

Colloidal Quantum Dot

Solar Cells



Nanlin Zhang
Mansfield College
University of Oxford
Supervised by Prof. Andrew A. R. Watt

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Abstract

This thesis presents three specific strategies to enhance colloidal quantum dot (CQD) solar cells' performances, including band alignment engineering, quantum dot passivation, and smart device architecture design.

Firstly, by inserting a PbS CQD layer with a relatively smaller band gap as the hole transport layer (HTL), the carrier extraction of the solar cells is much improved, so as the efficiency. The improvement is due to a better interfacial band alignment between the HTLs and the absorber layer, proved by Kelvin probe and cyclic voltammetry results. Small band gap PbS CQDs have deeper Fermi levels because of the easy oxidation. Coupled with a p-type inducing ligand, 1,2-ethanedithiol (EDT), a better valence band alignment is achieved to extract the holes more efficiently.

Secondly, alcohol-dissolvable CsI is used as the ligands to passivate QDs' surface with the aim of reducing dangling bonds and defects on the surface. Compared to the commonly used ligand, tetrabutylammonium iodide (TBAI), CsI resulted in better passivation, which was proved by the full ligand exchange, a narrow photoluminescence peak, fewer oxide defects, and the existence of Cs-S bond. A high efficiency of 10% is achieved, which is attributed to that fewer defects and better passivation lead to larger depletion region pushing its optimal thickness and current output higher, as well as the efficiency.

Thirdly, a microgroove-structured flexible PbS CQD micro-module solar cell is reported for the first time with a record V_{oc} of 9.2 V. This device was fabricated by automatic dip coating methods, and it avoids the complex recombination layers required in monolithic tandem devices. By e-beam depositing two electrodes on the two walls of the V-shape grooves, devices were connected in series in less than 100 μm width. By using three-dimensional characterisations, the reasons for low efficiency were explained.

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Statement of originality

This thesis is an account of work carried out by the author in the Department of Materials, the University of Oxford under the supervision of Professor Andrew A. R. Watt. Any work of others that have been utilised, directly or indirectly, is duly acknowledged in the text, and a list of references is presented at the end of the thesis. No part of this thesis has been submitted towards the completion of another degree at the University of Oxford or elsewhere. Parts of the thesis have been submitted to or published in the following scientific journals:

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List of abbreviations

(TMSi) ₂ S	Bis(Trimethylsilyl) Sulphide
Ag	Silver
Al	Aluminium
AM	Air Mass
Au	Gold
BDT	1,4-Benzenedithiol
BHJ	Bulk Heterojunction
CB	Conduction Band
CdS	Cadmium Sulphide
CQD	Colloidal Quantum Dot
CsI	Caesium Iodide
CV	Cyclic Voltammetry
C-V	Capacitance-Voltage
DMF	Dimethylformamide
EDT	1,2-Ethanedithiol
E _f	Fermi Level or Work Function
E _g	Band Gap
EQE	External Quantum Efficiency
ETL	Electron Transport Layer
FF	Fill Factor
FIB-SEM	Focused Ion Beam Scanning Electron Microscopes
FTIR	Fourier-Transform Infrared Spectroscopy
GRL	Graded Recombination Layer
HOMO	Highest Occupied Molecular Orbital
HTL	Hole Transport Layer
IQE	Internal Quantum Efficiency
I _{sc}	Short-Circuit Current
ITO	Indium Tin Oxide
I-V	Current-Voltage
J _{sc}	Short-Circuit Current Density
J-V	Current Density-Voltage
LBIC	Light-Beam-Induced Current
LiF	Lithium Fluoride
LUMO	Lowest Unoccupied Molecular Orbital
MEG	Multiple Exciton Generation
MoO ₃	Molybdenum Trioxide
NREL	National Renewable Energy Laboratory
OA	Oleic Acid
ODE	1-Octadecene
PbS	Lead Sulphide
PCE	Power Conversion Efficiency
PEDOT:PSS	Poly(3,4-Ethylenedioxythiophene) Poly(Styrenesulfonate)
PL	Photoluminescence

PV	Photovoltaic
QD	Quantum Dots
R_s	Series Resistance
R_{sh}	Shunt Resistance
TBAI	Tetrabutylammonium Iodide
TEM	Transmission Electron Microscope
TiO_2	Titanium Dioxide
UV-vis	Ultraviolet-Visible Absorption
VB	Valence Band
V_{bi}	Built-in Potential
V_{oc}	Open Circuit Voltage
XPS	X-Ray Photoelectron Spectroscopy
ZnO	Zinc Oxide

Chapter 1 Introduction

1.1 Energy and environment crisis and solar solution

The global energy consumption of 2015 was 13.1 billion tons of oil equivalent (153 PWh), with 85% of which is fossil fuel (Figure 1-1).¹ The burning of fossil fuel has released a massive amount of carbon to the atmosphere, mainly as the form of CO₂. Current total CO₂ equivalent (CO_{2e}) concentration in the atmosphere is >480 ppm,² of which CO₂ is about >400 ppm, while the CO₂ concentration is 278 ppm at the beginning of the industrial revolution. 75% of this rise happened since 1950, breaking the carbon cycle on earth which keeps the earth environment-friendly to all the lives. It is expected that the world population will increase to 8.8 billion by 2035 with 1.5 billion more than now, which will have about 130% energy consumption of 2015.¹ To meet the increasing demand of energy and reduce the carbon emission, more renewables are urgently required as predicted in Figure 1-1.

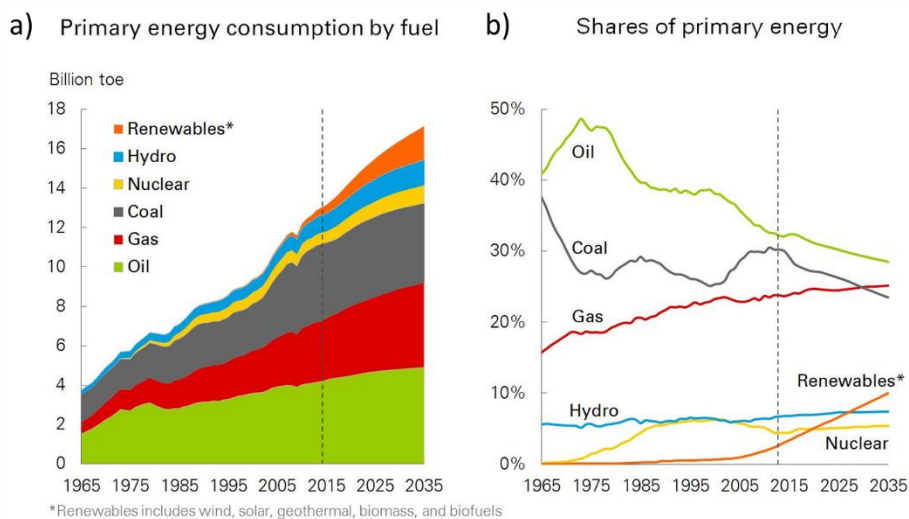


Figure 1-1 Energy outlook 2017: a) primary energy consumption by fuel; b) shares of primary energy. Graphs adapted from reference¹.

Solar cells, harnessing photon energy to be electricity in a clean and sustainable way, have been the research focus of scientists in the past few decades. The last decade has witnessed a rapid increase of the installation capacity, as shown in Figure 1-2.³ The

cumulative solar panel installation in 2017 has increased to be 355 GW. Assuming an annual sunshine hour of 2400 h, a capacity of 64 TW would provide all the energy we needed in 2015. By using commercial solar panels of 15% efficiency, a coverage of a size ($>424,720 \text{ km}^2$) like Spain can meet all the energy demand across the globe.

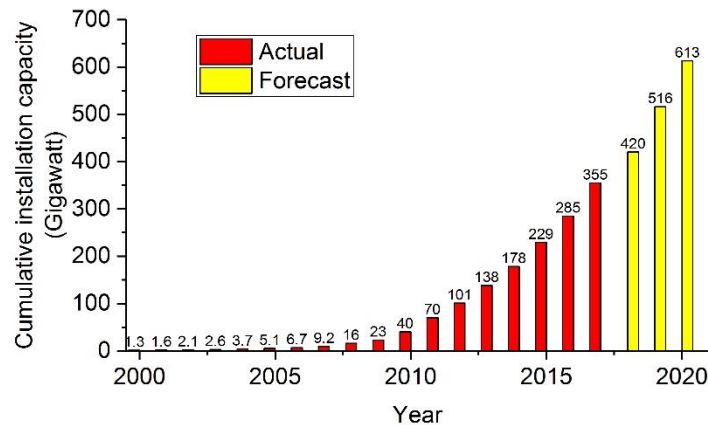


Figure 1-2 the cumulative photovoltaic installation capacity (GW) from 2000 to 2020. Data extracted from reference.³

Although the most important participants of the solar market are still crystalline silicon and thin film solar cells such as CdTe and CIGS, the emerging technologies have shown enormous potential to enhance solar cells' PCE and further lower down the cost. Except the rapid increased but not stabilised efficiency (about 22.1%) of perovskite solar cells,⁴ the efficiencies for the other third generation photovoltaics, such as dye-sensitised solar cells, organic solar cells, inorganic solar cells, and quantum dots solar cells, are all between 11-14% (Figure 1-3),⁴ and the best cells are all small area lab cells. To meet commercial standards, the efficiency needs to be further enhanced and stabilised, and the laboratory cells need to be extended to large area modules and panels for real-life use.

1.2 Solar cell physics

1.2.1 Solar spectrum

The light outside the Earth's atmosphere has an intensity of 1360 W/m^2 , which is represented by air mass (AM) 0. After being absorbed and reflected by the atmosphere, the average value received on the Earth's surface is about 1000 W/m^2 , represented by AM 1.5. In terms of power, AM 1.5 approximately has 52% infrared, 44% visible, and 4% ultraviolet light. Their spectrum intensity distribution is in Figure 1-4.

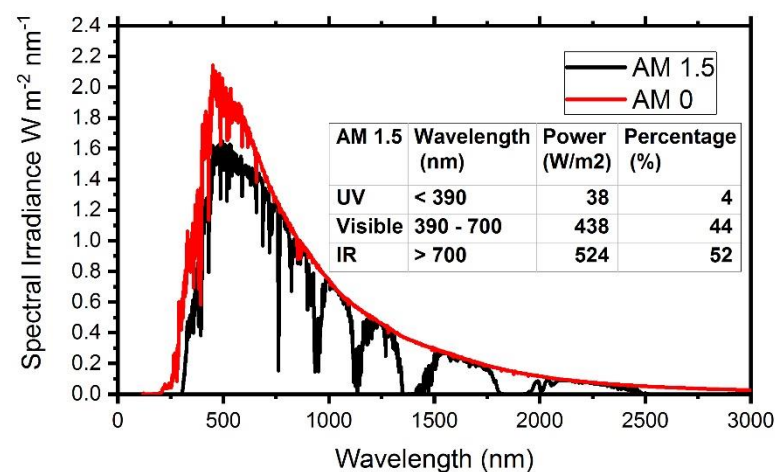


Figure 1-4 AM 1.5 and AM 0 spectrum intensity distribution.

1.2.2 Solar cell structure

Solar cells are devices converting photons from the light to be electrons, which then be extracted out by its internal p-n junction to become electricity. A typical solar cell usually has four different layers, which are an anode, an n-type layer, a p-type layer, and a cathode, as shown in Figure 1-5 a. The anode and cathode are conductive materials, for example, metal, or transparent conductive oxide. The n-type and p-type layers are usually semiconductors with different types of doping. These two layers will absorb the photons which have higher energy than the semiconductors' band gaps and create excited electrons and holes which will then be extracted out as electricity.

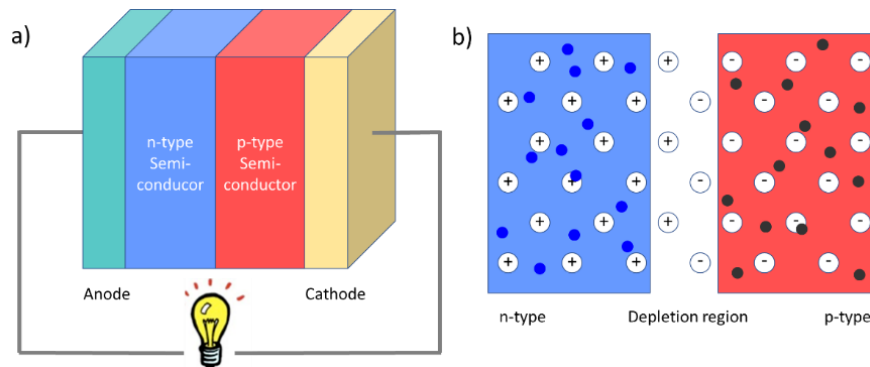


Figure 1-5 (a) schematic of the basic solar cell structure, and (b) the mechanism of p-n junctions.

1.2.3 P-n junction

A p-n junction is the most common way to sweep out the free electrons and holes. An n-type layer is a layer that has doping impurities with more valence electrons than its intrinsic materials, creating more free electrons, while a p-type layer is with doping impurities of fewer valence electrons, creating more free holes. When these two layers interact, the electrons will diffuse from high concentration n-type side to low concentration p-type side, leaving the n-type side positively-charged. The hole diffusion happens simultaneously, leaving the p-type side negatively-charged. This will form an internal electric field which is countering the diffusion direction. When the field becomes strong enough, the diffusion process will be balanced, and there will be no free electrons and holes existing in this region, which is called depleted region as shown in Figure 1-5 b. When free electrons and holes outside this region enter, it will immediately sweep electrons to the n-type side and holes to the p-type side, which will then be extracted out by the anode and cathode respectively.

1.2.4 I-V curves

To evaluate a solar cell's efficiency, an I-V test is usually conducted by changing the bias across the device under the light and monitoring its current output. A typical curve is shown in Figure 1-6. Four parameters are commonly used to demonstrate a solar cell's property. They are short circuit current (I_{sc}) or current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE). It will have a

maximum power point, where fill factor is calculated by its maximum power divided by $J_{sc} * V_{oc}$. The voltage and current at this point are V_{mp} and J_{mp} respectively.

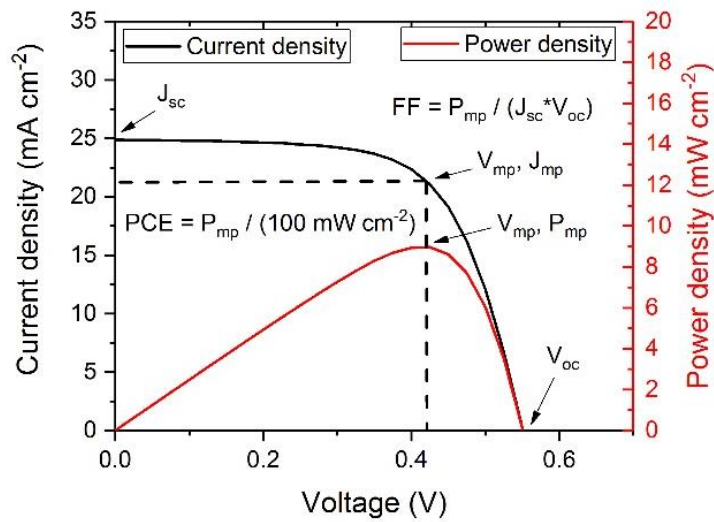


Figure 1-6 a typical I-V curve of a solar cell under the light.

1.3 Colloidal quantum dots (CQDs)

Colloidal quantum dots are nanoparticles with 1-20 nm diameter dispersed in a colloidal state. Protected by their long ligands on the surface, these CQDs are not fusing with each other, so that their properties can be well preserved. Lead sulphide (PbS) is one of the most common CQDs. Due to the quantum confinement effects, different size CQDs will have different band gaps. Depending on the applications, varieties of devices can be fabricated by just one kind of CQDs. Figure 1-7 a shows a typical TEM of 1.4 eV PbS CQDs with a mean diameter of 2.8 nm. The optical band gap of PbS CQDs (E_g) was determined by UV-vis absorption spectrum. Figure 1-7 b showed the UV-vis curves of the above PbS sample. The first excitonic peak position was used to calculate its band gap.

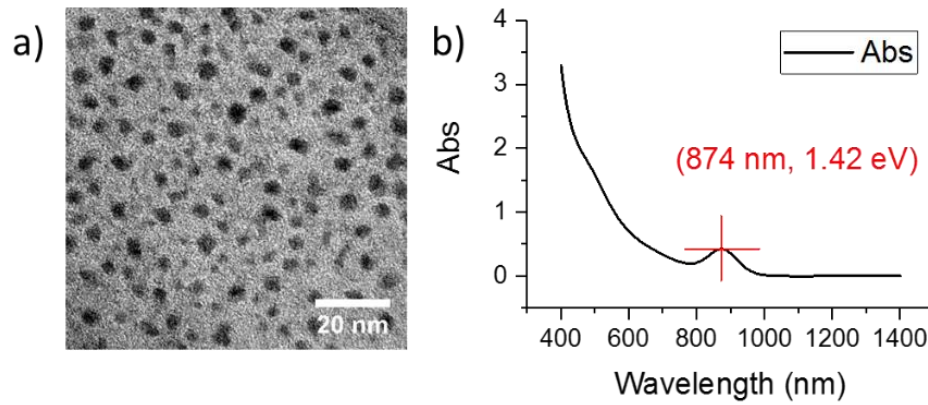


Figure 1-7 a) a typical TEM image of 1.42 eV PbS CQDs with a mean diameter of 2.8 nm.

b) a UV-vis absorption curve of PbS CQDs for determining its optical band gap.

1.3.1 Quantum confinement effects

Due to the quantum confinement effects, CQDs showed very different semiconductor properties from their bulk counterparts: the band gap of CQDs increases as their size decreases (Figure 1-8). In bulk materials, the energy states at the conduction band edge and the valence band edge are thought continuous. This is due to the exclusive principle that the same energy states of electrons on different atoms will split into many different ones forming a broad band, and infinite atoms in bulk materials will result in continuous bands. In CQD materials where there are limited atoms, the band edge will change from continuous to discrete, which results in narrower bands and larger bandgaps.

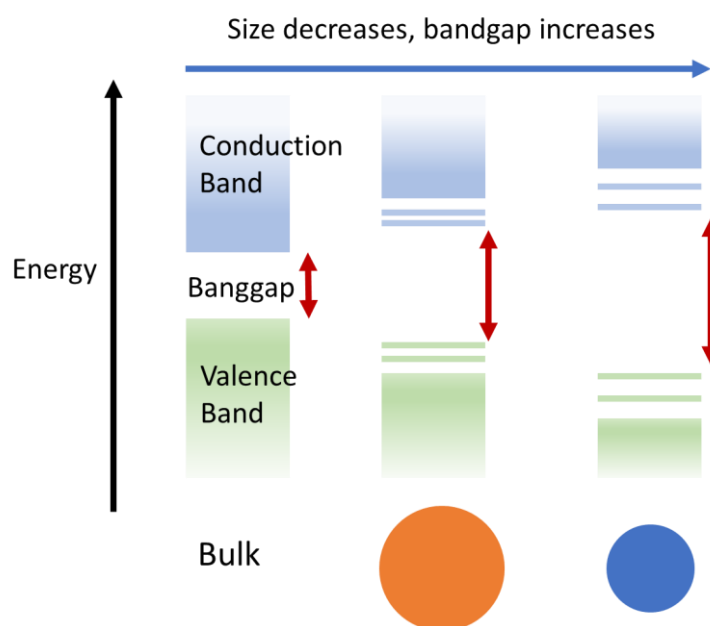


Figure 1-8 Diagrams for quantum confinement effects. As CQDs' size decreases, the band at the edges change from continuous to discrete.

The quantum confinement effects become obvious when CQDs' size is smaller than its exciton Bohr's radius, which describes how much the excitons are delocalised in CQDs. The Bohr's radius, which in hydrogen atoms is the mean radius of the ground-state electron orbit around its nucleus, represents the position of the maximum probability density for the excitons in CQDs, which varies between different materials.⁵ The value for PbS CQDs is about 18 nm, so PbS shows quite strong quantum confinement effect in nanoscales.⁵

1.3.2 CQD synthesis

There are three methods used in literature for CQDs' synthesis, including hot injection synthesis⁶, non-injection heat-up method⁷, and flow reactor synthesis⁸. In hot injection method Figure 1-8 a), nucleation occurs upon the injection of a room temperature precursor into a high-temperature surfactant. This is followed by reaction cooling leading to the growth phase. In the non-injection heat-up method (Figure 1-8 b), all precursors are mixed up from the beginning of the reaction and steadily heated to initiate nucleation and growth stages. In the flow reactor synthesis Figure 1-8 c), the

phases of synthesis are separated with a multistage, low volume, continual flow synthesis reactor.

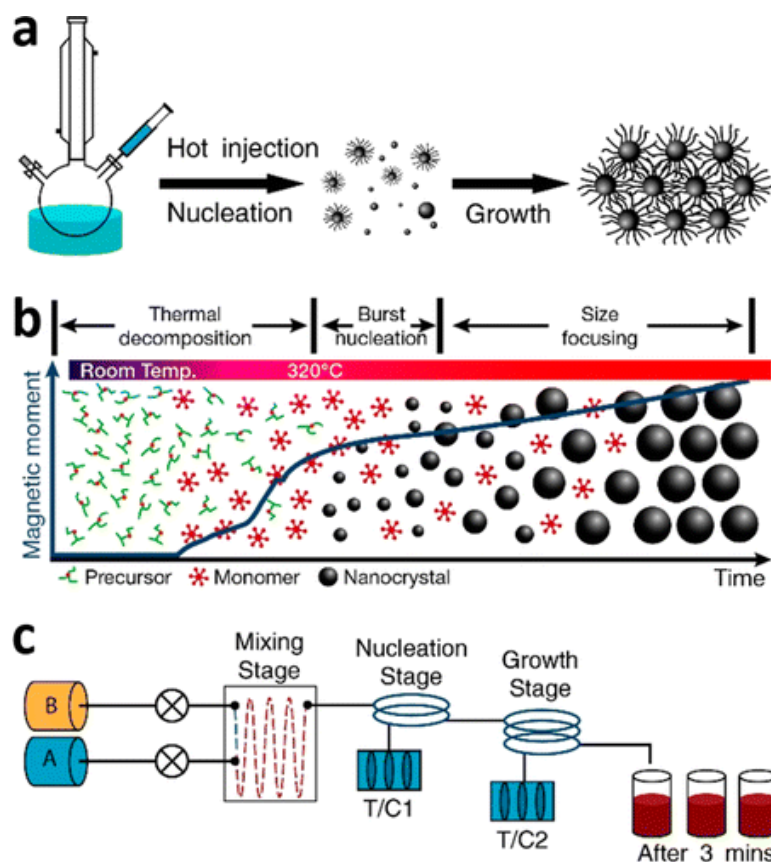
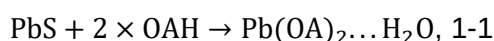


Figure 1-9 Schematics of CQD synthesis methodologies by hot-injection (a), heat-up (b), and flow-reactor (c). Obtained from reference.⁹

CQDs such as PbS quantum dots were usually synthesised using the hot injection method from Hines et al.^{10,10} Typically a lead oleate precursor is formed by mixing PbO and oleic acid in octadecene with degassing,¹¹ followed by the injection of bis(trimethylsilyl) sulphide (TMSi)₂S in octadecene. The reaction process is as listed below:



Once the room temperature (TMSi)₂S was injected, the nucleation started due to the induced supersaturation. The drop of the overall temperature will terminate the nucleation and commence the growth. A rapid nucleation and a slow growth are thought

to result in good mono-dispersity. The injection temperature is important as it will regulate the decomposition of the precursor.

Another variant method would be replacing lead oleate and TMS with lead chloride and elemental sulphur respectively in oleylamine.^{12, 13} The synthesis of ZnO nanoparticles was often adapted from Pacholski et al.'s reports.^{14, 15}

1.3.3 Carrier transport between CQDs

The carriers were transported mainly via the tunnelling current between quantum dots (Figure 1-10 a). The concept of tunnelling for quantum transport requires the understanding of coupling energy β , between two neighbouring CQDs (Figure 1-10 b). Coupling energy describes the extent to which wave functions of two neighbouring CQDs' states overlap and hence, the extent of exciton delocalisation.¹⁶⁻¹⁸ It is given by:

$$\beta \approx \frac{\Gamma}{h}, \quad 1-3$$

where β is the coupling energy, Γ is the tunnelling rates, and h is the Planck's constant. Γ can be approximately summarised as¹⁹

$$\Gamma \approx \frac{1}{e^{2 \times (2m^* \Delta E / \hbar^2)^{1/2} \times \Delta x}}, \quad 1-4$$

Where ΔE and Δx are the energy barrier's height and thickness, m^* is the effective mass of the carriers. It is obvious that the tunnelling rate decreases exponentially with Δx which equals to the nearest dot-to-dot distance.

