improvement at the interface between ZnO and perovskite caused by higher electron mobility of the thicker ZnO films. Moreover, they reported that any increase in thickness more than 30 nm reduces the PCE of the device owing to increase in the series resistance.

2.5.2(b) PKSC and FPKSC based on ZnO nanostructures ETM

Different ZnO nanostructures (such as nanoparticles, nanorods and quantum dots) were synthesized through various solution method at low temperature for use as ETM in PKSCs. Incorporating nanostructures can increase extraction of photogenerated charge carriers owing to its larger specific surface area and improved optical path length for higher light absorption in PKSCs by acting as scattering

centres. Liu and Kelly [71] demonstrated ZnO nanoparticles prepared via solution method at low temperature (65^{o}C) and spin coating deposition method is used to obtained thin films of different thicknesses from 0 to 70 nm. They studied ZnO nanoparticles film thickness effect on device performance. By increasing the thickness of ZnO film from 0 to 25 nm, the PCE was boosted from 2.4% to 14.4%, but declined to 12.9% with further increase in thickness to 70 nm. Besides, the improvement in the performance of the PKSC is attributed to the bigger grain size formed due to the absence of mesoporous layer which consequently increase absorption, carrier mobility and reduced carrier recombination rate. Another work is reported on the influence of ZnO nanoparticles film thickness on the PKSC performance [56] and the result is consistent with the Liu's and Kelly's findings [71].

Zhang et al., [72] investigated the impact of ZnO nanoparticle size on the performance of PKSCs. By using three different solvents (methanol, ethanol and n-propanol), ZnO nanoparticles of 25, 40 and 50 nm sizes were synthesized at 150 ^{o}C temperature via solvothermal technique. They observed that PKSC based on 25 nm size ZnO particles has the least PCE (11.86%) originated from the perovskite poor infiltration into ZnO small pores causing severe recombination, hence degrading performance. The highest PCE (15.92%) is obtained with 40 nm ZnO and is believed to be due to good perovskite crystallites grown over the ZnO mesoporous layer with suitable nanoparticle size, while the 50 nm ZnO yielded lower PCE of value 13.20% which is assigned to degradation in charge injection efficiency from perovskite to ZnO layer owing to low contact surface area between the two layers.

The low temperature processing of ZnO nanostructures coupled with high electron mobility as well as good optical transparency make it the first material employed as ETM in FPKSCs. Kumar et al., [73] demonstrated FPKSC based on ZnO

ETM for the first time. They prepared ZnO compact layer and ZnO nanorod ETM on ITO-coated polyethylene terephthalate PET (ITO/PET) via electrodeposition and chemical bath deposition methods, respectively. The FPKSC device fabricated based on this ETM exhibits moderate PCE of 2.62%. Later, Liu and Kelly [71] fabricated FPKSC based on low temperature prepared and spin coated ZnO nanoparticles film on ITO/PET substrate. They reported good FPKSC performance with PCE soared to 10.2%. Heo et al., [74] prepared ZnO ETM via spin coating nano-sol on ITO/PEN (polyethylene naphthalate) substrate with subsequent 150^{o}C heat treatment. The results for ZnO based FPKSC showed superior photovoltaic performance (with 15.5% PCE) and modest mechanical stability even after several bending.

Moreover, Najafi et al., [75] prepared a bilayer ETM based on PCBM/ZnO NPs. The PCBM is sandwiched between the ZnO layer and triple cation perovskite absorber in the FPKSC structure to inhibit degradation and improve stability. The ZnO layer enhanced electron extraction and hole blocking leading to higher efficiency of FPKSC device with PEN/ITO/NiO_x/ composite perovskite/PCBM/ZnO/Al structure.

ZnO quantum dot (QDs) is also employed as ETM in PKSCs. Thanks to its exceptional properties of enhanced electron injection ascribed to band gap increased caused by quantum confinement effect due to size (size quantization) and generation of multiple excitons when it absorbed a photon of light [76]. Due to its small size, the quasi-continuous energy levels of bulk materials are replaced by the separated electronic energy levels and the band gap will become larger. The increased band gap is mainly caused by the negative shift of the conduction band and the positive shift of the valence band, which will improve the electron injection efficiency and hole blocking. Therefore, ZQDs will be a promising ETM in PKSC. Ameen et al., [37] first

introduced ZQDs based PKSC. They synthesized ZQDs through solution process method and spin coated the as-synthesized ZQDs on flexible substrate. The study on the performance of PKSC with structure containing ZQDs layer show better PCE value (5.28%) as compared with the ZQDs layer-free PKSC which yielded PCE value of 2.89%. This significant improvement in the device PCE is ascribed to larger contact surface area of ZQDs. Furthermore, after atmospheric plasma jet treatment, an increase in PCE (9.73%) is recorded due to the improved light scattering at the ZQDs/perovskite interface resulted by enhancement in the contact surface area and porosity of ZQDs.

Wang et at., incorporated ZQDs through solution processing and spin- coating into the pores of TiO scaffold. Remarkable PV performance with efficiency enhancement from 14.5 to 17.2% were achieved. This is ascribed to enhanced specific surface area which yielded larger perovskite grain size, increased light absorption, improved charge transfer and reduced recombination [77].

Agada et al., fabricated PKSC based on quantum dot charge transport materials (ETM/HTL). The ETM is graphene-zinc oxide quantum dot prepared via facile solution-spin coating technique while the HTM is copper sulphide QDs. Varying the graphene-zinc oxide hybrid composition resulted in the same V_{OC} with slight improvement for 60:40 composition leading to highest efficiency of 2.3%. This could be attributed to the enhanced electron transport associated to graphene due to the observed higher lowest unoccupied molecular orbit [78].

Therefore, from the literature surveyed ZQDs enhanced electron transfer process in PKSC, however there is limited PKSC based on ZnO quantum ETM, this prompted the study to explore its potentiality in PKSCs.