Therefore, the dot-to-dot distance, which is controlled by the ligand length, is crucial for CQD films' conductivity. Longer ligands, lower tunnelling possibilities, poorer conductivity. For instance, in core-shell structures of PbS/CdS,²⁰ a thicker shell will result in the smaller effective CQD core and larger effective bandgap. However, as the dot-to-dot distance is increased as well, the tunnelling current decreases exponentially. Thus a very thin shell is needed.²¹

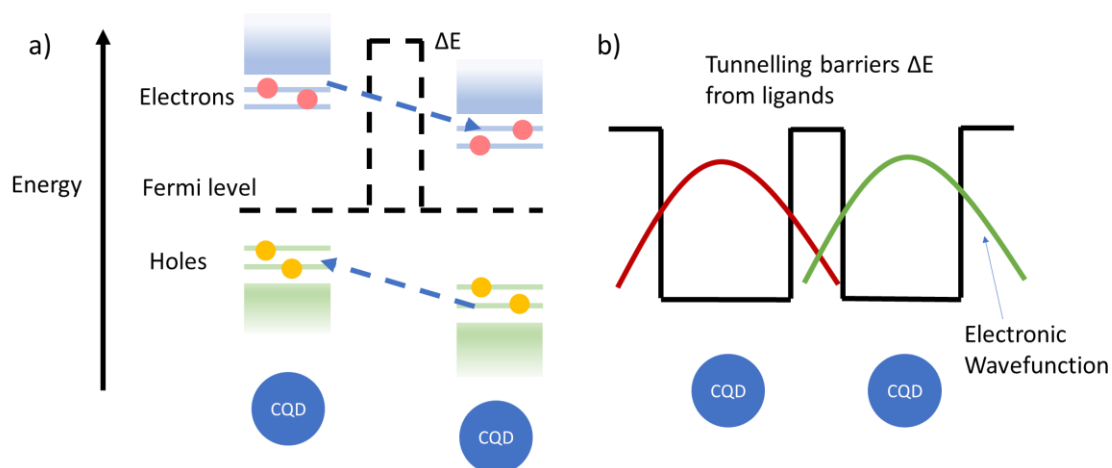


Figure 1-10 Diagrams for tunnelling transport between CQDs. a) quantum tunnelling happens even if the barrier is much larger than the carrier's energy. b) the coupling of two neighbours CQDs.

1.3.4 Trap states on CQDs

Due to the abrupt termination of the crystalline structure of CQDs on the surface, there are usually dangling bonds on the surfaces, resulting in trap states in the band gap. These trap states are detrimental to CQDs' optoelectronic properties. Except for dangling bonds, other causes for trap states include surface oxide impurities and unmatched ligand passivation. There are two types of trap states (Figure 1-11), the deep ones lying in the middle of the band gap and the shallow ones close to the band edges. The shallow states may slow down carrier transport, while the deep ones will result in carrier loss in the form of non-radiative recombination. Therefore, these states need to be removed by passivation. For example, OH bond is found crucial in the synthesis of PbS CQDs,¹¹ while it must be removed to improve CQD films' conductivities,²² which will be discussed further in Chapter 5.

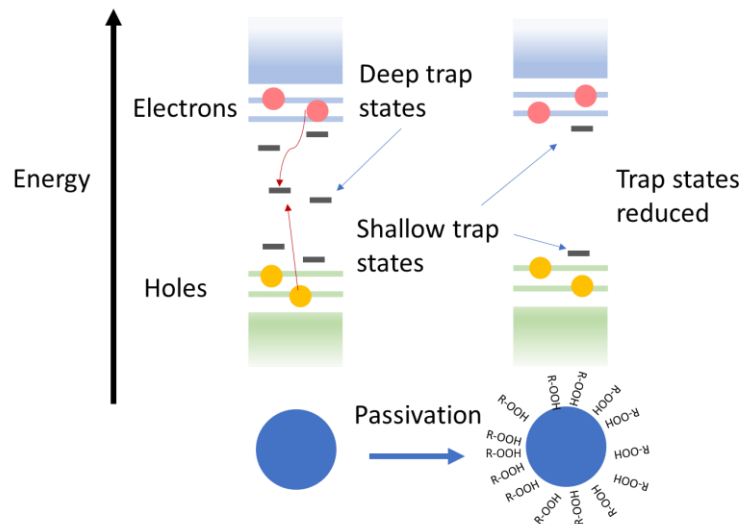


Figure 1-11 Diagrams of the trap states of CQDs and passivation by ligands reducing the trap states.

Because of the high surface atom percentage in CQDs, the ligands on the surface will ultimately influence CQDs' electronic structure. Due to the numerous surface defects, as synthesised CQDs will naturally be doped by these defects, showing either p- or n-type properties. By passivating these defects or enhancing its doping, CQDs with p- or n-type properties are both achievable.

1.4 CQD photovoltaics

1.4.1 Advantages and disadvantages

Solar cells based on PbS colloidal quantum dots (CQD) as the absorber have the potential to provide cheap, flexible, and highly efficient photovoltaic (PV) devices. As shown in Figure 1-12,²³ lead and sulphur are both abundant and low-cost materials that can be synthesised into colloids which absorb across the solar spectrum. For example, the band gap of CQD PbS can vary from 0.4 eV (3100 nm) to 2.4 eV (517 nm).^{24, 25} These colloids can be solution-processed into thin films with controlled semiconductor properties suitable for optoelectronic devices.^{26, 27}

The Elements According to Relative Abundance

A Periodic Chart by Prof. Wm. F. Sheehan, University of Santa Clara, CA 95053
Ref. Chemistry, Vol. 49, No. 3, p 17-18, 1976

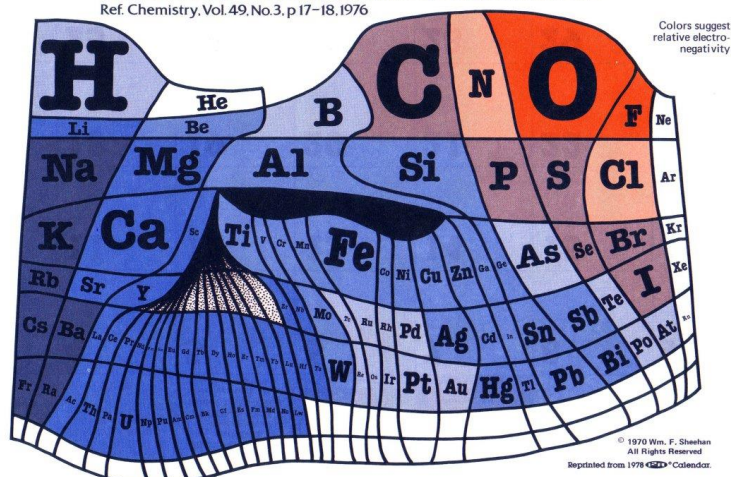


Figure 1-12 the periodical table according to the relative abundance on earth. Adapted from reference²³.

Because of the high absorption coefficient of CQDs such as PbS, the active layers can be very thin, usually less than 500 nm. For example, for the light at 550 nm (Table 1-1), the absorption coefficient of 31.3 nm PbS is at least $3.43 \times 10^5 \text{ cm}^{-1}$, and the absorption depth is less than 30 nm,²⁸ while for silicon the coefficient is only $6.39 \times 10^3 \text{ cm}^{-1}$ and the absorption depth is at least 1500 nm.²⁹ Due to the use of abundant, high production-volume primary metals and ultra-thin absorber layers, 25 TW_p PbS CQD PV, which will meet the global energy consumption of 2050, would only require the equivalent of 22 days of global lead production and 6 hours of global sulphur production.³⁰ In the past decade, the power conversion efficiency (PCE) of CQD solar cells has rapidly increased from less than 1% to 13.4%.³¹⁻³³

However, because of the disadvantages such as low carrier mobility and diffusion length, high surface defects etc., the overall performance is lower than some other emerging photovoltaics such as perovskite solar cells.⁴

Table 1-1 Optical property comparison for different materials at 550 nm at 300K. Data adapted from references.^{28, 29, 34}

Materials	Extinction coefficient k	Absorption coefficient α (cm ⁻¹)	Absorption depth(nm)
CdS	0.0073	1.67E+03	6000
Si	0.0280	6.39E+03	1565
alpha-Si	0.2432	5.56E+04	180
GaAs	0.2675	6.11E+04	164
CdTe	0.2918	6.67E+04	150
InP	0.3890	8.89E+04	113
Ge	1.7021	3.89E+05	26
PbS (bulk)	1.2300	2.81E+05	36
PbS (31.3nm)	1.500-2.000	(3.43-4.57)E+05	22-29

Firstly, the most important drawback is that the carrier diffusion length of quantum dot solar cells is low. The carrier diffusion length, which is determined by the carrier mobility and carrier lifetime according to Einstein equation, controls how thick the solar cell absorber layer can be, and this will determine the solar cells' current output. Because the carrier was transported via tunnelling current between quantum dots, the mobility is much lower than the one in crystalline materials such as monocrystalline silicon. Besides, the carrier lifetime is also lower, which is due to the high surface defects on quantum dots. These defects become the recombination centres for the free carriers.

Secondly, the voltage output is low as well. This is because the surface defects will also induce trap states in the band gap of the quantum dot semiconductors. These trap states lowered down the overall quasi Fermi level difference in n- and p-type layers, which subsequently lead to a lower voltage output.

To overcome the shortness discussed above, three common strategies are developed by scientists by optimising the quantum dot itself, creating advanced architecture solar cells, and engineering the band structure across the devices.

1.4.2 QD optimisation

It is commonly accepted that the chemistry on the CQD surface determines carrier properties as much as the QD's bulk properties.^{35, 36} Recent device improvements have been focused on improving carrier mobility and reducing recombination rates using a variety of treatments including solid or liquid state ligand exchange,³⁷⁻⁴⁰ and surface passivation.^{20, 41, 42} For example, Tang et al.⁴² showed that passivation using halide containing organic ligands, e.g. cetyltrimethylammonium bromide (CTAB), reduces the number of trap sites, and lowers the recombination rate of electrons and holes, compared to organic only counterparts, e.g. 1, 2-ethanedithiol (EDT). Ning et al.³⁷ invented ways to change p-type CQDs to be air stable n-type by iodide ligand passivation, and also found ways to build devices based on n-type inks.³⁸

1.4.3 Band alignment engineering

Besides optimising the quantum dots, interfacial band alignment engineering is also crucial for further improvements in fill factor, open circuit voltage, as well as the efficiencies of CQD solar cells.⁴³⁻⁴⁷ Chuang et al.⁴³ reported that replacing two layers of tetrabutylammonium iodide (TBAI)-modified PbS with EDT-modified PbS acts to block electron at the cathode resulting in a certified efficiency of 8.55%. The work of Brown et al.⁴⁴ tabulated the effects of various ligands on the Fermi levels and valence band positions of the QDs. Besides different ligands,⁴³⁻⁴⁵ QDs with different sizes⁴⁶⁻⁴⁸ also lead to changes in the band alignment effects. Hyun et al.⁴⁸ reported that QD's size also changes the energy level of the conduction band. In 2011 Kramer et al.⁴⁷ reported a quantum funnel CQD solar cell using large band gap PbS as a blocking layer at the rear contact with PCE of 2.7%. However, the mechanism behind band alignment in quantum dot solid is still open to debate. Ning et al.³⁷ suggest that it is a result of an extended depletion region, while Chuang et al.⁴³ ascribes it to the formation of an interface dipole.

1.4.4 Architecture improvement

Schottky junction CQD solar cells: the first type of CQD solar cells. Schottky junction CQD solar cells were the first type of quantum dot solar cells that provide another photovoltaic candidate apart from quantum dot dye-sensitised solar cells and makes people realise that quantum dots can also make a photovoltaic device.³¹ The typical architecture is shown in Figure 1-13 a. This technology uses the drift electrical field produced by the asymmetric electrodes with different work function, and the junction formed between p-type CQDs and shallow work function metal electrode as shown in Figure 1-13 c, is called Schottky junction. However, because the junction is usually at the back of the device, it resulted in long carrier transport distance and subsequently high recombination rates.

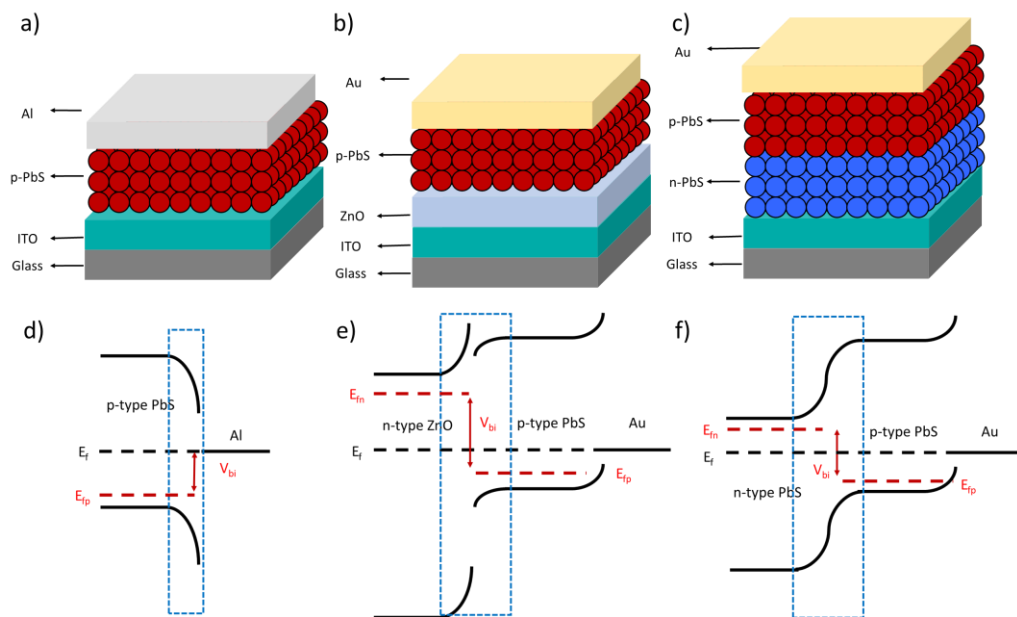


Figure 1-13 schematics and band diagrams of typical CQD solar cells with (a, d) Schottky junctions, (b, e) heterojunctions, and (c, f) quantum dot homojunctions. The blue regions are the depletion regions. The red marks are the quasi-Fermi levels, which define the built-in voltage of the device.

Heterojunction solar cells: the highest performed CQD solar cells. The architecture of Schottky CQD solar cells was changed by applying another wide bandgap n-type materials, such as ZnO,⁴³ TiO₂,⁹ etc., to form a p-n junction with p-type CQDs,

called heterojunction solar cells. The architecture is in Figure 1-13 b. In heterojunction solar cells, the photon generation occurs near the p-n junction so that the travelling distance for carriers is much less than that in Schottky junction solar cells. The depletion width in both p- or n-type materials can be tuned by changing their doping density. Although this architecture has provided the highest CQD solar cell efficiency as so far, the open-circuit voltage was still low due to the pinning of the CQDs' band edge as well as the wide-band-gap materials' band edge offset as can be seen in Figure 1-13 e.

Quantum dot homojunction solar cells: absorbing more high energy photons. Quantum dot homojunction solar cells (Figure 1-13 c) are developed to overcome the band edge offset drawback.^{21, 49, 50} It uses the same CQDs as both p- and n-type materials. This type of solar cells can absorb light at both p- and n-type layers, increasing the light harvesting. Besides, the band offset between p- and n-type layers can be tuned easily (Figure 1-13 f). The difficulty is in developing stable n-type CQD materials because oxidation is a cause of the p-type property. Excellent properties of materials have been achieved, but performance optimisation for devices need to be done.

Multiple-junction solar cells: using more infrared photons. Beyond the single junction solar cell, multiple-junction solar cells (Figure 1-14 a) are thought would absorb more infrared solar spectrum which takes account for about 52% in AM 1.5 as shown in Figure 1-4. A typical tandem solar cell's architecture is shown in Figure 1-14 a, consisting of a top visible cell and a bottom infrared cell. This can theoretically result in higher efficiency (Figure 1-14 b),^{26, 51} exceeding the Shockley-Queisser limit for single junction solar cells, which indicated that the highest theoretical efficiency of a single junction solar cell is around 33.7%⁵². The main efforts on tandem CQD solar cells were put on the recombination layers, which must be highly transparent, conductive, and with an appropriate band structure.^{53, 54} This technology can take the most advantage of the band-gap tunability of CQDs. Multiple junction cells by silicon or GaAs have been achieved successfully, but they are complicated to fabricate thus costly. However, with the ease of solution processed fabrication for CQD solar cells, this technology can very

possibly provide highly efficient, easy-fabricated, and air-stable photovoltaic applications with affordable price in the near future.

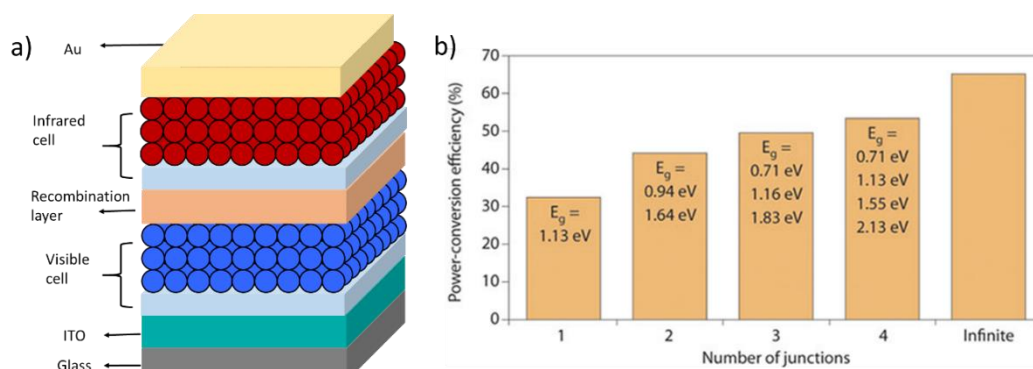


Figure 1-14 schematics of typical tandem CQD solar cells, and (b) the maximum efficiencies of multiple junction solar cells with a number of junctions. (b) is adapted from reference²⁶.

1.5 Aim and structure of this thesis

This thesis aims to explore ways of improving CQD solar cells' performance and understand the science that is involved. The structure of the thesis was listed as below.

The first chapter is background introductions and concept explanations. The second chapter is a literature review about three device-improvement strategies, including band engineering, surface passivation, and architecture improvements, and relevant advanced characterisation techniques. The third chapter is the experimental methods used for all the projects in this thesis. The fourth chapter is the first project by using better band alignment with a narrow band gap PbS HTL to improve CQD solar cells' performance. The fifth chapter is the second project by using a new ligand of CsI in alcohol to passivate the CQDs' surface to reduce the defects. The sixth chapter is the third project to apply CQDs into a microgroove-structured solar cell to gain super high voltage output. The seventh chapter is the fourth project to simulate the best tandem solar cells by a dichroic system and to optimise it by the comparison between the modelling and experiments. The eighth chapter is the conclusions and future work plans, which is followed by the references.

Chapter 2 Literature review

In this review, we will mainly talk about the advanced strategies scientists have used to enhance the performance of CQD solar cells, as well as the cutting-edge methods taken to characterise the optoelectronic properties of CQDs. Three aspects will be covered by how scientists had improved CQD solar cells' materials, architecture, and band structure. In the first section 2.1, quantum dot optimisation methods will be introduced such as ligand modification or surface passivation, and size and shape control of CQDs. In the second and third sections, the strategies by architecture engineering and band engineering would be detailed extended. Section 2.2 will mainly focus on the efforts taken on architecture engineering, and its relative advantages and disadvantages. Section 2.3 will introduce the band engineering work on absorber materials and extra extraction layers respectively. In the following section 2.4, the cutting-edge characterisation methods for optoelectronic properties of CQD and devices will be presented. Band edge energy measurement, carrier mobility, carrier lifetime and diffusion length, and doping density would be fully explained.

2.1 Quantum Dot Optimisation

Quantum dot optimisation is one of the many methods aiming at improving the photovoltaic performance of CQD solar cells. As the Fermi level of the CQDs was pinned due to its surface defects, the open circuit voltage is low, far below CQDs' actual band gap. Many methods have been used to optimise CQDs to solve this problem. For example, controlling its size and shape can tune the band gap value, and subsequently determine the light absorption. Besides, its surface modification will significantly influence the recombination rate as well as the build-in field.

2.1.1 Control of CQD size and shape

The main advantage of the CQD solar cells is that the band gap of CQDs can be tuned across a broad range by just changing their diameter. This range, such as from

0.4 eV to 2.4 eV for PbS QDs (Figure 2-1),^{24, 25} can cover almost the whole spectrum of the solar light (Figure 2-1),^{12, 25} implying CQD solar cells can provide potentially high efficiency with more light absorption.

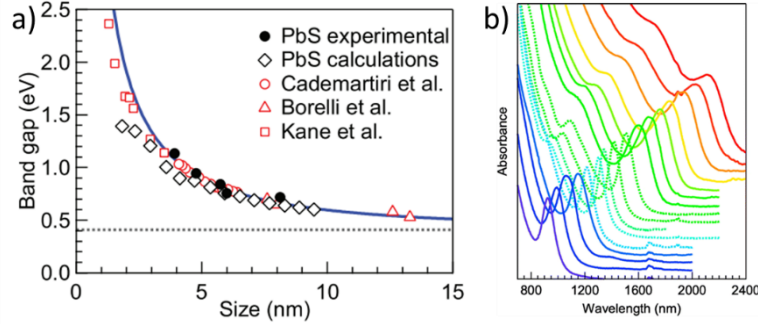


Figure 2-1 (a) PbS CQD band gaps and (b) absorbance changes with different QD sizes.

(a) is adapted from reference²⁵, and (b) is adapted from reference¹².

As explained by Brus,⁵⁵ who discovered CQDs, the increased band gap correlated to its QD size in the following Brus equation, especially for small bang gap materials:

$$E_0 = E_{\text{bulk}} + \frac{h^2}{8r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right), \quad 2-1$$

Where E_0 is CQDs' band gap, E_{bulk} is the bulk materials' band gap, h is the Planck's constant, r is the CQDs' radius, m_e^* and m_h^* are the effective mass of the excited electron and the excited hole respectively.

As to PbS CQDs, the size-dependent optical properties of CQD PbS were researched by Morseels et al.²⁵, and they found the relationship between band gaps of PbS and sizes can be expressed by the following equation, which is very similar to the above Brus equation:

$$E_0 = 0.41 + \frac{1}{0.0252d^2 + 0.283d}, \quad 2-2$$

where d is the PbS QD's size in nm, E_0 is the optical band gap in eV, and 0.41 eV represents the bulk PbS's band gap.

Size and shape control. The control of size and shape of CQD was conducted by changing the amount of surfactant and precursor, as well as reaction temperature. Less amount surfactant would result in smaller CQD size with larger band gaps

indicating a blue shift in the optical absorption or emission spectra. Higher temperature would usually result in bigger size QDs. Choi et al.⁵⁶ modified Hine's method to be two processes, nucleation and growth under different temperatures and gained stable and smaller size PbS to 1.5 nm.

Also, the shape transition of the nanoparticles is controlled by changing the size of the PbS. The shape transition of oleate-capped QDs from octahedron to cuboctahedron (Figure 2-2) is driven by the size-dependent surface energy of oleate-passivated Pb-rich QD facets, where the surface energy is defined as the excess energy at the surface of a material compared to the bulk. The oleate-capped octahedral small-size QDs are very stable in air, while cuboctahedral large-size QDs truncated with the unpassivated (100) surface are rather unstable against surface oxidation. Apparent stability transition around 4 nm is then observed (Figure 2-2).

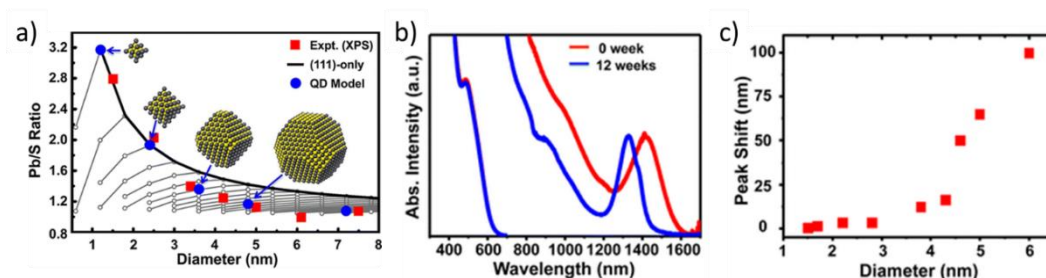


Figure 2-2 (a) PbS size and shape controls: Pb/S ratio of octahedral and cuboctahedral PbS QD models as a function of diameter. (b) Large and small size PbS absorption spectrum over 12 weeks. (c) The peak shift of different size PbS. Abrupt transition of stability around 4 nm was observed. (a-c) are all adapted from reference.⁵⁶

Different size QDs also lead to changes in band alignment effects.⁴⁶⁻⁴⁸ Hyun et al.⁴⁸ reported that QD's size obviously changes the energy level of the conduction band (Figure 2-3). This will further influence the performance of the solar cells.

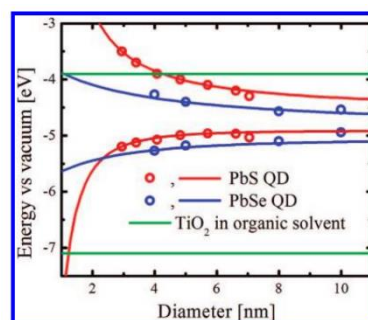


Figure 2-3 Different sizes resulting in different energy levels for PbS and PbSe QDs.

Extracted from reference.⁴⁸

2.1.2 Control of CQD surface passivation

Surface passivation is the most common and vital methods to enhance CQD solar cells' performance. The surface states of quantum dots influenced the overall properties as much as the bulk states. Surface ligand treatment will significantly change their carrier mobility, doping density, and energy levels. Different ligand modification would change the CQD surface energy level as well as the overall energy level.^{43-45, 57} Brown et al.⁴⁴ tabulated the effects of various ligands on the Fermi levels and valence band positions (Figure 2-4). Obvious changes with different ligand modification were observed.

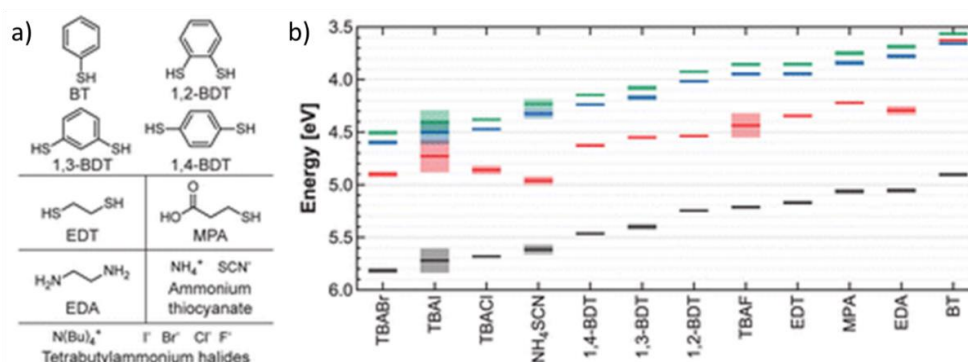


Figure 2-4 a) Different ligands used for passivation of PbS CQDs; b) Band edge positions of PbS CQDs with different ligand treatments. Obtained from reference.⁴⁴

Solid state ligand exchange. Solid state ligand exchange is a common method used for surface passivation. Usually, the QDs were capped by non-polar long-chain organic ligands which keep it stable and make it soluble in organic solvents. After a QD film was done by spinning coating or spray coating, short-chain ligand solvents will be

coated on the film. The short-chain ligands which have a stronger affinity towards the QD surface atoms will replace the long-chain ligand. Thus, the passivation of the surface was done. However, it is usually not sufficiently efficient to passivate all the surface atoms, leaving some cations on the surface uncoordinated and acting as defects. These defects would contribute a lot of trap energy levels in the band gap, limiting solar cells' performance. Therefore, single atom passivation and further hybrid passivation was reported to reduce the trap energy level's number.

Tang et al.⁴² found single halide atom treatment can improve the passivation of QDs' surface, resulting in obvious enhancement on the overall performance of solar cells. As can be seen in Figure 2-5, Br-capped QDs showed much lower absorption in the time-resolved infrared (TRIR) spectra, which indicated lower numbers of trap energy levels compared to both the MPA-capped and EDT-capped QDs. The broad features in the TRIR spectra are due to trap-to-band transitions, and the amplitude and shape of the spectra reflect the number and depth of trapped carriers. The narrow features appearing between 0.15 and 0.2 eV result from vibrational spectra of ligands that are perturbed by localisation of charges at surface trap sites.⁴²

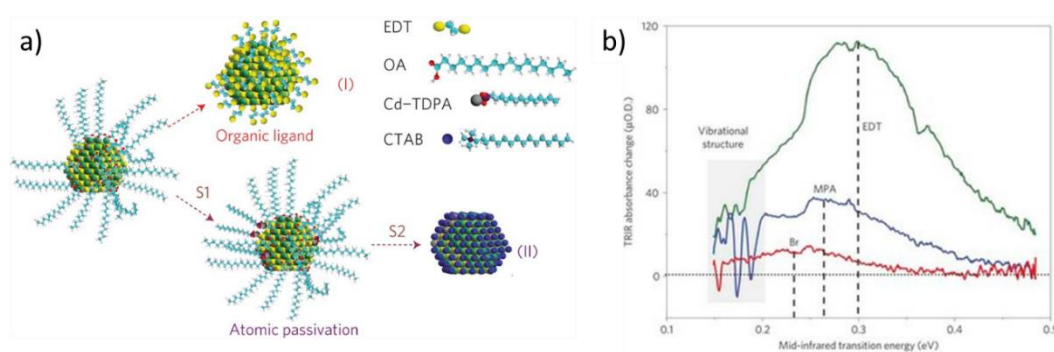


Figure 2-5 (a) schematic of passivation strategies by organic ligand EDT and atomic ligands Br. S1: Cd-TDPA (cadmium–tetradecylphosphonic acid) passivation for S, S2: CTAB (cetyltrimethylammonium bromide) passivation for Pb and Cd. (b) their corresponding TRIR transient absorption spectra. MPA: 3-mercaptoparboxylic acid. (a-b) are adapted from reference.⁴²

Ip et al.⁴¹ further introduced hybrid passivation method using atomic and organic ligands together, which further reduced the trap energy levels between the band gap. Firstly, a halide treatment was employed at the end of PbS QD synthesis. CdCl_2 dissolved in oleylamine and tetradecylphosphonic acid (TDPA) was added to the reaction solution when it was cooling down. MPA passivation was conducted during the film fabrication process. In Figure 2-6, the hybrid passivated QDs showed clearer band gap than organic and inorganic QDs, which means better passivation and fewer trap sites on the QDs' surfaces. And the PCE of hybrid ones (7.0% certificated) is also higher than the others.

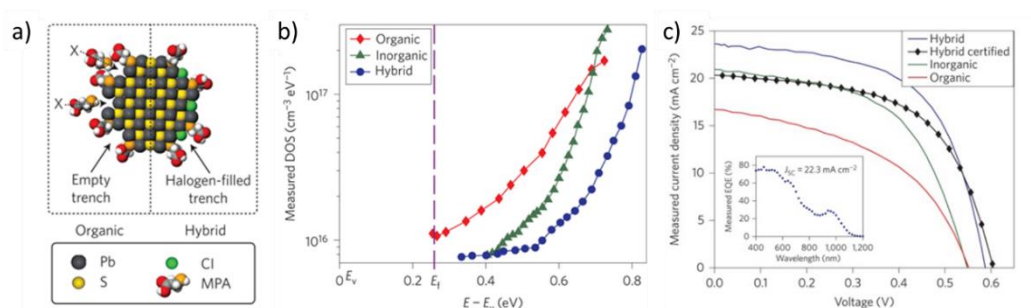


Figure 2-6 (a) schematic of hybrid passivation, (b) measured density of state (DOS) in the band gap by transient photovoltage measurements, and (c) I-V performance comparison. The hybrid QDs showed clear band gap compared with organic and inorganic QDs, so the performance is also better. (a-c) are obtained from reference.⁴¹

Some pre-treatments have been reported as well to improve the passivation before the film fabrication. Molecular iodine I_2 was reported improving the passivation.⁵⁸ 0.5 mL I_2 -toluene ($25 \times 10^{-3} \text{M}$) solution was added, in a drop-by-drop fashion, to the PbS nanocrystal solution (2.5 mL, 150 mg/mL) in a vial in a glove box. After 24 h, the CQDs was precipitated by methanol and re-dispersed in toluene (50 mg/mL) for solid-state ligand exchange. This resulted in a PCE of 9.9%.

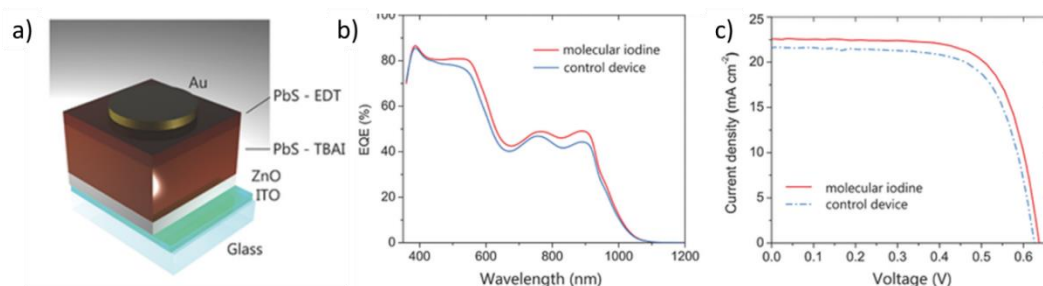


Figure 2-7 molecular iodine pre-treatment improving PbS passivation: a) the device structure; b) EQE; and c) I-V curves. (a-c) are reproduced from reference.⁵⁸

The highly reactive nature of molecular iodine can lead to uncontrolled fusion of PbS CQDs. Because it is very sensitive to the iodine amount in the above method which may influence its reproducibility, another method of milder iodine source MAI was reported following it.⁵⁹ A co-solvent system was employed to tune the solvent polarity in order to achieve the solvation of MAI and the dispersion of hydrophobic PbS CQDs simultaneously in a homogeneous phase. 1.5 mL toluene-DMF (2:1 vol%) dispersed MAI (40 mM) solution was added to 2 mL PbS CQDs (100 mg/mL) in a vial slowly (1 drop per 10 s). Gentle shaking, instead of strong stirring was applied to facilitate the formation of a homogeneous solution. Too fast injection of MAI solution resulted in irreversible precipitation of CQDs. After 12 h in the glovebox, methanol was employed to precipitate the CQDs, which were re-dispersed in octane (50 mg/mL) after fully drying. A PCE of 10.14% was announced with higher I (64%) replacing OA on PbS CQDs' surface.

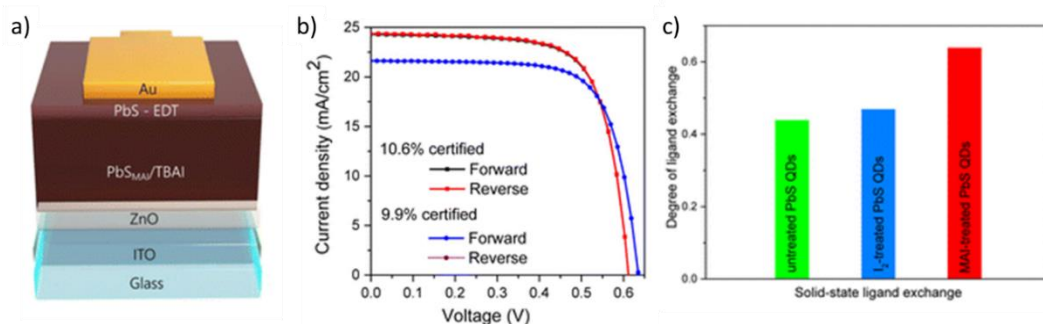


Figure 2-8 the MAI pre-treatment improving ligand amount on CQDs' surface: a) the device structure; b) I-V curves; and c) the I ligand ratio to Pb. (a-c) are obtained from reference.⁵⁹

Liquid state ligand exchange. Liquid state ligand exchange is aimed to significantly simplify the fabrication process and replace the complex layer-by-layer solid state ligand exchange. Butylamine,^{60, 61} or pyridine^{62, 63} has been used to replace the long organic chain with shorter ones. However, fully exchanging initial ligands in solution without causing aggregation is difficult. Anderson et al.⁶⁴ and Ning et al.⁶⁵ found that halides, including chloride, bromide or iodide, have a high affinity towards surface cations enabling room temperature, solution-phase ligand exchange.

In Ning et al.'s work,⁶⁵ *solution halide precursor* (TBAI precursor) was prepared as follows: TBAI was dissolved in oleylamine by heating at 200 °C for 2 hours under N₂ in Schlenk line and then pumping for 2 hours at 100 °C. A precursor with a concentration of 0.6 M was obtained by dissolving TBAI (2.21 g, 6 mmol) in oleylamine (10 mL). For solution halide treatment, untreated dots in toluene were added to TBAI precursor in a vial. The solution was stirred at room temperature for 15 minutes. Ethanol was added to precipitate the dots, and the solution was centrifuged to separate the CQDs powder from the solution. The nanocrystals were finally dispersed in octane. The ligand exchange process was carried out in a dry nitrogen glovebox (Oxygen level below 2 ppm and moisture level below 10 ppm). Furthermore, Ning et al.³⁷ reported air-stable n-type PbS quantum dot films based on this solution processed QDs. After depositing such n-type PbS, solid-state ligand exchange by TBAI was used, resulting in air-stable n-type PbS film. The efficiency of the solar cell by this method showed no noticeable change over almost four days (Figure 2-9). The iodide-modified device is inert for oxidation according to the Rutherford backscattering spectrometry results in Figure 2-9 e.

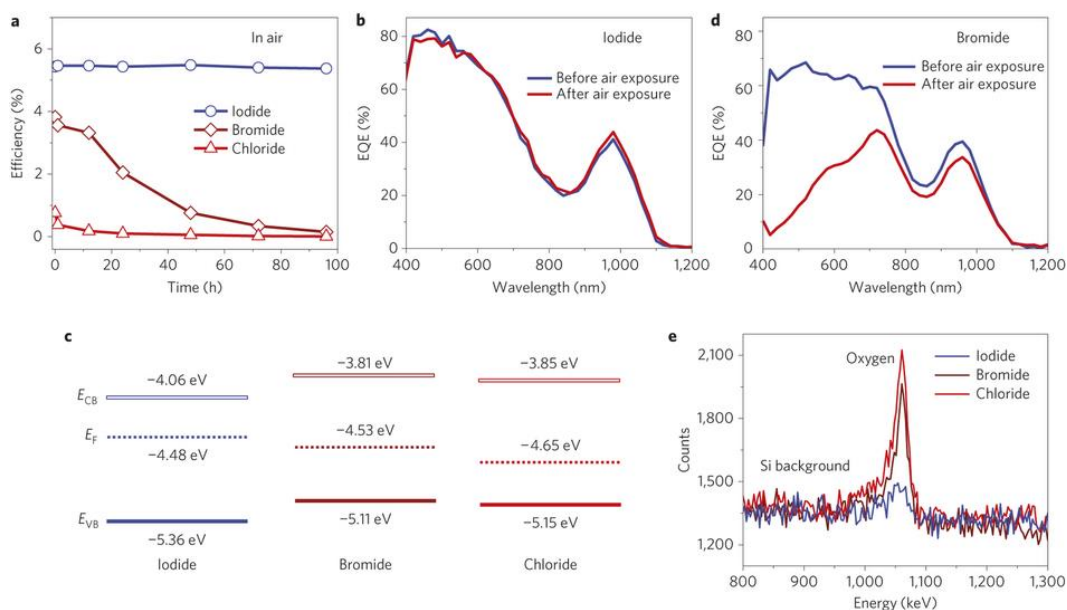


Figure 2-9 As-prepared Iodide-, bromide-, and chloride-modified device comparison: a) PCE in the air; EQE of iodide-(b), and bromide-(d) devices; c) band structures; and e) the amount of oxide. (a-e) are obtained from reference.³⁷

Their further research established a PbS quantum dot ink by judicious choice of solvents and ligands, which is capped using halide-based ligands alone.⁶⁶ And this method leads to the single-step fabrication of CQD solar cells.

Sargent's group reported three different strategies in a row by using a two-phase ligand exchange method to achieve the single step ink. PbS CQDs dispersed in octane (10 mg/mL) was added to target ligand dispersed DMF. These were mixed vigorously for several minutes until the CQDs moved from the top octane solvent to the bottom DMF phase. The DMF solution was washed by using octane. This solvent/antisolvent purification process was repeated twice to remove the residual oleic acid (OA), and the purified CQDs were finally re-dispersed in dry butylamine to yield a concentrated ink (200 mg/mL) in a solvent with a low boiling point.

First, they used $\text{CH}_3\text{NH}_3\text{I}$ as the ligand. A homogeneous and thick colloidal quantum dot solid is applied in a single step, which simplifies the fabrication process. After film fabrication, an annealing process is thought to remove the residual chain as Figure 2-10 shows. By using this ink with a PbS-MPA layer as the HTL, a PCE of 6.1% was reported.

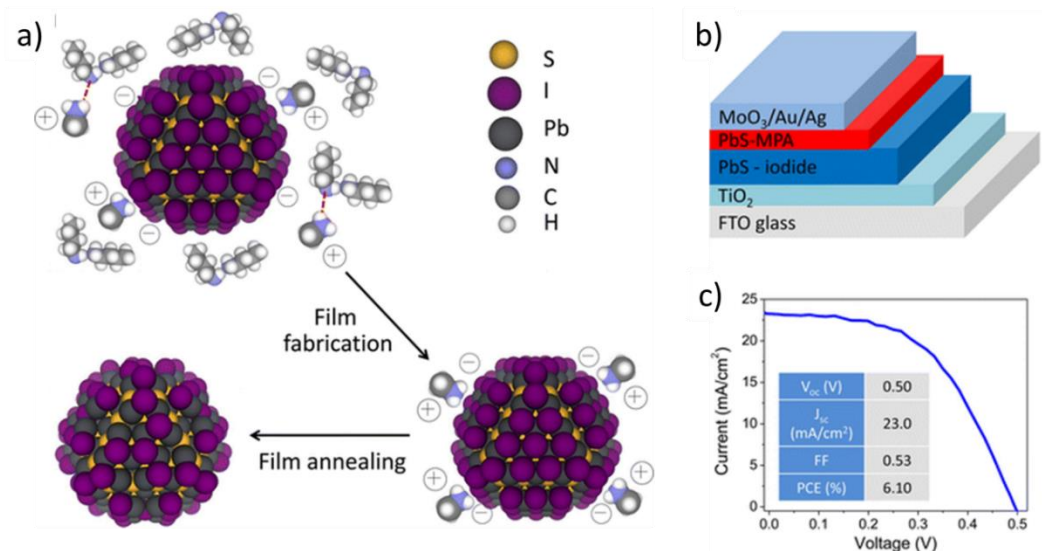


Figure 2-10 MAI passivated PbS by liquid state ligand exchange: (a) schematic of surface ion distribution in quantum dot inks and films; (b) the device structure; and (c) the I-V curve. (a-c) are obtained from reference.³⁸

A following research work was done by mixing MAI ligand with PbI₂ together to form a perovskite shell outside PbS CQDs with a similar method as above.⁶⁷ Instead of using 80 mg/mL MAI/DMF, a dimethylformamide (DMF) solution containing MAPbI₃ perovskite precursors (MAI and PbI₂, 0.3 mol/L) was mixed with the PbS solution. The MAPbI₃ ligand passivation renders CQDs soluble in DMF that can then be reprecipitated upon addition of toluene. This results in an optimised PbS thickness of 250 nm with a PCE of 8.95%.

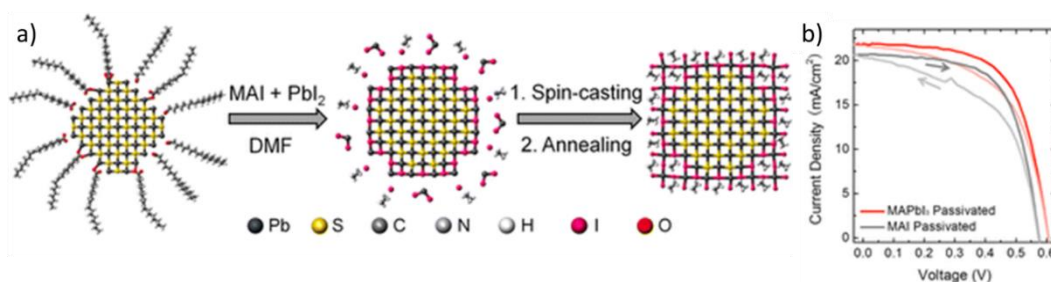


Figure 2-11 the perovskite shell passivated liquid state ligand exchange: a) schematic of the ligand exchange process. b) I-V curves. (a-b) are obtained from reference.⁶⁷

This work was further enhanced by applying PbI₂, PbBr₂ and NH₄Ac as the ligands together, and a PCE of 11.28% with an optimized PbS thickness of 350 nm was reported.⁶⁸ Lead halides (lead iodide 0.1 M and lead bromide 0.02 M) and NH₄Ac (0.04 M)

are pre-dissolved in DMF as the ligand precursor. During the ligand exchange process, the $[\text{PbX}_3]^-$ anions replaced the OA ligands with the aid of ammonium protons. Both $[\text{NH}_4]^+$ and $[\text{PbX}]^+$ were thought to contribute to nanocrystal colloidal stabilization in the polar solvent. The NH_4Ac organic residues were taken away by the anti-solvent precipitation process instead of the annealing process used above. This hybrid CQD ink maximises the number of halides on the surface thus reduced the band tailing. Due to the inter-dot distanced was reduced by small ligands, the pack intensity of the films is higher, so as the efficiency.

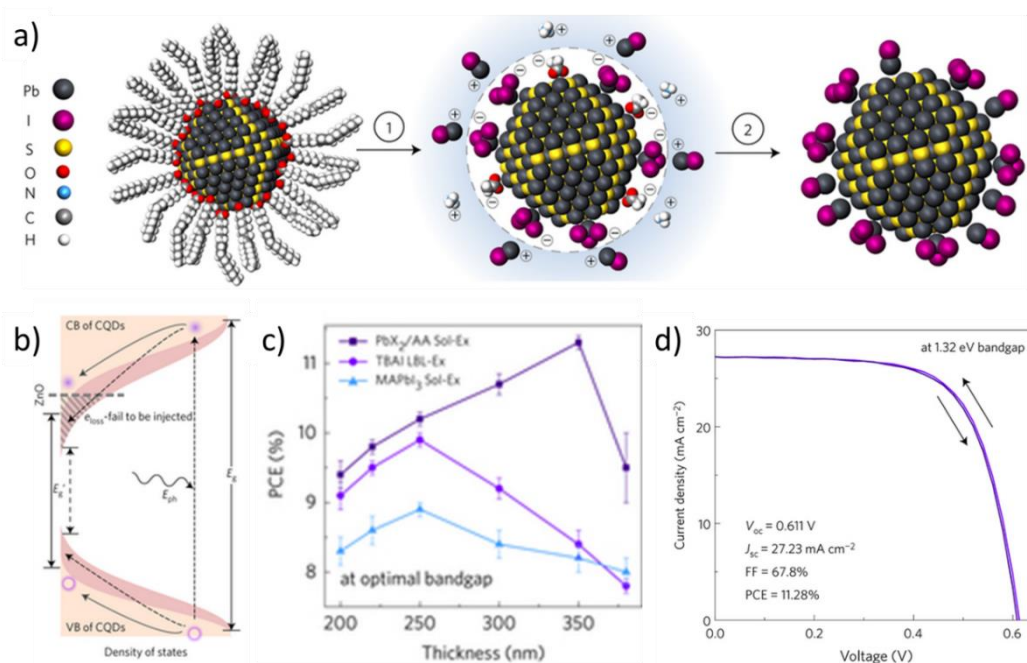


Figure 2-12 PbX₂/NH₄Ac passivated PbS liquid state ligand exchange: a) schematic of the ligand exchange process, b) flattening of the band tails, c) PCE optimisation, and d) I-V curves. (a-d) are obtained from reference.⁶⁸

Besides, Aqoma et al.²² reported a PbI_2 -only way for liquid state ligand exchange by the same two-phase method. PbI_2/DMF (0.3 M, 5mL) was mixed with PbS/octane (15 mg/mL, 5mL) for 15-30 min at 40 degree Celsius. After CQDs transfer and washing step, the solution was directly centrifuged at 9000 rpm for 5 min to separate the CQDs from the yellow supernatant. After fully drying in vacuum for 1h, CQD powders were dispersed in butylamine (150 mg/mL) for device fabrication. Less oxide amount was thought the

origin for the performance enhancement from solid state ligand exchange to single step ink.

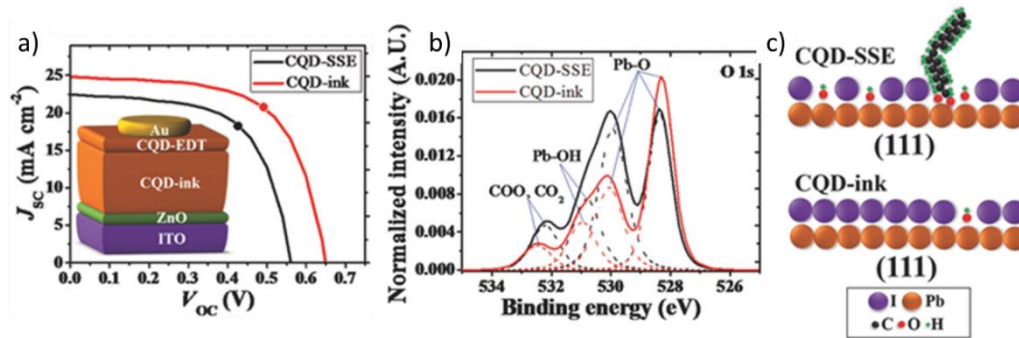


Figure 2-13 PbI₂ passivated PbS by liquid state ligand exchange: a) I-V curves; b) oxide species comparison by XPS; and c) schematic of passivation. (a-c) are obtained from reference.²²

2.1.3 Control of CQD component and structure

Changing CQDs' component and structure can also contribute to the improvement of the CQD solar cells' performance. For example, doping p-type PbS QDs with trivalent bismuth cations can shift the Fermi level, resulting in n-type PbS QDs.⁴⁹ This will change the optical properties dramatically despite that the shape of QDs is not affected.

Besides, building the core-shell structure of QDs is thought another way to improve QDs' quality.²⁰ This is a stronger passivation method to release the surface energy and reduce the trap sites. PbS/CdS was proved to be a good core/shell choice. A thin CdS shell of 0.1 nm provided near-complete surface passivation (Figure 2-14), because of which the built-in voltage was improved from 0.48 V to 0.66 V in EDT passivated devices. The improvement in V_{oc} is due to the deep traps being passivated by the thin CdS shell, which suppressed the nonradiative recombination. However, it comes at a large loss of current. As PbS/CdS is type-I core-shell structure and the energy barriers between dots are increased, the tunnelling current for carrier transportation is then largely reduced in an exponential way.

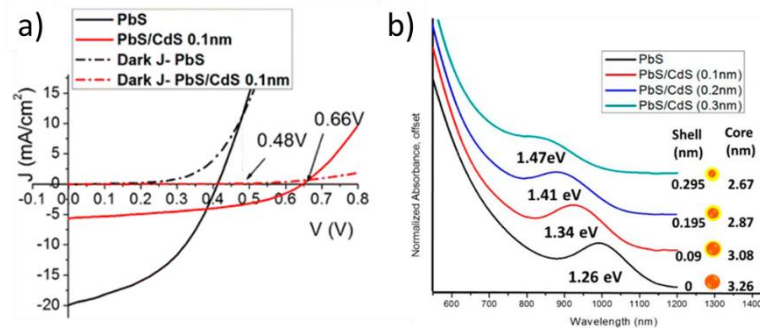


Figure 2-14 PbS/CdS core/shell structure: (a) I-V curves and (b) absorbance spectra of PbS/CdS CQDs with different shell thicknesses via a cation exchange process. (a-b) are obtained from reference.²⁰

2.2 Architecture Engineering

Architecture engineering is an efficient way to improve the performance of CQD solar cells because it will determine where the p-n junction is, how large the depletion width is, and how long the carrier need to transport. Advance has been achieved by building heterojunction, quantum dot homojunction, or even multiple junctions, compared to the very first Schottky junction devices. Light harvesting and carrier transport have both been improved a lot in the past decade, but further enhancement is still required.

2.2.1 Schottky CQD solar cells

The first Schottky junction CQD solar cell, using CQD layers as the absorbers, was reported in 2005.³¹ Transparent conductive metal oxide such as ITO or FTO and metal were used as two electrodes. A layer of CQDs was sandwiched between these two electrodes, like the SEM image in Figure 2-15 shows. It provided another photovoltaic candidate apart from quantum dot dye-sensitised solar cells. This technology uses the rectifying junction formed between p-type CQDs and shallow work function metal electrode, such as Al. At the interface between the metal and the semiconductor, due to the shallow work function of the metal, the band structure in the semiconductor would be downwards bending (Figure 2-15). The difference between the p-type PbS and metal work function determines the built-in potential.

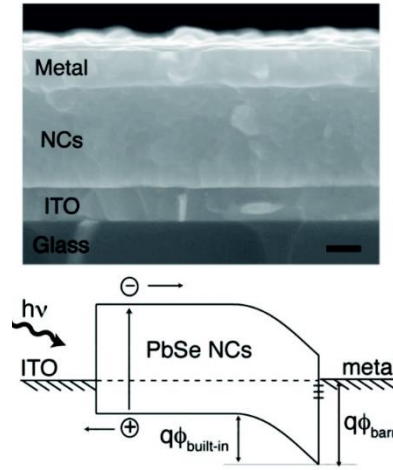


Figure 2-15 SEM of a typical Schottky CQD solar cell and its band diagram. Obtained from reference.⁶⁹

The larger PbS's band gap is, the higher the open circuit voltages are (Figure 2-16 a), as the electron and hole difference in energy is larger (Figure 2-15). The shallower metal's work function is, the higher the open circuit voltages are (Figure 2-16 b), as the anode and cathode work function difference is larger. The best Schottky device was reported by Piliego et al.⁷⁰ in 2013. The current record Schottky CQD solar cell has an efficiency of 5.2%.

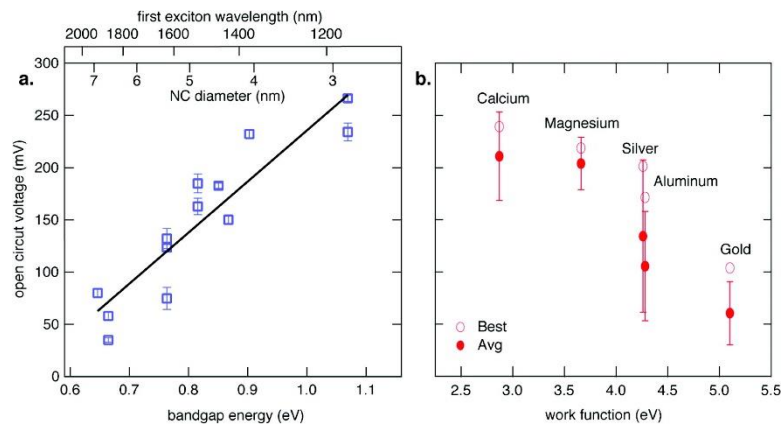


Figure 2-16 Trends in V_{OC} with NC size and metal work function. (a) Dependence on NC size. (b) Dependence on metal work function ($E_g = 0.82$ eV). (a-b) are obtained from reference.⁶⁹

Schottky junction devices have several advantages such as ease of fabrication and a limited number of interfaces. However, its drawbacks are also obvious. As this junction is usually at the back of the device, the photo-generated carrier will transport

across a long distance before being separated by the junction. Subsequently, the recombination rates are high. Besides, Fermi level pinning at the metal-CQD interface results in an upper bound on the open-circuit voltages.

2.2.2 Heterojunction CQD solar cells

Heterojunction CQD solar cell replaces the Schottky junction by applying another wide bandgap n-type materials, such as ZnO, TiO₂, etc., to form a p-n junction with p-type CQDs, called heterojunction. Highly doped metal oxides would be deposited on ITO or FTO coated glass substrates, followed by a layer of p-type absorbing CQD film. The stack is finished with the final ohmic contact consisting of a deep work function materials, for example, Au or highly doped oxide (MoO₃) followed by Ag or Al, so that the bending at the semiconductor-metal interface would be upwards benefiting the hole transport. The architecture and SEM of a typical heterojunction device are like Figure 2-17 shows.

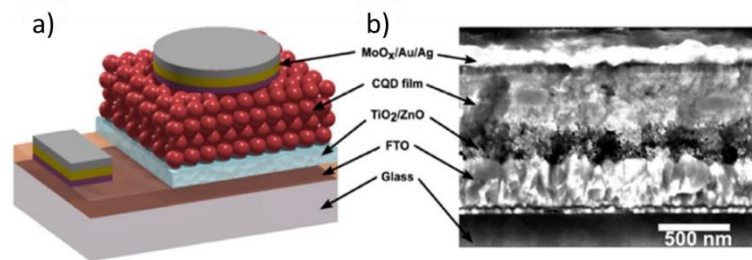


Figure 2-17 Schematic (a) and SEM (b) of heterojunction CQD solar cell. Graphs obtained from reference.⁹

Heterojunction solar cells make the photogeneration occurring near the p-n junction ensuring active carrier can be quickly separated. The depletion width in both p- or n-type materials can be tuned by changing their doping density. The wide bandgap n-type materials are usually highly doped so that the main depletion region will fall across the CQD layers.

Since the first certified heterojunction CQD solar cell (PCE 2.94%) with ZnO and PbS nanocrystals⁷¹, the performance was improved rapidly relying on several materials and device engineering advances. Band alignment between CQD films and TiO₂ or ZnO layer is critical and must be tuned so that the electron affinity difference benefits injection

of electrons to the highly doped n-type materials without sacrificing the open circuit voltage. Ohmic contact at the metal-semiconductor interface also needs special care to avoid Schottky junction. Advanced ligand treatments also reduce the trap sites and increase the diffusion length. These advances would be extended in the next chapter.

Another method such as building bulk heterojunction was also researched to increase the junction interface area and further reduce the carrier transport distance before being separated. TiO_2 nanorod⁷² or ZnO nanowire⁷³ was fabricated as the bulk n-type materials. The architectures and I-V performances of planar and bulk heterojunction solar cell devices are compared in Figure 2-18.

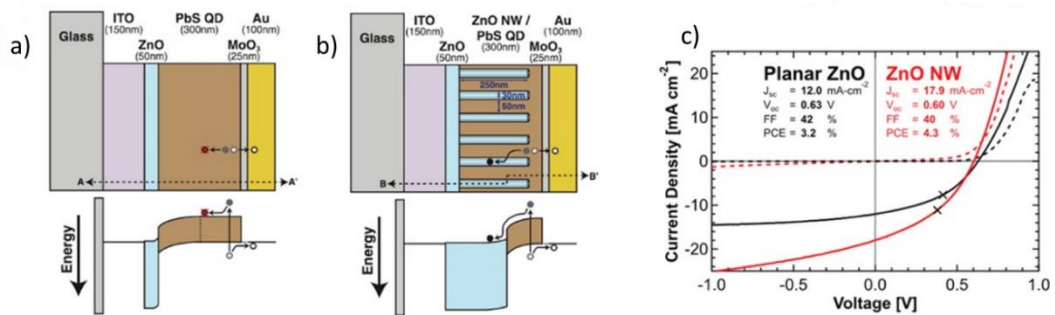


Figure 2-18 The architectures (a-b) and I-V performances (c) comparison of planar and bulk heterojunction PbS/ZnO CQD solar cell. Graphs taken from reference.⁷³

Although this architecture has provided the highest efficiency of CQD solar cells as so far,⁷⁴ the open-circuit voltage was low due to pinning of the CQDs' Fermi level as well as the wide-bandgap materials' band edge offset. And limited absorption of infrared photons at the single junction devices also limits the overall performance, which needs to be further improved.

2.2.3 Quantum dot homojunction solar cells

Quantum dot homojunction solar cells are researched to overcome the band edge offset drawback by using CQDs as both p- and n-type materials (Figure 2-19 a-b), and more high-energy photons will be absorbed.^{21, 49, 50} By using the same band gap materials in both p- or n-type layers, the built-in field as well as the open circuit voltage

was expected to increase (Figure 2-19 c). Besides, the depletion width will also increase because n-type layers can also absorb photons.

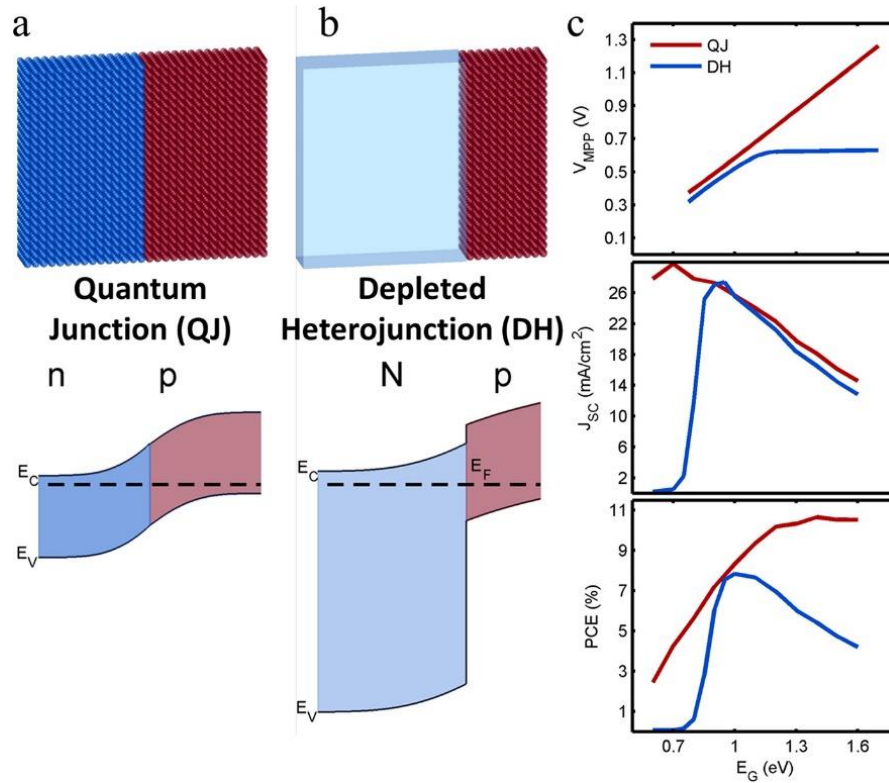


Figure 2-19 The band diagram of the quantum dot homojunction (a) and depleted heterojunction (b), and their simulated solar cell performances (c). (a-c) are obtained from reference.⁷⁵

The difficulty is in developing stable n-type CQD materials due to the action of oxygen as a p-type dopant⁷⁶. And progress is still on the way.^{37, 75} Ning et al.^{37, 65} found that the iodide treatment can change the p-type materials to be air-stable n-type materials. And their inverted quantum dot homojunction solar cell achieved a high efficiency of 8.0%.

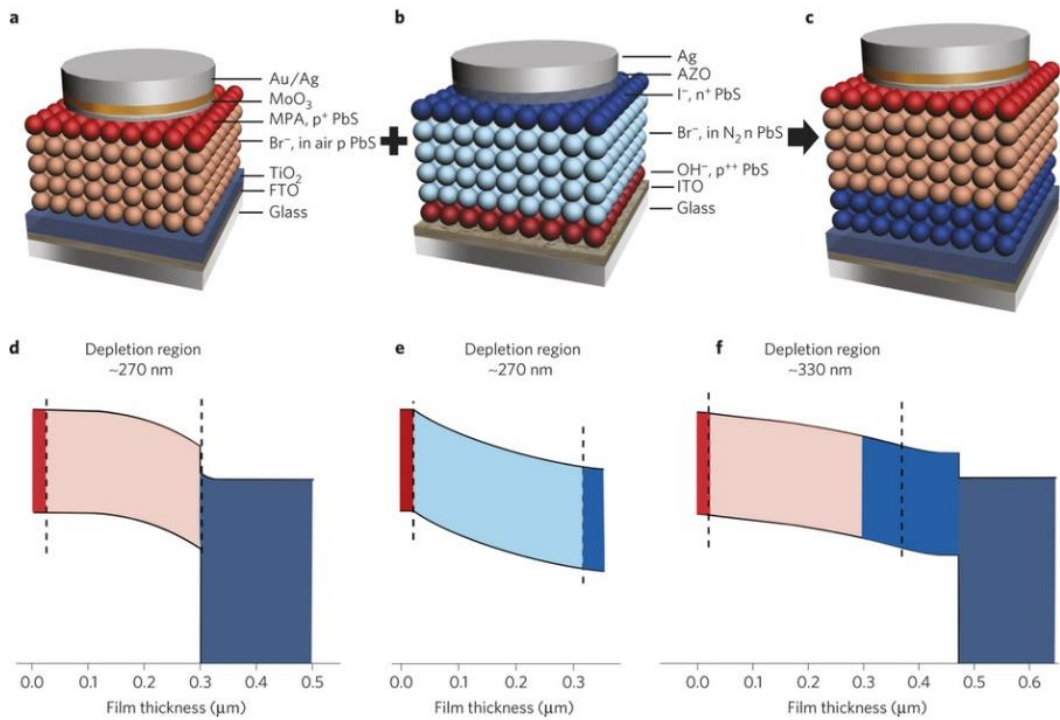


Figure 2-20 Quantum dot homojunction solar cell architectures. Inverted quantum dot homojunction CQD (c, f) showed the broadest depletion region about 330 nm compared to the heterojunction (a, d) and conventional quantum dot homojunction ones (b, e).

Graphs obtained from reference.³⁸

Quantum dot homojunction devices show high efficiency which may result from broader depletion region, while the open circuit voltage is not enhanced as expected. The trade-off of absorption and voltage output makes enhancement based on bandgap changing impossible. And the Fermi level is still pinned. Another method beyond single junction solar cell to enhance the voltage output is needed.

2.2.4 Multiple-junction CQD solar cells

Beyond the single junction solar cell, multiple-junction solar cells are thought would absorb more infrared solar spectrum and provide the sum of the open circuit voltage of two or more cells. This can very possibly result in higher efficiency, thus break the Shockley-Queisser limit⁵². This technology can take the most advantage of the band-gap tunability of CQDs.

Tandem CQD solar cells, as the most straightforward multiple junction devices, consist of two cells: a visible cell and an infrared cell (Figure 2-21 a).^{53, 54} Large band

gap QDs such as PbS would be used in the visible cell in the front of the tandem device, because its adsorption range mainly covers the visible light spectrum like the green fraction in Figure 2-21. This is followed by an infrared cell made by small band gap QDs to absorb the infrared like the red fraction in Figure 2-21

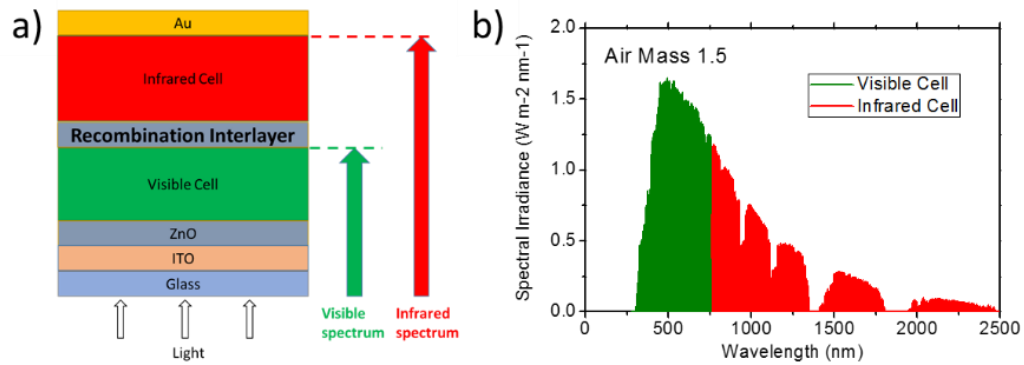


Figure 2-21 Typical tandem CQD solar cell structure (a) and corresponding absorption fraction in Air Mass 1.5 (b).

There are usually two strategies to connect the two cells: a tunnel junction or recombination layers. The tunnel junction is that the p-type layers of one cell are connected to the n-type layers of the other cell directly. At the interface, both layers are heavily doped. Thus, the p-n junction here can be very thin, less than the tunnel length of the electrons, which allows the tunnelling current happening. This junction is called tunnel junction which overcomes the carrier transport barrier by tunnelling current. The tandem solar cells using a tunnel junction to combine two subcells are marked as tunnel junction solar cells in the following discussion.

Three junction GaInP/GaInAs/Ge is a typical tunnel junction solar cell. In the tunnel junctions in Figure 2-22, highly doped p- and n-type materials were used to ensure the tunnel junction region is thin enough. With the lattice-matched three-junction solar cells, an efficiency of 40.1% at 135 suns was reported,⁷⁷ while in the lattice-mismatched (or metamorphic) case in Figure 2-22 smaller band gap middle and top cells can be grown on the bottom cells which allows a better band gap combination.

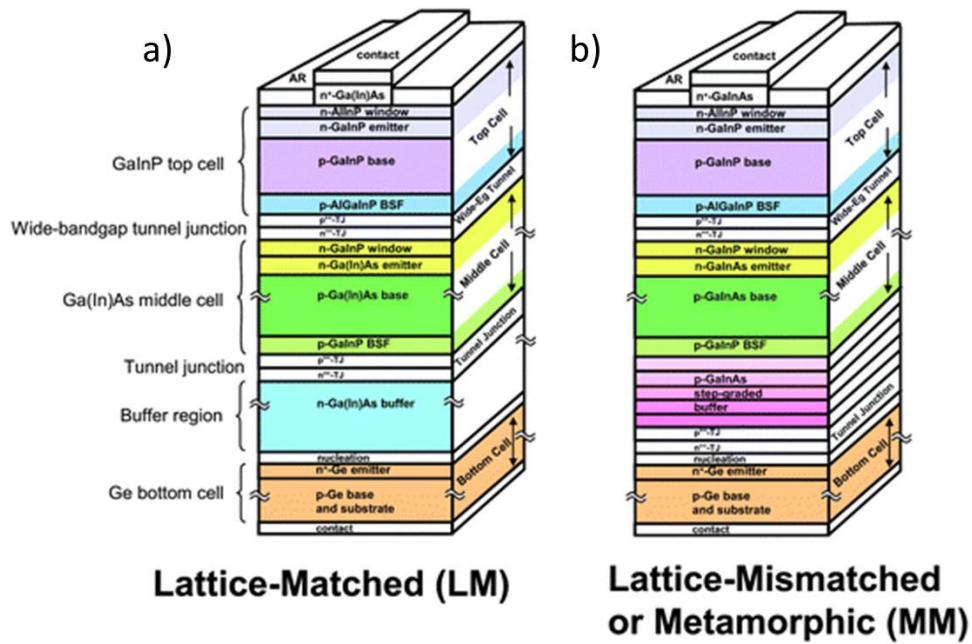


Figure 2-22 Cross-sections of lattice-matched (a) and metamorphic (b) GaInP/GaInAs/Ge 3-junction cell structures. (a-b) are obtained from reference.⁷⁸

The other strategy is to use recombination layers, which is a possible case for the emerging photovoltaic technologies. These two cells are connected in series by a conductive and transparent layer, called recombination layer where the electrons and holes from two cells meet and recombine here without any energy loss. Scientists' main efforts on CQD tandem devices have been taken on the recombination layers, which must be highly transparent, conductive, and with an appropriate band structure. The band gap, thickness, and ligand treatment of two cells need to be tuned to ensure the current matching when imposed in a tandem device. If the current did not match well, there would be energy loss for both cells.

Wang et al.⁵³ reported a graded recombination layer in tandem CQD solar cells and achieved an efficiency of 4.2% (Figure 2-23 a). This device showed the sum output voltage (1.05 V) of two separated cells successfully (0.35 V and 0.7 V respectively), indicating good current matching and excellent recombination performance at the interlayer. This highly efficient recombination resulted from the graded band structure, benefiting electrons' and holes' transport to the interlayer. The latest advances in atomic passivation⁴² and band engineering^{43, 79} on absorbers provide a potential improvement

in photovoltaic performance of tandem devices in the future. Besides, liquid state ligand exchange⁶⁸ can replace the layer-by-layer fabrication method, simplifying tandem's fabrication process significantly.

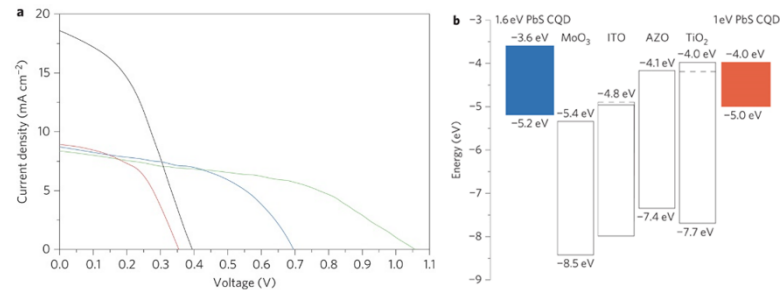


Figure 2-23 (a) I-V performances of tandem (green), visible (blue), infrared (black), and infrared with the visible cell as the filter (red); (b) the graded recombination layer's energy diagram. (a-b) are obtained from reference.

Besides, Choi et al.⁵⁴ reported a layer of ZnO/Au/pH 7 PEDOT:PSS as the recombination layer to build up a CQD tandem device with efficiency of 1.27%. The PEDOT:PSS layer was neutralised to prevent the acidity of the PEDOT dissolving the underlying ZnO layer. With the insertion of a 1 nm gold layer, the S curve disappeared in Figure 2-24.

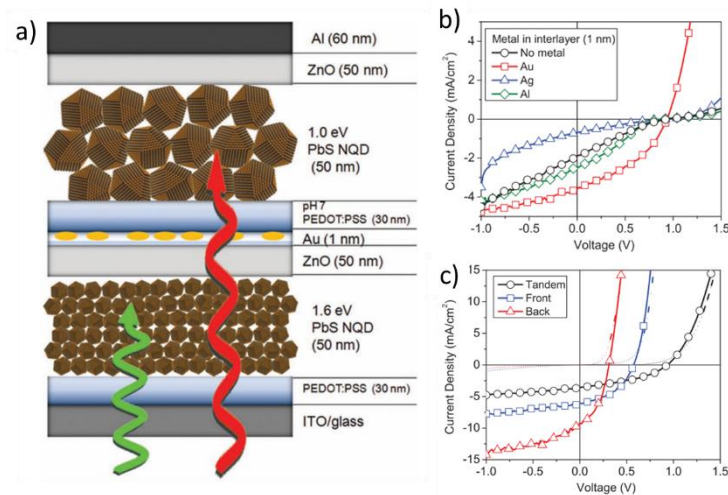


Figure 2-24 tandem CQD solar cells with ZnO/Au/PEDOT:PSS as interlayers: a) the device structure; b) I-V curves with different recombination layers; and c) I-V curves of the tandem and individual cells with gold as the recombination layers. (a-c) are obtained from reference.⁵⁴

With more advanced ligand strategies by a TBAI/EDT combination, Shi et al.⁸⁰ reported a tandem CQD solar cell by using an interlayer of Au or PEDOT, as shown in Figure 2-25. 1 nm Au was deposited through e-beam deposition, or a modified n-PEDOT (20 nm) was deposited on top of PbS-EDT layers at 2000 rpm followed by annealing at 100 °C for 10 min. 1 mL n-PEDOT (Clevious n-PEDOT) was diluted with 1.5 mL deionized water before the addition of 10 mg of surfactant (Capstone Dupont FS-31). With the all solution processed PEDOT recombination layer, a PCE of 7.7% was achieved, while with the e-beam processed Au recombination layer, the PCE was enhanced to be 8.9% with the help from doping the ZnO layer with TBAI for higher electron concentration.

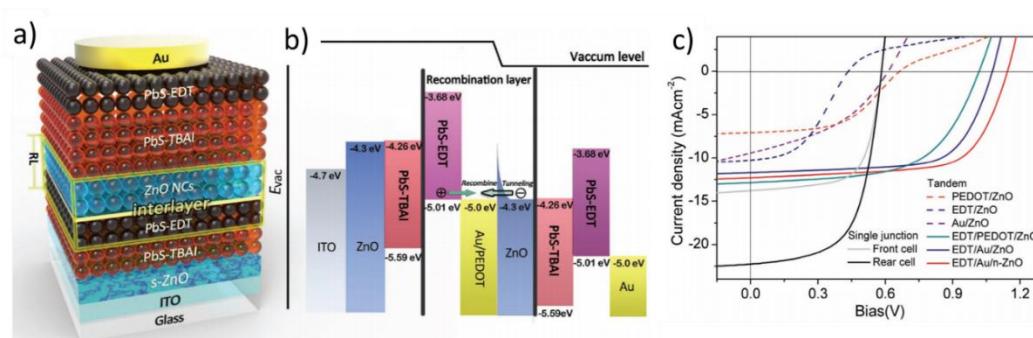


Figure 2-25 PbS CQD tandems with TBAI/EDT structures and an Au or PEDOT recombination layer: a) the device structure; b) the energy diagram; and c) the I-V curves. Graphs obtained from reference.⁸⁰

Organic tandem solar cells reported by Kim et al.⁸¹ used a junction of TiO_x and PEDOT:PSS as the recombination layer here. A transparent TiO_x layer was used to collect the electrons and to be the solid foundation of the fabrication of the back cell. From the SEM in Figure 2-26, the sharp boundary of each layer was observed, which means there were no interlayers. And the best PCE at 6.5% was demonstrated.

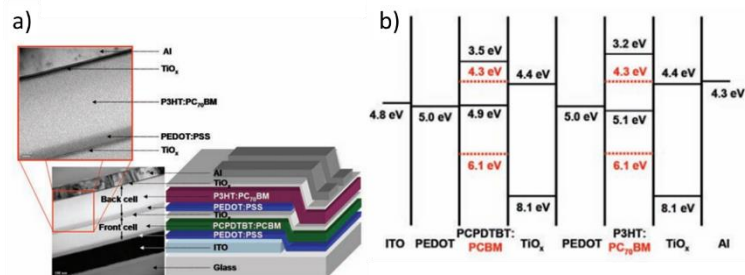


Figure 2-26 Organic tandem solar cells with recombination layers: a) the device structure; and b) the energy diagram. Graphs extracted from reference.⁸¹

Hybrid tandem solar cells are also of significant interests for scientists because they can combine the advantages of both cells such as CQDs' high absorption coefficient and perovskite's high efficiency.

CQDs/organic tandem has been reported a lot in the past three years. The first case is reported by Speirs et al.⁸² by using PbS with 1, 4-benzenedithiol (BDT) ligands as the front cell and P3HT: PCBM as the back cell, providing a PCE of 1.8% as shown in Figure 2-27. The interlayer was deposited by thermal evaporation of Al (1 nm), and WO₃ (15 nm). The rear active layer was spin coated with a solution of P3HT and PCBM (1: 0.8 wt/wt) in 1,2-dichlorobenzene. The as-cast film was subsequently annealed at 120 °C for 5 minutes. The device was finished by thermal evaporation of LiF (1 nm) and Al (100 nm). The low PCE is due to the unmatched spectrum and less advanced PbS passivation and cell architecture.

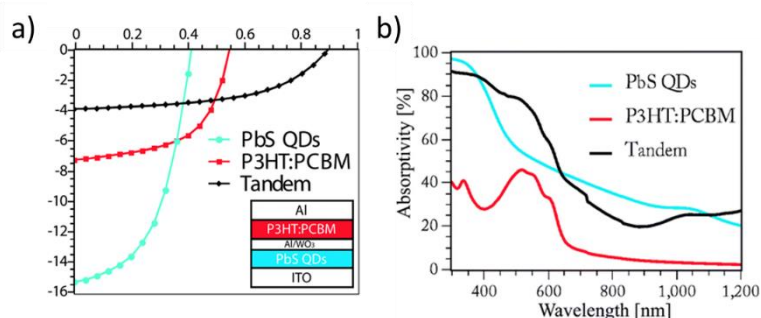


Figure 2-27 hybrid tandem cell: ITO/PbS/Al/WO₃/P3HT:PCBM/LiF/Al: a) I-V curves; b) absorption curves. (a-b) are obtained from reference.⁸²

Another work was reported following the above. Kim et al.⁸³ improved it by using MPA as the ligand and a heterojunction in the front PbS cell and a low band gap

PTB7:PC71BM as the back cell as shown in Figure 2-28. With thermal evaporated MoO_x and ZnO, and spin coated poly[(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) as the recombination layer, a PCE of 5.3 % was achieved. Following this work, another recombination layer⁸⁴ (Figure 2-28) was reported by replacing the ZnO by a thin layer of Au (1 nm), pushing the PCE to be 7.9%.

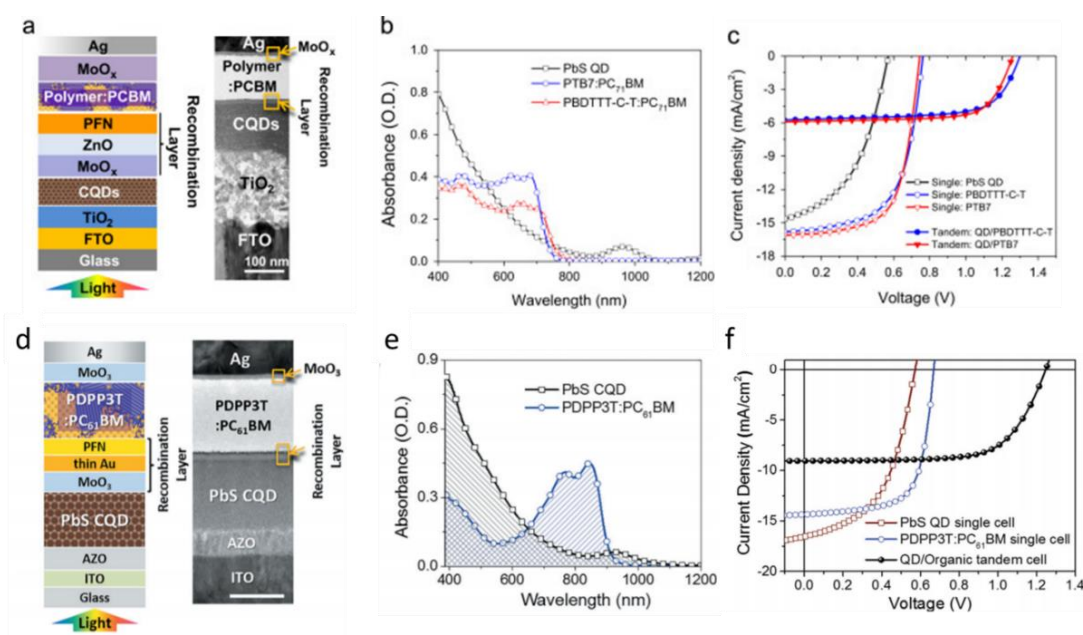


Figure 2-28 Diagrams of architectures, absorbance, and I-V curves of (a-c) glass/FTO/TiO₂/QD/MoO_x/ZnO/PFN/polymer:fullerene/MoO_x/Ag (Graphs obtained from reference⁸³) and (d-f) glass/ITO/AZO/QD/MoO_x/Au/PFN/PDPP3T:PC₆₁BM /MoO_x/Ag (Graphs obtained from reference⁸⁴)

This is further enhanced by another work⁸⁵ by swapping the sequence of the two cells, which will improve the spectrum matching. A recombination layer of spiro-MeOTAD(150 nm)/MoO_x(10 nm)/Ag(0.5 nm)/Polyethylenimine(PEIE, 2nm) was used, as shown in Figure 2-29. A PCE of 7.4% was obtained.

With a structure similar as the above, a recombination layer of MoO_x(20nm)/Au(1nm)/ZnO(20nm) was used by another team,⁸⁶ resulting in a PCE of 8.3% (Figure 2-30).

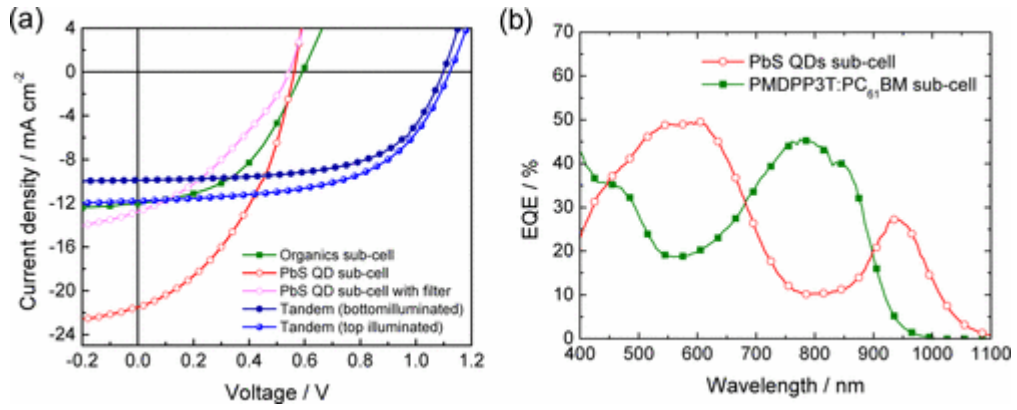


Figure 2-29 Glass/ITO/ZnO/PbS/Spiro-MeOTAD/MoO₃(10nm)/Ag(0.5nm)/PEIE/MDPP3T :PC₆₁BM/PEDOT:PSS-T (Top Illuminated): a) I-V curves; b) EQE. (a-b) are obtained from reference.⁸⁵

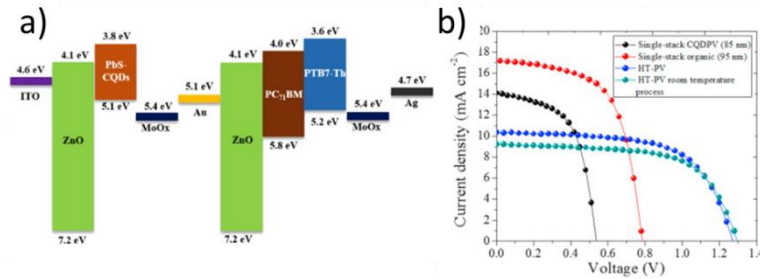


Figure 2-30 Glass/ITO/ZnO/PbS/MoO_x(20nm)/Au(1nm)/ZnO(20nm)/PC71BM:PTB&-Th/MoO_x(20nm)/Ag: a) the energy diagram; b) I-V curves. (a-b) are obtained from reference.⁸⁶

2.3 Band Engineering

Band engineering is also a significant method to optimise CQD solar cells. It can lower down the transport barrier for carriers at the interface and accelerate carriers' transport and extraction.

2.3.1 Band engineering of absorbers

An appropriate band structure throughout the device is beneficial for carrier separation, transport, extraction, and collection. Therefore, band engineering, including graded doping⁵⁷ and quantum funnel⁴⁷, has drawn a lot of attention from scientists.

Yuan et al.⁵⁷ reported an n/p/p+ graded doping heterojunction device reaching an efficiency of 7.2% (Figure 2-31). By building 280 nm of p-type PbS CQD layers treated with 3-mercaptopbutyric acid (3MBA) on TiO₂, a p-n junction was formed, followed by

employing higher doped 3-mercaptopropionic acid (MPA) treated PbS CQDs to form a graded doping device. High built-in potential and wide depletion region are both achieved at its maximum power point.

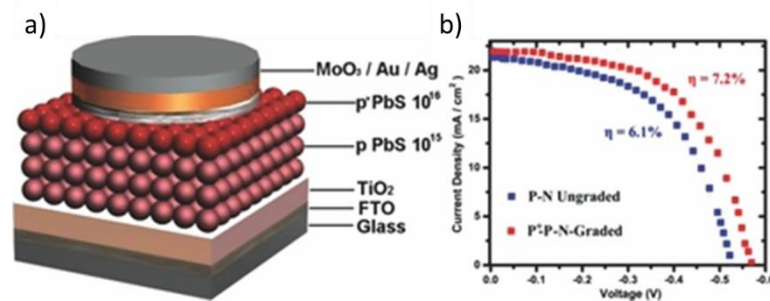


Figure 2-31 (a) schematic of an n/p/p+ graded doping heterojunction device and (b) its I-V performance. (a-b) are obtained from reference.⁵⁷

Chuang et al.⁴³ showed that replacing two layers of tetrabutylammonium iodide (TBAI)-modified PbS with EDT-modified PbS (Figure 2-32) acts to block electron at the cathode resulting in a certified efficiency of 8.55% in a heterojunction device. Because of the effect of oxidation on PbS-EDT layers,⁸⁷⁻⁸⁹ more p-type property is expected on PbS-EDT. This work significantly improved the performance and stability of CQD solar cells. Most of the following world record devices in CQD solar cells are still using the same structure as this one.

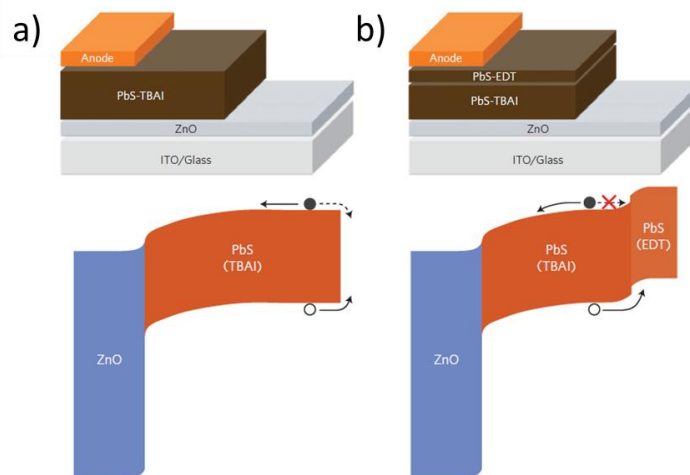


Figure 2-32 the architectures and band diagrams of PbS-TBAI (a) and PbS-TBAI/EDT (b). (a-b) are obtained from reference.⁴³

Ning et al.²¹ reported a quantum dot homojunction device with p+/n/n+ structure like Figure 2-33 shows. They found the addition of n+ top layers enable increased quasi-

Fermi level splitting and open circuit voltage, as well as higher PCE. And the different doping levels are achieved by using different types and amount of ligand treatment.

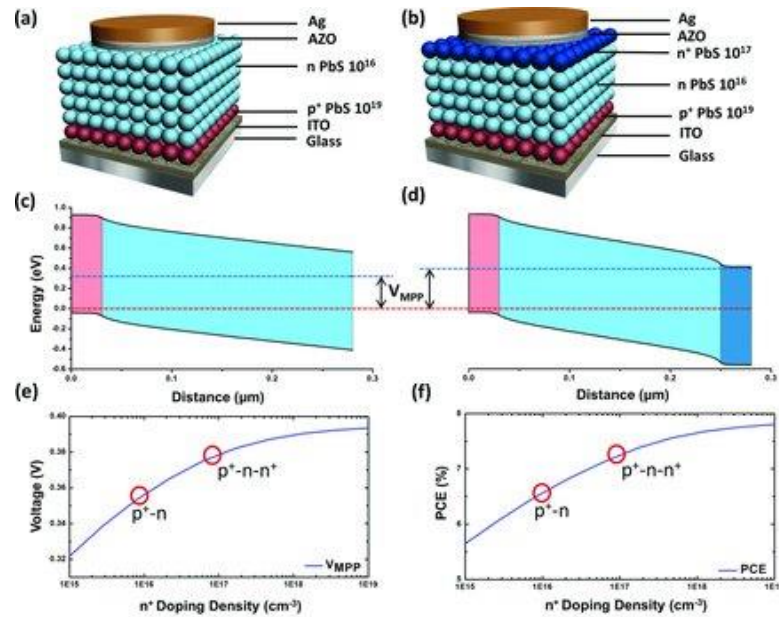


Figure 2-33 comparisons of a p+/n device and a p+/n/n+ device in architecture (a, b), quasi-Fermi level splitting (c, d), V_{oc} (e), and PCE (f). (a-f) are obtained from reference.

Quantum funnel is also a beneficial way to build an aligned band structure by just changing the size of the QDs. Kramer et al.⁴⁷ reported the first CQD quantum funnel solar cell with different PbS QDs modified by 3MPA. PbS with a small band gap was deposited on TiO_2 , followed by the large ones. This built a graded band structure like Figure 2-34 shows. The large band gap at the back efficiently blocked the electrons from p-type PbS to the metal electrode, reducing the recombination rates at the interface. And the graded device had the highest efficiency of 4.2% among the ungraded, graded, antigraded devices like presented in Figure 2-34.

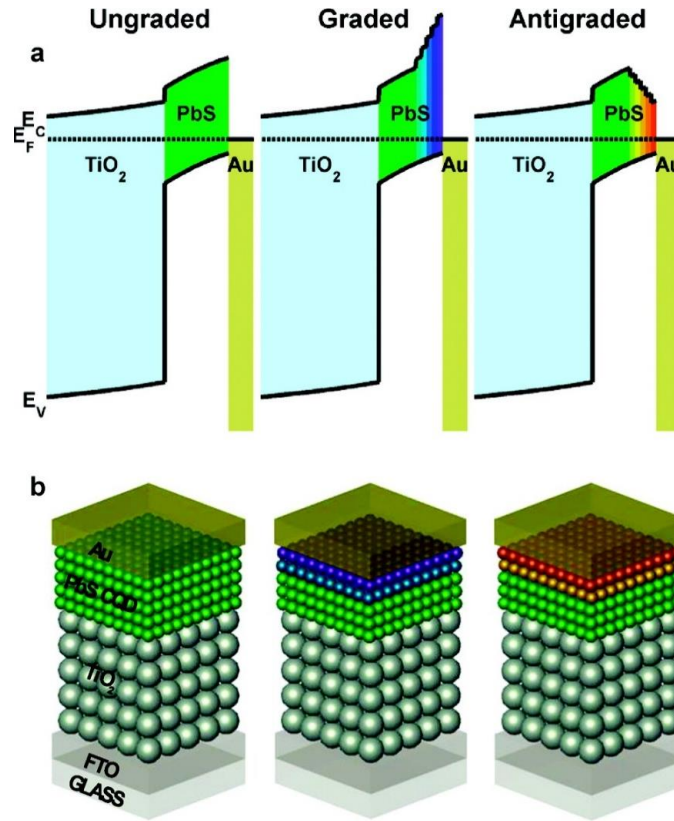


Figure 2-34 the band diagrams (a) and architectures (b) of different types of CQD devices. (a-b) are obtained from reference.⁴⁷

2.3.2 Extraction layer development

Extraction layer, known as hole transport layer (HTL)^{90, 91} or electron blocking layer (EBL)⁹², was thought to boost the efficiency of CQD solar cells dramatically.

Au was widely used in the inverted heterojunction devices as a cathode because gold has a deep work function (5.1 eV), which helps build an upward bending band structure at the interface of a metal and a p-type semiconductor. This upward bending would benefit hole collection. An alternative method was researched by applying a layer of LiF in front of Ni or Al, which can also prevent recombination and reduce the usage of high-cost material.

Gao et al.⁹⁰ reported that n-type transition metal oxides consisting of molybdenum oxide (MoO_x) and vanadium oxide (V₂O_x) were used as an efficient hole extraction layer (HEL) in heterojunction ZnO/PbS CQD solar cells. A 4.4% certificated device based on the MoO_x HEL with Al as the back contact materials was achieved

(Figure 2-35), representing a more than 65% efficiency improvement compared with the case with Au contacting the PbS layer directly. The hole transport was though enhanced through the shallow gap states in the MoO_x layer.

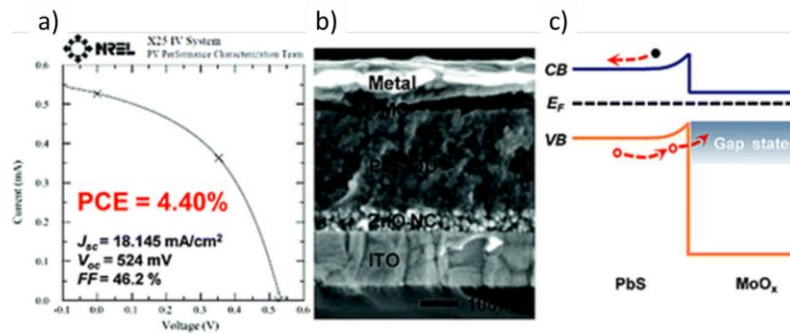


Figure 2-35 MoO_x as the hole transport layer in heterojunction solar cells: a) the I-V curve; b) SEM; c) the band diagram. (a-c) are obtained from reference.⁹⁰

Another research also showed that the insertion of MoO_x removed the reverse-bias Schottky diode present at the CQD-metal interface.⁹¹ As shown in Figure 2-36 a, with the increasing of the MoO_3 thickness, the single junction simulation for dark current fits the experimental results better and better, which indicates the removal of the reverse-bias Schottky diode because of the deep work function of MoO_3 . In Figure 2-36 b, the increase on the forward-bias dark currents on three electrodes after the insertion of the MoO_3 layer also proved this conclusion.

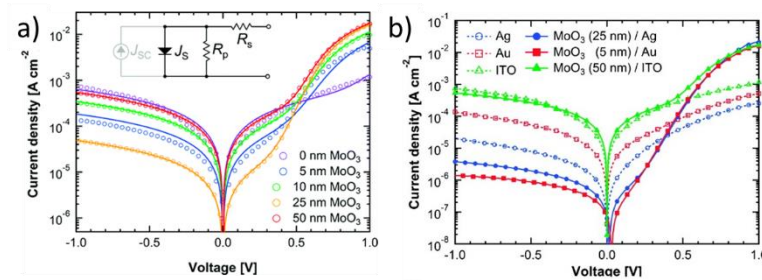


Figure 2-36 (a) Experimental and simulated dark currents for heterojunction solar cell devices with different thickness of MoO_3 as the hole transport layer. (b) dark current comparison before and after the insertion of MoO_3 on three electrodes. (a-b) are obtained from reference.⁹¹

Electron collection work has been mainly focusing on n-type semiconductors such as TiO_2 or ZnO . Changing the conduction band offsets between p-type CQDs and TiO_2 acceptor by doping TiO_2 with Zr or Sb would result in optimised carrier extraction.⁹³ ZnO conduction band position, as well as band gap values, can also be tuned by doping it with Mg.⁹⁴

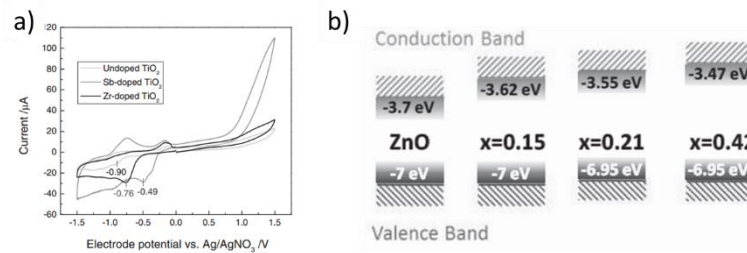


Figure 2-37 the tuning of TiO_2 (a) or ZnO (b) conduction band position by doping. (a-b) are obtained from reference.⁹⁴

Passivation of ZnO is also thought an effective way to tune its band alignment with PbS layers. Chloride passivation is reported to passivate the oxygen vacancy well,⁹⁵ improving the better alignment between the ZnO and PbS layers.

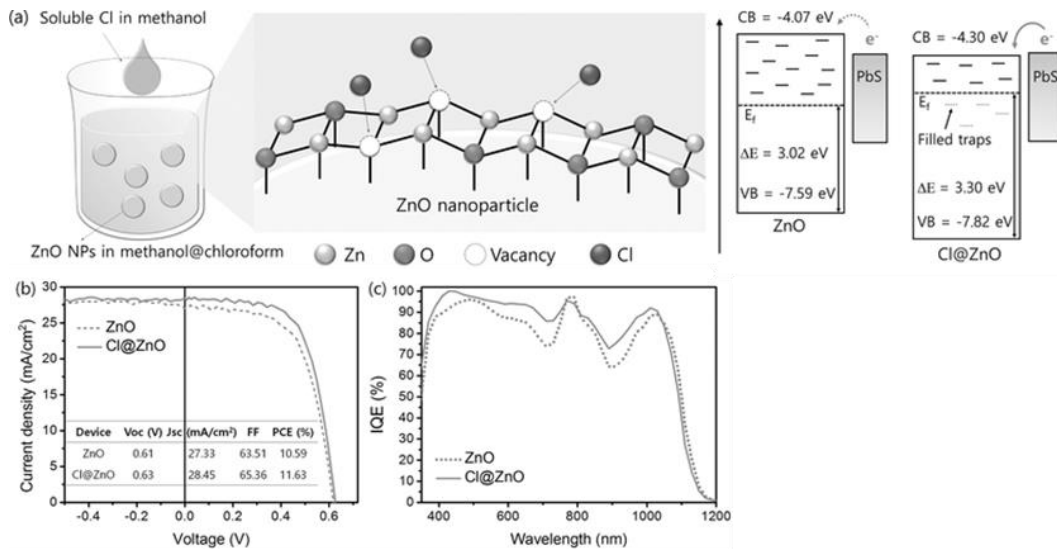


Figure 2-38 chloride passivation of ZnO improving band alignment at PbS/ZnO interfaces: a) schematic and the energy diagram; b) the I-V curves; and c) the IQE curves. Graphs adapted from reference.⁹⁵

Regarding the interface between metal oxide and semiconductor, recombination here is also a crucial problem. Several strategies have been used to overcome it. For example, insertion of a thin ZnO buffer layer between CQDs and TiO_2 results in almost

a 2-fold reduction of the interface recombination rate (Figure 2-39 a-b).⁹⁶ PCBM was also used as the buffer layer and electron transport layer at the same interface, which has resulted in an efficiency of 8.9% (Figure 2-39 c).⁹⁷ Doping ZnO with NH_3 also benefit reducing the recombination rates at the metal-oxide-semiconductor interface.³³

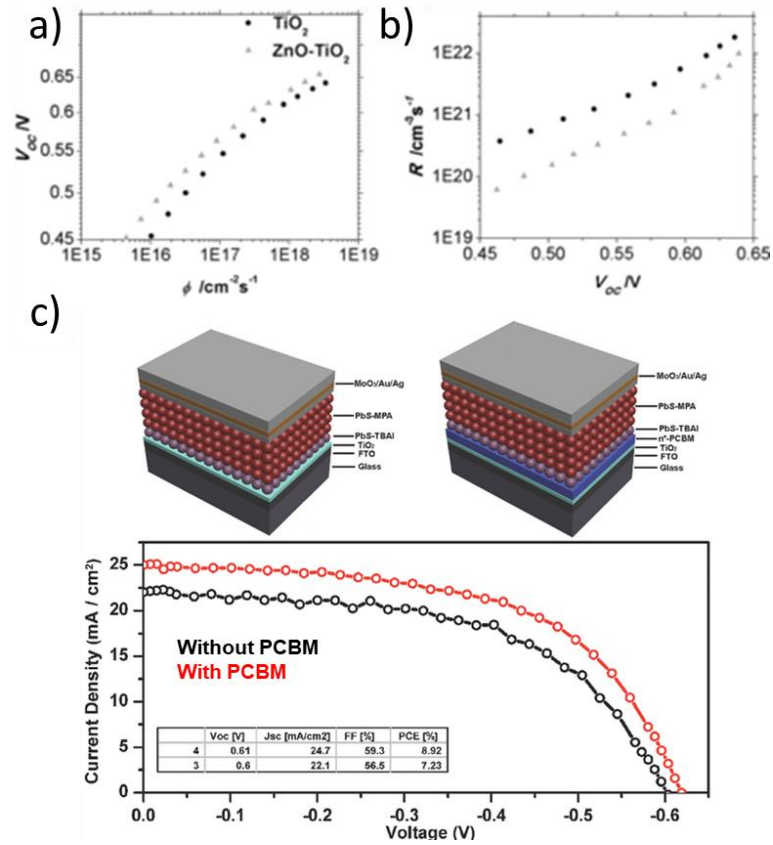


Figure 2-39 Insertion of buffer layer ZnO (a, b) and PCBM (c) to reduce recombination rates and enhance I-V performances. (a) the V_{oc} and (b) the recombination rate comparison with and without ZnO buffer layers on TiO_2 . (c) the architectures and I-V curves of devices with and without PCBM buffer layers. (a-b) are from reference⁹⁶, and (c) is from reference⁹⁷.

Methods working on the electron-accepting electrode can also be used to enhance the depletion width in CQD films. A highly doped, shallow work function electrode would increase the free carrier concentration in n-type electrode via charge injection doping. This makes the low-temperature TiO_2 application to be possible without sacrificing the performance.⁹⁸ The following work with shallow work function FTO

provides an efficiency of 8.5%.⁹⁹ Research on graphene electrode was also conducted.¹⁰⁰

2.4 Characterisation of CQDs' Optoelectronic Properties

Characterisation of CQDs and devices is really important to help us understand the physics and further find improvement pathways. Some conventional methods to characterise properties of CQDs and devices consist of UV-visible absorption, I-V test, external quantum efficiency (EQE), internal quantum efficiency (IQE), electron microscopy (EM), X-ray diffraction (XRD), and X-ray photoemission spectroscopy (XPS). However, some unusual and significant optoelectronic properties, such as band edge positions, carrier mobility, carrier lifetime, diffusion length, and doping density, could not be determined by these conventional approaches. Therefore, cutting-edge methods have been developed to probe these properties.

2.4.1 Band edge energy

Band engineering is a significant way to improve the performance of solar cells. Thus the precise measurement of band edge energy of CQD thin films, such as conduction band edge positions (E_c), valence band edge positions (E_v), as well as Fermi level (E_f), is necessary for scientists to design a graded band structure and appropriate band bending at p-n interfaces as well as metal-semiconductor interfaces.

Fermi level, or work function, dominated the property of semiconductors in solar cells, such as the quasi-Fermi level differences determining the open-circuit voltage of a solar cell, Fermi level differences at the metal-semiconductor interfaces defining the band bending is upwards or downwards. It can be measured by Kelvin Probe, ultraviolet photoemission spectroscopy (UPS)^{43, 44, 49, 53}, or valence band X-ray photoemission spectroscopy (VB-XPS)¹⁰¹. Kelvin probe tests the relative work function between the probe and the thin film. With the calibration by Au and Al, the work function of the thin film can be determined.

UPS (Figure 2-40), or VB-XPS (Figure 2-41) analyses the kinetic energy of the photoemission electrons under ultraviolet or X-ray with a certain energy to determine the Fermi level. Besides, they can also be used to test the valence band edge (HOMO). From the lowest spectrum edge (Figure 2-40 left), the value of Fermi level can be determined according to the certain beam energy. From the highest spectrum edge (Figure 2-40 right), HOMO can be determined. The analysis for the HOMO level in VB-XPS is similar (Figure 2-41).

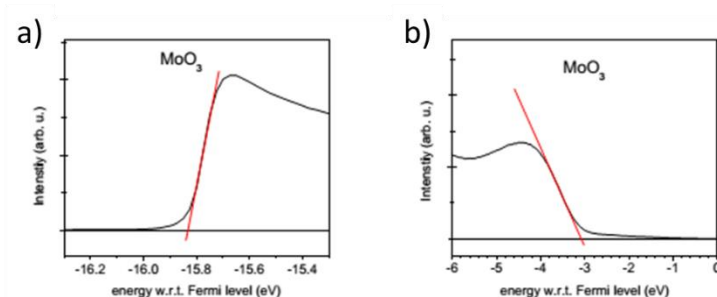


Figure 2-40 UPS analysing MoO₃'s Fermi level (a) and HOMO (b). (a-b) are adapted from reference.⁵³

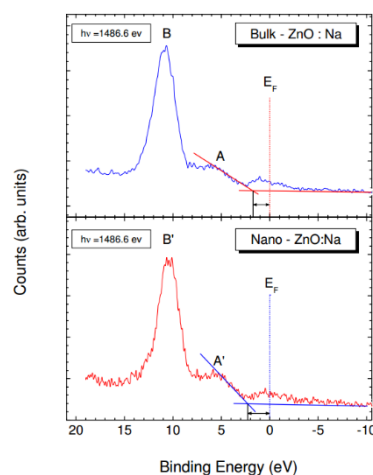


Figure 2-41 VB-XPS analysing ZnO's Fermi level and HOMO. Obtained from reference.¹⁰¹

Other methods for example cyclic voltammetry^{48, 93} are helpful to test LUMO positions (the conduction band edge or the electron affinity). CQDs were modified in the three-electrode system: CQDs films coated on Pt or glassy carbon electrode as the working electrode, Pt wire as the counter electrode, and a standard reference electrode. All measurement is usually conducted in 0.1 M Bu₄NClO₄ in acetonitrile. The working

electrode will be linearly swiped under different potentials referred to the reference electrode, such as Ag/AgCl in standard NaCl which is thought 4.7 eV below the vacuum level.⁴⁸ The first reduction peak below 0 V (about -1.15 V in Figure 2-42) is thought the behavior of LUMO. Thus, the energy level of LUMO can be calculated ($E_c = -4.7 \text{ eV} - E_{\text{peak}}$). Additionally, with the help of bandgap analysis by UV-visible absorption, HOMO or the valence band edge can then be also determined.

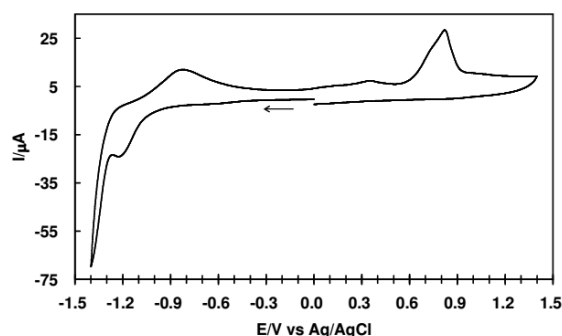


Figure 2-42 PbS/Oleic acid (3 nm) QDs cyclic voltammetry curves in 0.1 M Bu₄NClO₄ in acetonitrile at 100mV/s: $E_{\text{peak}} = -1.2 \text{ V}$. $E_c = -4.7 \text{ eV} + 1.2 \text{ eV} = -3.5 \text{ eV}$. Obtained from reference.⁴⁸

2.4.2 Carrier mobility

Carrier mobility was defined as the carrier drift velocity under the unit electrical field.^{102, 103} It is a crucial parameter determining the recombination rates of solar cells, which has always been a drawback of quantum dot solar cells compared to other types of photovoltaic technology such as perovskite solar cells, silicon-based solar cells, because of the large transport barriers between different QDs.

Carrier mobility can be tested through carrier extraction by linearly increasing voltages (CELIV),¹⁰⁴ time of flight (TOF),^{104, 105} J_{sc} transient decay,¹⁰⁶ and field effect transistor (FET)¹⁰⁷ methods on CQD thin films or devices. CELIV and TOF measurements have the similar setups. The setup schematic is what Figure 2-43 shows.¹⁰² The only difference between these two methods is that CELIV needs a voltage pulse, while TOF requires a laser pulse. Both ways can be used to test hole or electron mobility, which only depends on the electrical field.

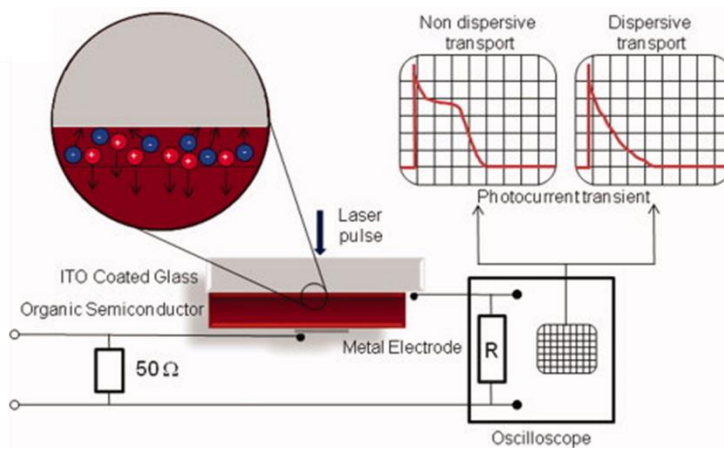


Figure 2-43 The setup schematic for carrier mobility measurement by TOF. Obtained from reference.¹⁰²

CELIV. Figure 2-44 a shows a typical CELIV transient curve.¹⁰⁴ The carrier mobility was determined by the time required for the current to reach a maximum value, as the following equation shows.

$$\mu_h = \frac{2d^2}{3At_{\max}^2 (1 + 0.36 \frac{\Delta j}{j_d})} \quad ,2-3$$

where μ_h is the hole mobility, d is the film thickness, A is the slope of the voltage increasing pulse, j_d is the displacement current, and Δj is the maximum drift current.

ToF. ToF measurement is based on semiconductor films. The transient current curve is what Figure 2-44 b shows.¹⁰⁴ A short-time light pulse will produce photogenerated carriers within a very thin layer from the transparent electrode. Under a certain electrical field, the carrier (holes or electrons) will be drifted towards the other electrode. The transient current would be monitored. The transient time is determined by the cross position of the two lines. If the light pulse is too strong, there will be obvious disperse transport resulting in non-linear curves. To make sure the precision of this measurement, TOF was only used on thick films usually exceeding 1000 nm, particularly in high-mobility films.

$$t_{tr}^{-1} = \mu_e d^{-2} V \quad ,2-4$$

Where μ_e is the electron mobility, d is the device thickness, t_{tr} is the transient time, and V is the bias applied.

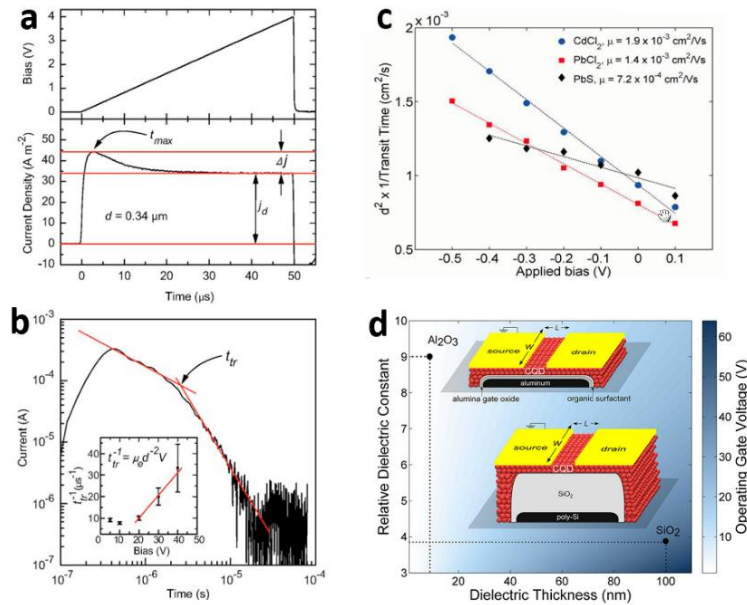


Figure 2-44 CELIV (a), and TOF (b) for PbS CQDs capped with EDT. The inset in (b) shows the bias dependence of the transit time. J_{sc} transient decay curves (c), and FET diagrams (d). (a-b) are adapted from reference¹⁰⁴, (c) is from reference¹⁰⁶, and (d) is from reference¹⁰⁷.

J_{sc} transient decay. J_{sc} transient decay can also be used to measure the minority carrier's mobility.¹⁰⁶ This measurement is based on devices. The time for photocurrent to decay to 1/e of its maximum value was recorded over a range of applied biases. The carrier mobility was extracted from the slope of the curve of the square of the film thickness divided by the transient time as a function of the bias (Figure 2-44 c). As can be seen in Figure 2-44, PbS treated with CdCl₂ or PbCl₂ has obviously higher electron mobility than pure PbS CQDs.

J_{sc} dependence of the light intensity. Space charge can also reflect the mobility difference of electrons and holes.¹⁰⁸ Due that one type of the carriers' mobility is much lower compared to the other, the slower carrier will accumulate at the extraction electrode interface region, resulting in the build-up of space charges. The current

through this region will be limited under high carrier generation intensities (or higher light intensities).¹⁰⁹

This measurement is based on devices as well. The short circuit current (J_{sc}) dependence of the incident light intensity was researched to see if there is space charge on the device.

$$J_{sc} \propto I^\alpha, \text{ 2-5}$$

If J_{sc} changed linearly with the incident light intensity, it demonstrated that the electron and hole transport was balanced inside the devices.^{87, 110} Deviation of α from 1 means the formation of the space charge region.^{72, 110}

Field effect transistor. Field effect transistor is a device which uses one electric field applied on the gate electrode to control the source-drain current under certain bias, transferring patterns of signal fluctuation from a small input signal to a more significant output signal. Figure 2-44 d shows the basic FET architecture. The voltage on the gate electrode has the effect of controlling the ease with which current can move between the source electrode and the drain electrode. According to the following equation, the carrier mobility can be then calculated.

$$\mu_e = \frac{1}{C_i V_d} \times \frac{L}{W} \times \frac{\delta I}{\delta V_g}, \text{ 2-6}$$

where I is the source-drain current, V_g is the current applied on the gate electrode, V_d is the voltage applied between the source electrode and the drain electrode, C_i is the capacitance of the device, L is the channel length, and W is the channel width.

In Figure 2-44 d, Al/Al_2O_3 was employed as a gate dielectric to replace the commonly used Si/SiO_2 . The high permittivity of Al_2O_3 allows the use of a very thin gate film and much lower gate voltage, which effectively reduces the effect of charges in the gate.¹⁰⁷ However, the FET measurement gives an upper bound to the carrier mobility, considering that deep traps are filled during the FET scanning process.⁹

2.4.3 Carrier lifetime and diffusion length

Open circuit voltage decay^{22,28} and photoluminescence decay^{20, 111} can be used to test the carrier lifetime. Open circuit voltage decay is a relatively common way to check minority carrier lifetime.^{104, 112} A solar cell's open circuit will be monitored under a light pulse. The open circuit will decay linearly within a very short period right after the light is off (Figure 2-45), due that the behaviour at this stage is the result of the internal recombination of photocarriers.¹¹² The slope is inversely proportioned to the minority carrier lifetime like the following equation shows.

$$\frac{dV}{dt} = \frac{kt}{q\tau}, \quad 2-7$$

where V is the voltage output of the device, τ is the carrier lifetime, k is the temperature, t is the time initiating when the light is off, q is the elemental charge. Thus, the carrier lifetime can be determined.

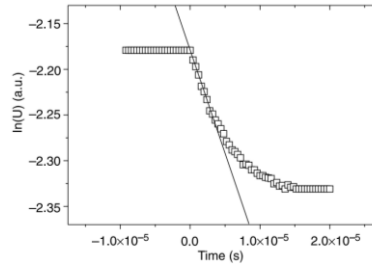


Figure 2-45 Open circuit voltage decay for crystalline solar cell(measured decay time $\tau=40 \mu\text{s}$). Obtained from reference.¹¹²

The diffusion length can be then estimated based on carrier mobility and carrier lifetime according to Einstein's relation.¹¹¹

$$L_D = \sqrt{D \cdot \tau} = \sqrt{\frac{\mu k_B T}{q} \cdot \tau}, \quad 2-8$$

where D is the diffusion coefficient, τ is the lifetime, k_B is Boltzmann constant, and μ is the mobility.

2.4.4 Doping density

Doping density determines the Fermi level position of material, which is a critical parameter for solar cells' open circuit voltage. It can be determined by the capacitance-

voltage study.⁵⁷ The linear regions in Figure 2-46 a-c correspond to the changes of the depletion width with the bias across the devices. The doping density is calculated according to Mott-Schottky analysis over this range and is shown in Figure 2-46 d-f respectively. As can be seen, MPA-PbS showed a higher doping density than 3MBA-PbS, and the device treated with 3MBA and MPA together showed a graded doping structure.

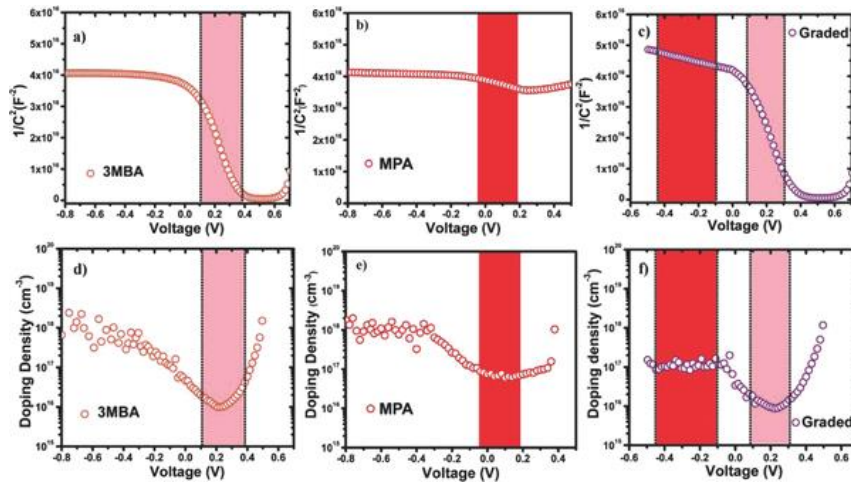


Figure 2-46 Capacitance-voltage studies about 3MBA-PbS (a, d), MPA-PbS (b, e), and 3MBA/MPA-PbS (c, f). The red ranges represent the linear change of $1/C^2$ in (a-c) and the plateau in (d-f), which is due to the change of depletion width. Graphs obtained from reference.⁵⁷

2.4.5 Trap states

The trap sites in the band gap can be estimated by the absorption or photoluminescence spectra. A sharp peak indicates less band tailing or fewer trap sites.

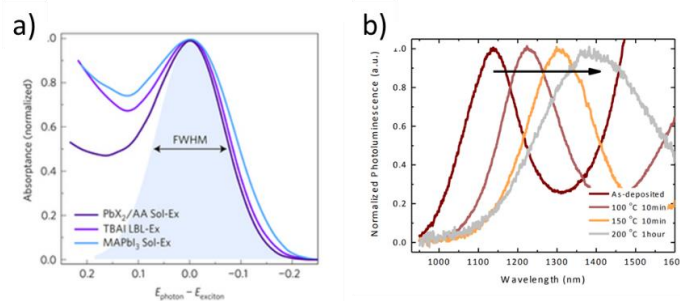


Figure 2-47 the full width of half maximum of the absorption (a) and PL (b) to establish the trap states in the band gap. (a-b) are obtained from reference.⁶⁸

2.5 Conclusions

To overcome the drawback in CQD solar cell technology such as high amount of surface defects, low carrier diffusion length, and the existence of the trap states in the band gap, quantum dot optimisation, device architecture improvement, and band engineering are three main approaches.

Dramatic enhancement has been achieved due to advanced passivation method providing high-quality QDs, solution process simplifying the fabrication, band engineering research optimising the overall band structure of the devices, and cutting-edge physical and chemical characterisation methods helping understand the underneath mechanism. Reducing trap energy sites on QDs' surfaces, engineering band structure throughout the devices, and building multiple junction devices are all potential ways to harvest CQD solar cells' performances further. Based on advanced characterisation methods, further understanding of carrier generation, transport, separation, recombination, and extraction will also be crucial and beneficial for enhancing photovoltaic performance further.

The current photovoltaic technique is not good enough to compete with fossil fuels in a free market. The current CQD solar cell is not the best photovoltaic technology as well. Other types of photovoltaic research, such as perovskite solar cells, organic solar cell etc. can provide many useful experiences for CQD solar cells. Hybrid solar cells, such as CQD and organic hybrid solar cell, may utilise organic materials' unique band structure to help build better band engineering. CQD and perovskite hybrid solar cell may benefit from the high mobility of perovskite materials and the stability of CQDs. The combination between CQD and thin film Si may result in highly efficient tandem solar cells, as CQD can absorb the infrared well. Different kinds of photovoltaic devices all have pros and cons. If we can take advantages of the merits of varying type solar cells, it will be possible to help humans find a better way to utilise solar energy.

Chapter 3 Experimental methods

The experiment methods introduced in this chapter mainly cover the common experiments used in all the work of this thesis, such as CQD synthesis, planar device fabrication, optoelectronic characterisations, and materials property characterisations. Parts of them were conducted by my group colleagues. For example, Kelvin probe results were measured by Mr Yujiro Tazawa. TEM images were taken by Mr Daniel Gregory. PL data was acquired by me with the help of Miss Zhanet Zaharieva. Besides, XPS data were obtained by Dr Phil Holdway from Oxford Materials Characterisation Service. Cyclic voltammetry experiments and analysis were conducted by Dr Xiuting Li from the Physical and Theoretical Chemistry Laboratory, Department of Chemistry. All the other experiments in this chapter unless specified were all conducted and analysed by myself.

3.1 Synthesis of CQDs

3.1.1 Hot injection synthesis of PbS CQDs

Oleic-acid-capped PbS CQDs were synthesised by the hot injection method with Schlenk line techniques following the literature with minor modifications.^{10, 20} 1.40 eV PbS was synthesised as shown in Figure 3-1. Lead oxide (0.46 g), 1-octadecene (10 g), and oleic acid (OA, 1.45 g) were mixed first (Figure 1-1 left). After degassing at 105°C for 2 hours, no clear bubbles should be seen, and a clear solution was obtained. The temperature of the lead precursor mixture was then lowered down to 80°C under degassing for another 30 min. Separately, hexamethyldisilathiane (210 µL) was dissolved in pre-degassed 1-octadecene (5 g) at 80°C as the sulphur precursor (Figure 1-1 right), which was then injected rapidly into the lead precursor solution (Figure 1-1 left) under vacuum. After 1 min reaction, the flask was cooled down in a water bath to room temperature. PbS CQDs were then precipitated by acetone via centrifugation. Next, a methanol/hexane mixture was used to wash the QDs twice, followed by vacuum drying

for overnight. The PbS CQDs were finally dispersed in octane (50 mg mL^{-1}) for device fabrication. Different band gap PbS CQDs were synthesised in the same way by varying the injection temperature or the amount of oleic acid.¹¹³

The molar ratio used for Pb, S, and OAH was about 2:1:5, with excess Pb and OAH. The 1-octadecene for $(\text{TMSi})_2\text{S}$ was also pre-degassed to make sure that no water impurity was involved in the injection. The temperature of $(\text{TMSi})_2\text{S}$ solution was also controlled the same as the lead precursor, for the purpose that the overall temperature is not changed randomly after the injection. The injection was done under vacuum conditions to ensure it is rapid enough for an immediate uniform nucleation process. The nucleation was terminated, different from literature by a drop of temperature, by a reduction of concentration. The growth process was kept for 1 min upon injection, which was then quenched into a water bath. The quenching process will result in a rapid cooling down of the whole flask, thus the growth differences will be minimised, and a good monodispersity was achieved.

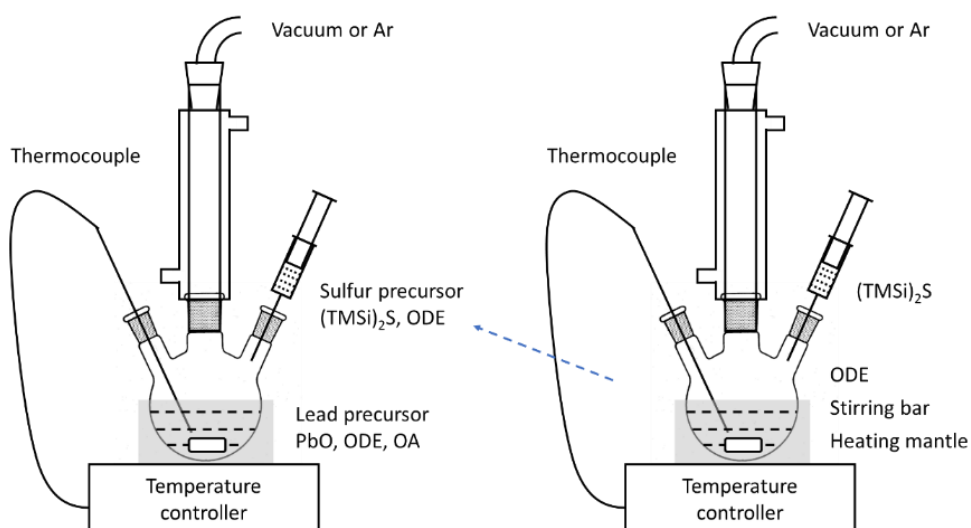


Figure 3-1 Illustration of the PbS CQD synthesis via the hot injection method

3.1.2 Synthesis of ZnO nanoparticles

The synthesis of ZnO nanoparticles was adapted from the literature.^{14, 15} Zinc acetate dihydrate (2.95 g) was dissolved in methanol (125 mL) by stirring at 60°C . Potassium hydroxide (1.50 g) dissolved in 65 mL methanol was added dropwise to the

zinc acetate dihydrate solution, which was then kept stirring at 60 °C for 2.5 h. The diagram is shown in Figure 3-2. After the solution was cooled down naturally to room temperature, it was then washed by using dispersion and centrifuge induced precipitation with methanol for three times. Finally, the ZnO nanoparticles were dispersed in a chloroform-methanol (1:1) mixture at about 40 mg mL⁻¹.

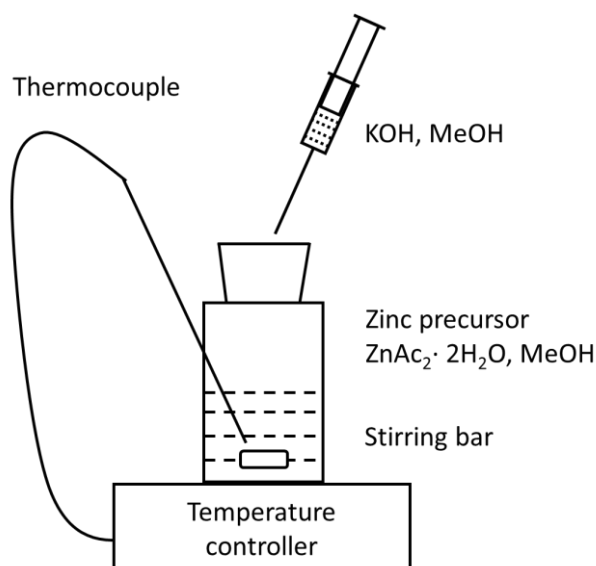


Figure 3-2 Illustration for the synthesis of ZnO nanoparticles

3.2 Device fabrication

3.2.1 Transparent electrode patterning and cleaning

The substrates for solar cell fabrications, usually ITO coated glass, were pre-patterned first before cleaning as shown in Figure 3-3. A tape of 2-2.5 mm in width was pasted in the middle of thoroughly covered ITO/glass before it was submerged into an acid solution with HCl: H₂O: HNO₃ as 25: 25: 2 at 60 °C. After 5 mins of etching, the substrates were removed and rinsed with deionised water for three times to remove all the acid before peeling off the tape. A cotton bud was then used with isopropanol to clean any glue left on the surface. The parameters of the pre-patterned ITO are shown in Figure 3-3 as well.

The pre-patterned ITO coated glass substrates were then cleaned by sonication sequentially in Decon-90, deionised water, acetone, and isopropanol at 55 °C for 10 min.

After the substrates were thoroughly dry, it was followed by an oxygen plasma treatment for 3 min or a UV ozone treatment for 15 min. The substrates were then used for device fabrication right after the cleaning.

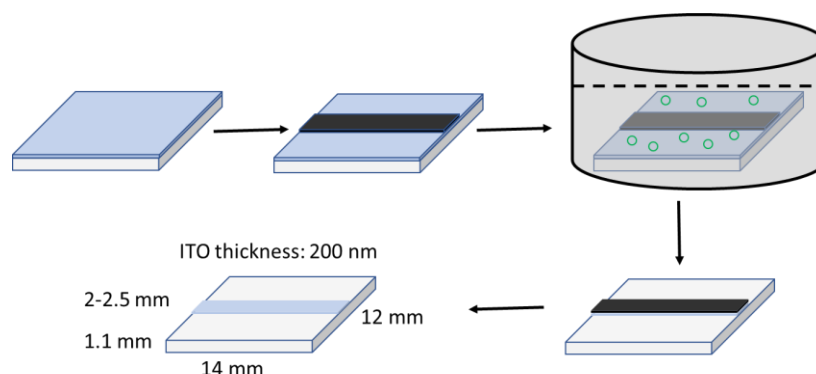


Figure 3-3 Schematic of ITO patterning process

3.2.2 ZnO and PbS coating by spin coating

In an inverted solar cell (structures shown in Figure 3-5), the substrates were coated with ZnO solution first (40 mg/mL) by spin coating at 2000 rpm for 30 s, which were then annealed on a hot plate in the air at 100 °C for 10 mins to remove all the solution residue. After the ZnO film was cooled to room temperature, PbS CQD ink (50 mg/mL) was spin-coated on top of it layer-by-layer with the solid-state ligand exchange. 15 mg/mL TBAI-methanol solution was coated on the PbS film for 1 min, which was subsequently washed away by five drop methanol. The spinning speed for PbS coating is 2000-3000 rpm, while the rate used for drying and rinsing is 6000 rpm. This PbS coating process was repeated 6-10 times until the desired thickness was reached. Another two layers of PbS-EDT were coated subsequently as the hole transport layers. Two drops of 2% EDT-acetonitrile solution was dropped on the PbS film while it was spinning, followed by five drop acetonitrile for rinsing. After this, the films were ready for metal electrode evaporation.

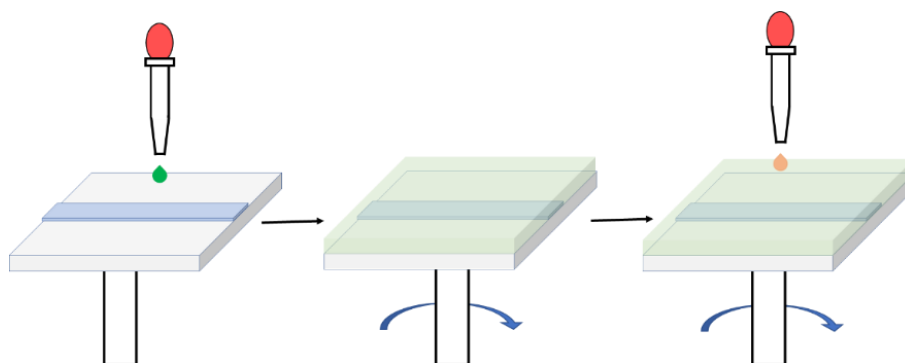


Figure 3-4 Schematic for solar cell fabrication by spin coating

3.2.3 Metal thermal evaporation

The films were placed into a shadow mask for Au evaporation with defining electrode width at 1 mm. The systems were vacuumed for 2 h or overnight until 10^{-5} torr before starting evaporation. A deposition rate of 0.1 nm/s was conducted for Au until a thickness of 100 nm was reached.

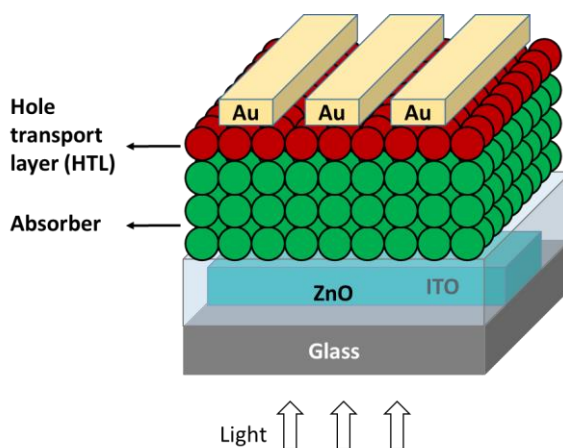


Figure 3-5 Schematic of a typical structure for an inversed heterojunction PbS solar cell

3.3 Characterisations of CQDs

3.3.1 TEM and XPS

Transmission electron microscope (TEM) images were taken on JEOL 2100 LaB6 with an accelerating voltage of 200 kV by my group colleague Mr Daniel Gregory. A copper grid with carbon films covered by graphene oxide was dipped into a diluted

PbS CQD octane solution, then dried naturally for use. The sample preparation and data analysis were done by me.

X-ray photoelectron spectroscopy test was carried out on Thermo Scientific™ K-alpha™ compact XPS by Dr Phil Holdway from Oxford Materials Characterisation Service (OMCS). PbS films were built upon glass by drop casting or spin coating. 284.5 eV C1s peak was used for calibration. Because of the overlapping between S 2p peaks and background peaks, S 2s peak was analysed for better accuracy. The sample preparation and data analysis were done by me.

3.3.2 UV-vis, PL, FTIR, and reflection

UV-vis spectroscopy was performed by using a Cary Varian 4000 UV-vis-NIR spectrophotometer. A zero/baseline mode was used to calibrate the background. Quartz cuvettes were used for liquid samples, and glass substrates or ITO/glass substrates were used for thin films. The first excitonic peak positions of PbS samples were used to calculate the optical band gap.

Photoluminescence was tested on an Agilent Cary Eclipse Fluorescence Spectrophotometer by me with the help of my group colleague Miss Zhanet Zaharieva. An excitation wavelength of 600 nm was used for PbS samples, and an excitation wavelength of 350 nm was used for ZnO samples. Quartz cuvettes were used for liquid samples, and glass substrates or ITO/glass substrates were used for thin films. The sample preparation and data analysis were done by me.

FTIR spectroscopy was carried out by using a Varian Excalibur Series FSE 3500 spectrometer. A background scan was done in the air before each test. Glass substrates or ITO/glass substrates were used for thin films.

The reflectance test was conducted with an integrating sphere with a detection range from 178 nm to 1248 nm. Reflectance measurements were taken by backing the device stacks with a mirror and measuring the total reflectance using an Ocean Optics ISP-REF Integrating Sphere coupled to an LR1 spectrometer.¹¹⁴ Reflectance was then

compared to a NIST-calibrated diffusive reflectance standard (WS-1, Ocean Optics). Transmission of light was considered as minimal at the wavelengths tested.

3.3.3 Kelvin probe and cyclic voltammetry

Fermi level positions were measured by using a KP Technology Scanning Kelvin Probe System 2001 by my group colleague Mr Yujiro Tazawa. For each sample, 25 measurements were taken at three arbitrarily chosen points. The instrument was calibrated by using aluminium (4.1 eV) and gold (5.1 eV) thin films. The sample preparation and data analysis were done by me.

The conduction band edge positions of different PbS QD films were determined by cyclic voltammetry, which was conducted in a double Faraday cage with an Autolab potentiostat (Metrohm-Autolab BV, Netherlands) using a three-electrode system (Figure 3-6 a) at 298 K. The experiments and analysis were conducted by Dr Xiuting Li from the Physical and Theoretical Chemistry Laboratory, Department of Chemistry.

PbS CQD films spin-coated on ITO were used as the working electrodes, with Ag/AgCl in saturated KCl as the reference electrode and a platinum foil as the counter electrode. All the measurements are carried out in acetonitrile (99.9%, Sigma Aldrich) with 0.1M Bu₄NClO₄ (Fluka) as the supporting electrolyte. Before the measurements, the solution was purged with an N₂ flow for 5 min to remove O₂, and an atmosphere of N₂ was maintained during the whole experiment. Scanning range is from -2.0 V to 1.4 V at a scan rate of 100 mV s⁻¹. The applied potential starts from 0.0 V and follows a negative-going direction at first. The conduction band edge energy is calculated by the first reduction peak position (the inset in Figure 3-6 b), based on that the energy level for Ag/AgCl in saturated KCl electrode is -4.7 eV vs vacuum.⁴⁸ Valence band edge positions were then derived based on the conduction band edge and the optical band gaps from UV-vis.

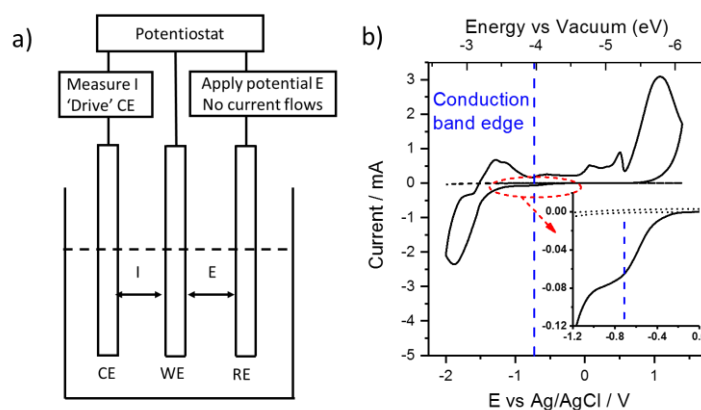


Figure 3-6 a) schematic of a three-electrode system. b) cyclic voltammetry determining the conduction band edge energy of a PbS sample. Solid: PbS on ITO/glass. Dash: bare ITO/glass.

3.4 Characterisations of optoelectronic properties

3.4.1 I-V and EQE

All the planar solar cell devices, unless specified, were loaded into a sealed testing chamber with N_2 continually purged through testing. I-V curves were measured by using a Keithley 2400 Source Meter. An AM 1.5 solar spectrum illumination was produced by a Newport solar simulator (model 67005) with an AM 1.5 filter, or an ABET Sunlite solar simulator (model 11002). The old Newport solar simulator was used in Chapter 5, and the new ABET one was used in all the other chapters. The power density of the light source was calibrated with a calibrated Si reference cell from ABET Technologies (model 15151). To avoid overestimation of the performance due to edge effects, a mask (1.28 mm^2) slightly smaller than the actual overlapping area of the cathode and the anode ($2\sim 2.5 \text{ mm}^2$) was used when conducting the I-V curve tests.

EQE was performed with an Oriel 1/8 m monochromator coupled to a quartz tungsten halogen lamp (used in Chapter 5) or a Cemax Xenon lamp (used in other chapters). 410 nm, 600 nm, and 1000 nm filters were used to remove the second order grating effects. Calibrated photodiodes from Newport (818-UV and 918-IR) were employed to measure the photon flux of the beam. The beam was chopped at a

frequency of 220 Hz by a Bentham 218 chopper controller, and a Xenon lamp was simultaneously shone on the devices to provide the white light bias. Solar cells were placed under constant N_2 flow and connected to a Bentham 227 pre-amplifier, a Bentham 225 lock-in amplifier (used in Chapter 4) or a Stanford Research 530 lock-in amplifier (used in other chapters), and a Keithley 6485 picoammeter.

3.4.2 Capacitance-Voltage measurements

Capacitance-voltage measurements were usually used to determine the semiconductor films' carrier concentration, built-in voltage, and diffusion length in the devices. As a simple description of the process, the device is stimulated with a small amplitude, single-frequency voltage by an LCR meter, and the phase shift and amplitude of the resulting current are recorded to calculate the impedance of the devices. The details were introduced in Figure 3-7.¹¹⁵ An AC voltage was supplied out of the high current terminal (HCUR), while the current through the solar cell is recorded by the low current terminal (LCUR). The voltage of the solar cell is measured by the high and low potential terminals (HPOT and LPOT). The voltage and current are recorded in a phase-locked manner that accurately measures the phase angle between them. Based on the known amplitude and phase angle, the desired AC impedance parameter can be obtained.

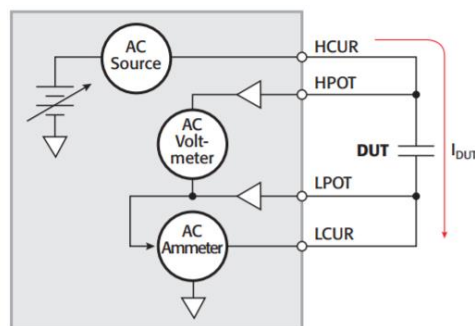


Figure 3-7 a schematic of an LCR meter. Obtained from reference.¹¹⁵

In this thesis, the C-V data was taken by an Agilent E4980A option 001 Precision LCR Meter. An amplitude of 20 mV was used for all the measurements in this thesis. A

scan between -1 V and 1 V with a step size of 20 mV was conducted on the devices in the dark.

Instead of directly reading the capacitance from the Agilent machines, the real and imaginary impedance are recorded ($Z = R + iX$, where Z is the impedance, R is the real component, and X is the imaginary component). This is because the machine will automatically adapt circuits which are not the actual cases for the solar cell devices, leading to inaccurate capacitance. For precise measurements, a commonly used circuit for a solar cell is assumed as shown in Figure 3-8.

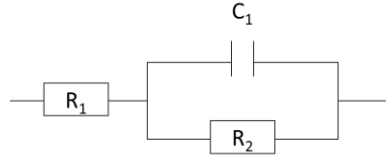


Figure 3-8 the most common circuit assumption for a solar cell

The impedance of a solar cell is thus given by

$$z(f) = R_1 + \frac{1}{\frac{1}{R_2} + i2\pi f C_1} = R + iX, \quad 3-1$$

where f is the frequency of the perturbation signal, C_1 is the capacitance, and R_1 and R_2 are the series and shunt resistance respectively.

A high-frequency test at 2 MHz was carried out first to obtain the series resistance R_1 under different bias, as the parallel part contributes so less to the overall resistance that the real impedance is almost equal to R_1 . A low-frequency test at around 100-1000 Hz was then followed to obtain the R and X , which were used in the following equations to calculate C_1 :

$$\frac{1}{\frac{1}{R_2} + i2\pi f C_1} = R - R_1 + iX, \quad 3-2$$

$$\frac{R - R_1 - iX}{(R - R_1)^2 + X^2} = \frac{1}{R_2} + i2\pi f C_1, \quad 3-3$$

$$C_1 = \frac{-X}{2\pi f((R - R_1)^2 + X^2)}, \quad 3-4$$

Mott-Schottky analysis. The Mott-Schottky analysis in solar cells describes the relationship between the reciprocal of the square of the capacitance ($1/C^2$) and the bias (V) applied to solar cells. In heterojunction devices, a full depletion approximation was

used. It assumes that the depletion region is fully depleted and the transition between the depleted and the quasi-neutral region is abrupt so that the electron and hole intensity is zero.

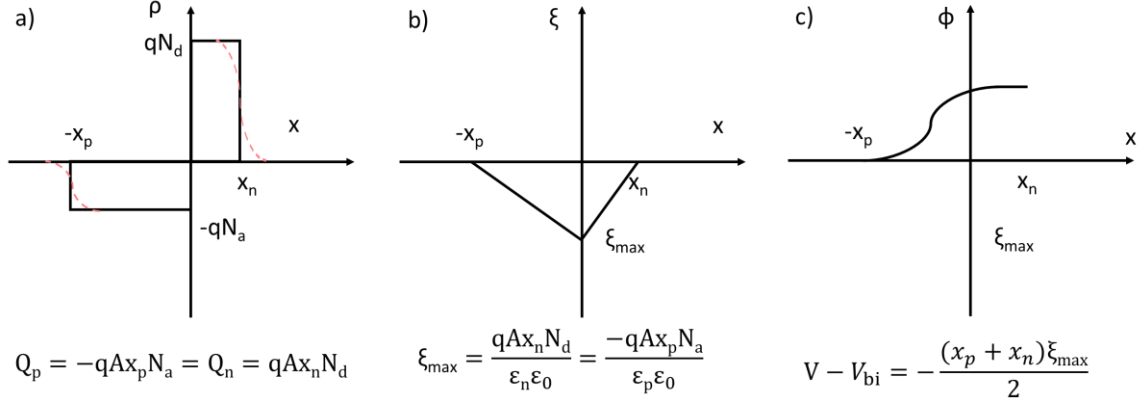


Figure 3-9 (a) Charge density ρ in a heterojunction, (b) Electric field ξ , and (c) Potential ϕ diagram: x is the distance to the p-n interface forwards n-type layers, x_p and x_n are the depletion width in p- and n-type layers, q is the electron charge, Q_p and Q_n are the charges, ϵ_p and ϵ_n are the permittivities, N_a and N_d are the carrier concentrations, A is the area, V is the applied bias, V_{bi} is the built-in voltage. Figures redrawn from references.¹¹⁶

Thus, according to Figure 3-9 a,

$$x_n \times N_d = x_p \times N_a, \quad 3-5$$

It also assumes that the quasi-neutral region has no charge so that the applied bias all falls into the depletion region. Thus, according to Figure 3-9 b-c,

$$V - V_{bi} = \frac{qAx_n^2N_d}{2\epsilon_n\epsilon_0} + \frac{qAx_p^2N_a}{2\epsilon_p\epsilon_0}, \quad 3-6$$

Combining Equation 3-5 and 3-6, one can obtain:

$$x_p = \sqrt{\frac{2\epsilon_p\epsilon_n\epsilon_0(V_{bi}-V)}{q(N_a\epsilon_p+N_d\epsilon_n)} \frac{N_d}{N_a}}, \quad 3-7$$

$$x_n = \sqrt{\frac{2\epsilon_p\epsilon_n\epsilon_0(V_{bi}-V)}{q(N_a\epsilon_p+N_d\epsilon_n)} \frac{N_a}{N_d}}, \quad 3-8$$

Thus,

$$C = \left| \frac{dQ(V)}{dV} \right| = qAN_a \frac{d(x_p)}{dV} = \sqrt{\frac{A^2q\epsilon_0}{2(V_{bi}-V)\left(\frac{1}{N_a\epsilon_p} + \frac{1}{N_d\epsilon_n}\right)}}, \quad 3-9$$

In the case of PbS/ZnO heterojunction, V_{bi} is the built-in voltage, N_a and N_d are the carrier concentration of PbS and ZnO, and ϵ_p and ϵ_n are the permittivities of PbS and ZnO. Therefore, the Mott-Schottky plot can be obtained according to 3-9:

$$\frac{1}{C^2} = \frac{2(V_{bi} - V)}{A^2 q \epsilon_0} \left(\frac{1}{N_a \epsilon_p} + \frac{1}{N_d \epsilon_n} \right), \quad 3-10$$

The carrier concentration of PbS, N_a , can be addressed with the assumption that the carrier concentration of ZnO, N_d , is $1E+17 \text{ cm}^{-3}$. The depletion width in the PbS layer (w_p or x_p) is calculated according to the following equation

$$w_p = \sqrt{\frac{2\epsilon_p \epsilon_n \epsilon_0 (V_{bi} - V) N_d}{q(N_a \epsilon_p + N_d \epsilon_n) N_a}}. \quad 3-11$$

3.4.3 V_{oc} decay

Open circuit voltage decay was used to determine the carrier lifetime, which has been covered in the previous chapter. A white light LED pulse was applied to the devices, and the V_{oc} decay process was recorded on an oscilloscope.¹¹⁷ The intensity of the LED was set to make sure that the device showed an open circuit voltage the same as under AM 1.5.

3.4.4 J_{sc} dependence on light intensity

The short circuit current (J_{sc}) dependence of the incident light intensity was investigated to test whether there is space charge in the device, which has been covered by in the previous chapter. Two ways are commonly used to vary the light intensity from the solar simulator: inserting different intensity filters and modifying the distance between the light sources and the devices. The former one was used in the case of the Newport solar simulator, while the latter one was used in the case of the ABET solar simulator.

Chapter 4 Narrow band gap PbS HTLs improving carrier extraction

ABSTRACT. In this chapter, the band structures of colloidal quantum dot (CQD) bilayer heterojunction solar cells are optimised by using a combination of ligand modification and QD band gap control. Solar cells with power conversion efficiencies of up to $9.33 \pm 0.50\%$ are demonstrated by aligning the absorber and hole transport layers (HTL). Key to achieving high efficiencies is optimising the relative position of both the valence band and Fermi energy at the CQD bilayer interface. By comparing different band-gap CQDs with various ligands, we find that a smaller band gap CQD HTL in combination with a more p-type-inducing CQD ligand can enhance hole extraction and hence device performance. We postulate that the efficiency improvements observed are mainly due to the synergistic effects of narrower band-gap QDs causing an upshift of valence band position due to 1, 2-ethanedithiol (EDT) ligands and a lowering of the Fermi level due to oxidation.

The Kelvin probe tests were done by Mr Yujiro Tazawa. Cyclic voltammetry experiments were conducted and analysed by Dr Xiuting Li. FIB-SEM images were taken by Prof. Andrew Watt. All the other experiments and data analysis were done by me.

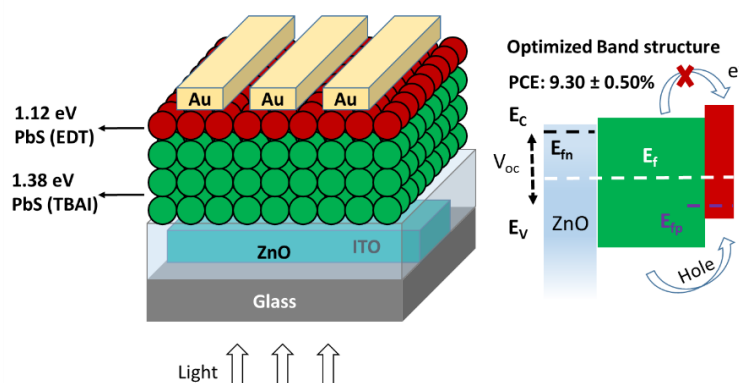


Figure 4-1 table of contents for narrow bandgap PbS HTLs. The optimised PbS CQD solar cell architecture used in this work and its band structure.

4.1 Introduction

Solar cells based on lead sulphide colloidal quantum dots as the absorber have the potential to provide cheap, flexible, and highly efficient photovoltaic devices.^{43, 118} Lead and sulphur are both abundant, low-cost materials that can be synthesised into nanocrystal colloids which absorb across the solar spectrum.^{24, 25} These colloids can be solution-processed into thin films with controlled semiconductor properties suitable for optoelectronic devices. The power conversion efficiencies (PCE) of PbS solar cells have increased from less than 1% to 11.3%.^{4, 32, 118}

To be a viable solar energy technology, improvements in fill factor (FF) and open circuit voltage (V_{oc}) are still required. Recent device improvements have focused on carrier mobility and recombination using a variety of treatments including solid or liquid state ligand exchange,³⁷⁻⁴⁰ surface passivation,^{20, 41, 42} and band alignment engineering^{43-47, 119}.

This project focuses on controlling the coupling between QDs using a combination of QD band gap and surface chemistry to create an optimised band. Kramer et al.⁴⁷ reported a quantum funnel CQD solar cell using large band gap PbS as a blocking layer at the rear contact with PCE of 2.7%. In this design, there was proper conduction band alignment but poor valence band alignment as the large band gap PbS gave rise to a deeper valence band position.⁴⁸ In this work, a thin PbS layer with a smaller band gap is inserted between the PbS absorber and the gold cathode to act as a hole transport layer using a combination of different band gaps and ligand treatments to optimise the band alignment as shown in Figure 4-1. This work optimises both absorber and HTL layers devices to improve PCE.

4.2 Experiments

4.2.1 PbS CQD synthesis of different band gaps

The PbS CQD synthesis is introduced in the experimental chapter above. Different band gaps of PbS CQDs are achieved by changing the injection temperature of the $(\text{TMSi})_2\text{S}$ solution. Figure 4-2 shows how the band gap changes with different injection temperature. It is found that higher injection temperature resulted in the larger size of CQDs and smaller band gaps.

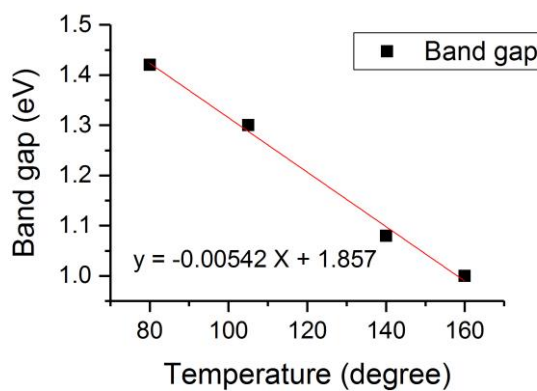


Figure 4-2 the relation between the injection temperature and CQDs' band gap in PbS synthesis

4.2.2 Device fabrications for optimised devices

A structure of glass/ITO/ZnO/PbS-TBAI/PbS-EDT/Au is used in this project as shown in Figure 4-3 a. The fabrication by spin coating is the same as introduced in the experimental method chapter. The thickness of each TBAI and EDT layer is 29 nm and 35 nm respectively as determined by using cross-sectional FIB-SEM images in Figure 4-3 b-c. The combination of band gaps from absorber table (1.52 eV, 1.37 eV, and 1.30 eV) and HTL table (1.38 eV, 1.20 eV, 1.12 eV, and 1.00 eV) was conducted to optimise the device band structure.

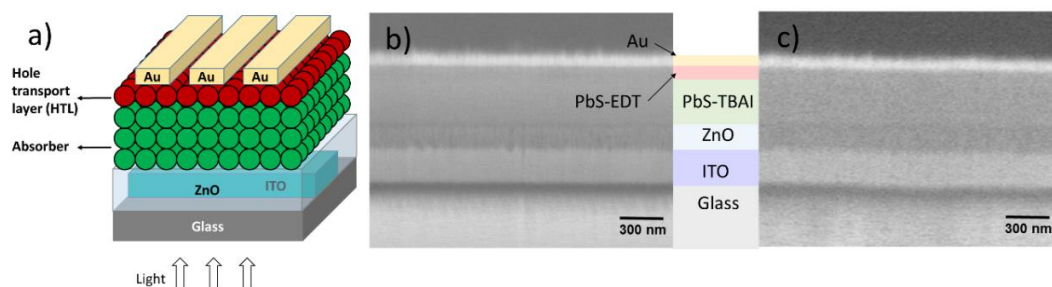


Figure 4-3 a) The architecture of colloidal quantum dot solar cells used in this work. b) Cross-sectional SEM images of the optimised device. c) Cross-sectional SEM images of the reference device. The thickness of each layer is 210 nm for ITO, 150 nm for ZnO, 290 nm for PbS-TBAI, 70 nm for PbS-EDT, and 50 nm for Au. FIB-SEM images were taken by Prof. Andrew Watt.

4.3 Bandgap optimisation for both absorber and HTLs

A series of devices were first fabricated to optimise the absorbers' band gap using 1.52 eV, 1.37 eV, and 1.30 eV CQDs modified by TBAI as absorbers respectively, with 1.20 eV CQDs modified by EDT as hole transport layers. The results are shown in Table 4-1, among which the 1.37eV/1.20eV (absorbers/HTL) CQD device demonstrated the best device performance.

Table 4-1 Absorber band gap optimisation: devices presented with mean and standard deviation. The error bars are based on statistics.

Absorber/HTL Band gap	$J_{sc}(\text{mA cm}^{-2})$	$V_{oc}(\text{V})$	FF	Efficiency
1.52 eV/1.20 eV	21.73±1.51	0.58±0.004	0.51±0.02	6.47±0.54%
1.37 eV/1.20 eV	24.65±3.09	0.60±0.008	0.60±0.05	8.97±0.56%
1.30 eV/1.20 eV	26.97±0.38	0.49±0.004	0.56±0.02	7.58±0.41%

With the optimum absorber band gap around 1.37 eV, the EDT-modified HTL's band gap was next optimised. Devices with absorber/HTL combinations of 1.38eV/1.38eV, 1.37eV/1.20eV, 1.38eV/1.12eV, and 1.38eV/1.00eV were fabricated and compared, as Table 4-2 shows. With the HTL band gap decreasing, the PCE peaked at 1.12 eV with the highest efficiency of 9.33±0.50%.

Table 4-2 HTL band gap optimisation: devices presented with mean and standard deviation. The error bars are based on statistics.

Absorber/HTL Band gap	$J_{sc}(\text{mA cm}^{-2})$	$V_{oc}(\text{V})$	FF	Efficiency
1.38 eV/1.38 eV	31.68±4.51	0.59±0.008	0.48±0.06	8.86±0.26%
1.37 eV/1.20 eV	24.65±3.09	0.60±0.008	0.60±0.05	8.97±0.56%
1.38 eV/1.12 eV	25.30±2.11	0.59±0.007	0.63±0.02	9.33±0.50%
1.38 eV/1.00 eV	21.49±0.47	0.53±0.010	0.53±0.01	6.03±0.40%

To understand why the optimised 1.38eV/1.12eV device achieved the highest PCE, its optoelectronic properties are now compared to a reference device with an absorber/HTL combination of 1.38eV/1.38eV. Figure 4-4 a) compares the current–voltage (I–V) curves of optimised and reference devices. The mean PCE is 9.33% with standard deviation of 0.50% for the optimised devices while the reference’s mean PCE is 8.86% with standard deviation of 0.26%. With prolonged exposure to an air atmosphere, the performance of both the optimised and reference devices became stable after the first ten days. As previously reported,⁴³ the TBAI/EDT device structure is air stable. After three months of storage in the air and the dark, the PCE (Figure 4-4 c) did not show any noticeable decrease. Besides PCE, the open circuit voltage (Figure 4-4 e) and fill factor (Figure 4-4 b) are also higher in the optimised device than that of the reference. However, the short circuit current (J_{sc} , Figure 4-4 d) in the optimised device is lower.

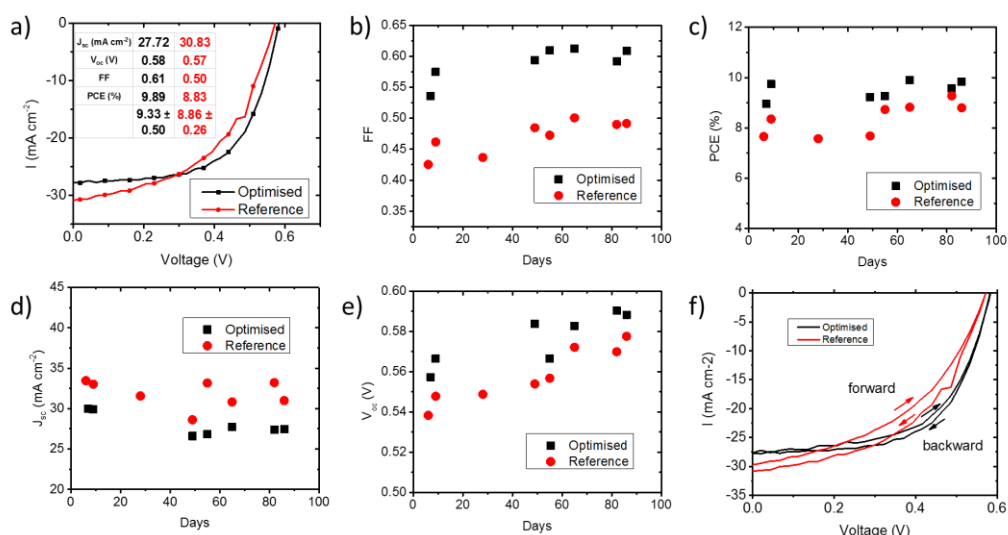


Figure 4-4 Optimised and reference devices' photovoltaic performances: I-V curves (a), variations of fill factor (b), PCE (c), J_{sc} (d), and V_{oc} (e) over 80 days, and the hysteresis (f).

4.4 Band position characterisation

We hypothesise that the higher V_{oc} , FF, and PCE observed are related to the different band structures which result from various QDs' size and ligand modification for the absorber and HTL with TBAI and EDT respectively. To prove this a combination of UV-vis, Kelvin probe and cyclic voltammetry is used.

The effect of different QD sizes and ligands on band gaps was determined by using UV-visible absorption spectroscopy as shown in Figure 4-5. The starting OA-capped QDs have bandgaps of 1.38 eV and 1.12 eV respectively. In Figure 4-5 a-c, TBAI ligand exchange led to a redshift of the excitonic peak, while EDT led to a blue shift. This is due that replacing OA with shorter ligands like TBAI, the inter-particle distance was reduced, so as the quantum confinement effect. The band gap decreased from 1.38 eV to 1.33 eV for the TBAI ligand exchange. However, different from air stable PbS-TBAI which is inert to oxidation⁴³, PbS-EDT, which can be easily oxidised, had its band gap increased. PbS-EDT showed larger band gaps (1.42 eV and 1.16 eV) compared to the diluted solution ones with OA ligands (1.38 eV and 1.12 eV).

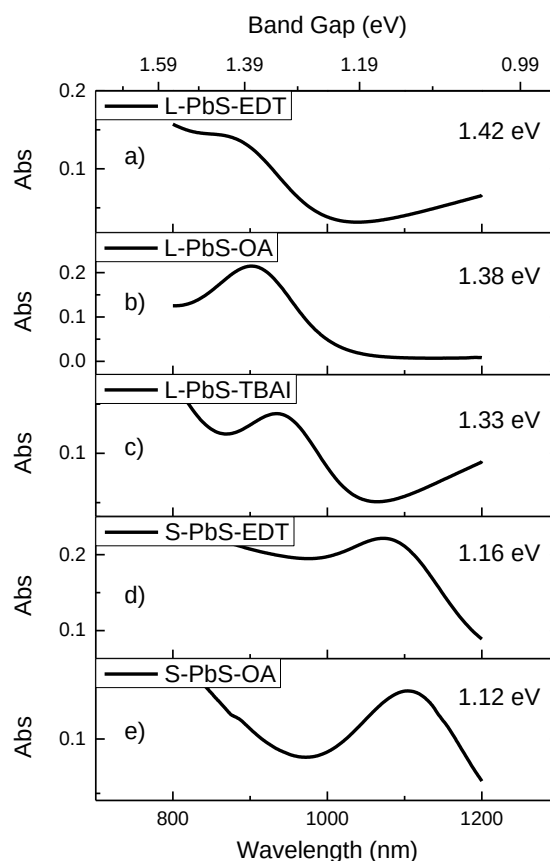


Figure 4-5 UV-visible absorption comparison for different ligand capped PbS based on large (1.38eV) and small (1.12) band gap PbS-OA respectively. TBAI and EDT curves were tested on solid samples of ITO coated glasses with the blank of the same, and OA curves were tested on solution samples in quartz cuvettes with the blank of the same: a) Large-band-gap-PbS-EDT; b) Large-band-gap-PbS-OA; c) Large-band-gap-PbS-TBAI; d) Small-band-gap-PbS-EDT; and e) Small-band-gap-PbS-OA.

The conduction band edge of PbS CQDs is determined by cyclic voltammetry, and the valence band edge energy is then calculated based on the band gaps. For each PbS QD in Figure 4-6, the CV scans exhibit a cathodic peak in the potential range of -0.3 ~ 1.3 V which is used to determine the conduction band edge energy by assuming that the energy level of Ag/AgCl in saturated KCl is 4.7 eV below the vacuum level.⁴⁸ A subsequent sharp current increase starting around -1.3 V was observed and assigned to the direct reduction of the lead ions (Pb^{2+}) to form Pb. For more precise measurement, the first reduction peak position for each PbS QD was determined after subtraction of

the background current assuming an exponential fit for the latter, as shown in Figure 4-7 a-e. The peak potential for each PbS QDs is shown in Table 4-3.

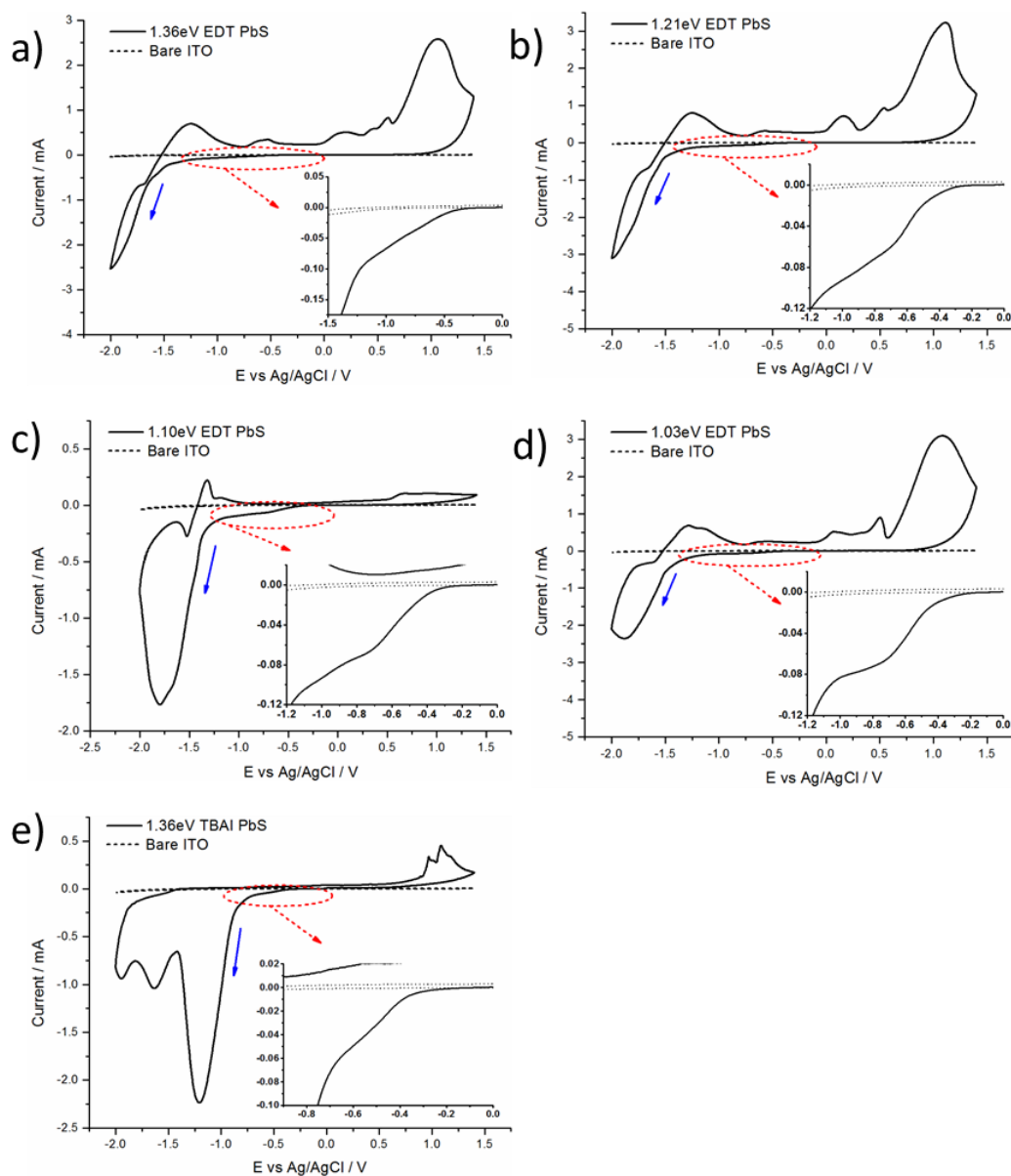


Figure 4-6 Cyclic voltammetry results of different PbS films including: a) 1.36eV-EDT, b) 1.21eV-EDT, c) 1.10eV-EDT, d) 1.03eV-EDT, and e) 1.36eV-TBAI. Cyclic voltammetry experiments were conducted by Dr Xiuting Li.

A further comparison for all PbS QDs is presented in Figure 4-7 f) after normalisation of the background subtracted curves. It was found that the peak potential shown in CV shifts more negatively with increasing the bandgap of the PbS QDs with the same ligand, which is consistent with the previous work.^{48, 120} For the PbS QDs with the equal bandgap but different ligands, 1.36 eV PbS-EDT and 1.36 eV PbS-TBAI, a

clear energy level shift was indicated by the observation of a peak shift of the potential from the -0.94V of 1.36 eV PbS-EDT to -0.55 V of 1.36 eV PbS- TBAI, which matches with the optical results⁴⁴.

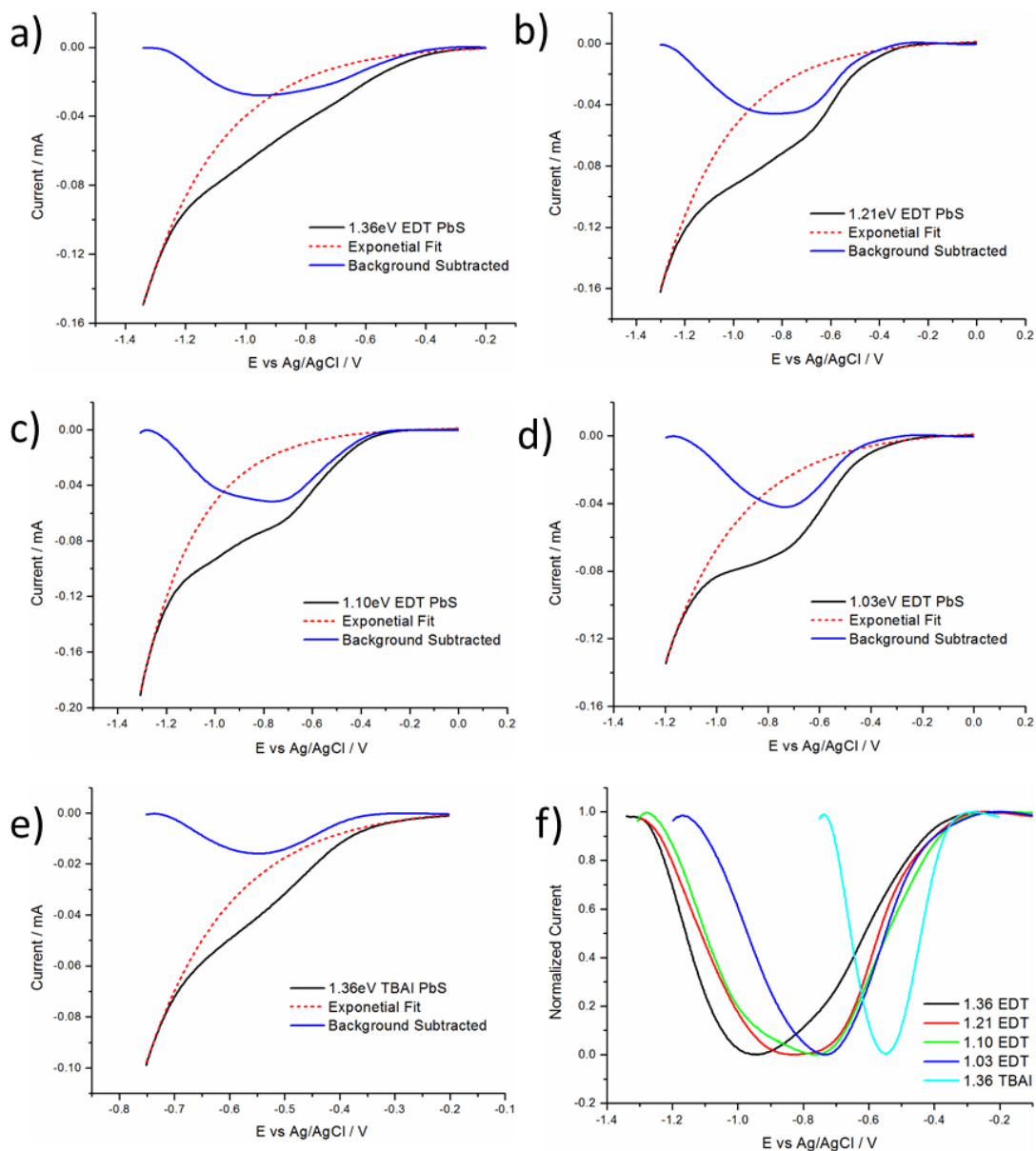


Figure 4-7 the first reduction peak determination of different PbS films including: a) 1.36eV-EDT, b) 1.21eV-EDT, c) 1.10eV-EDT, d) 1.03eV-EDT, e) 1.36eV-TBAI, and f) the first reduction peak comparison of different films. Cyclic voltammetry results were analysed by Dr Xiuting Li.

Table 4-3 Peak potentials and band energy levels from CV of PbS QDs. The error bars are based on statistics.

PbS QD films	E_p/V vs Ag/AgCl	E_c/eV	E_v/eV	STD/V or eV
1.36eV-EDT	-0.94	-3.76	-5.12	0.02
1.21eV-EDT	-0.83	-3.87	-5.08	0.03
1.10eV-EDT	-0.76	-3.94	-5.04	0.02
1.03eV-EDT	-0.73	-3.97	-5.00	0.01
1.36eV-TBAI	-0.55	-4.15	-5.51	0.01

Figure 4-8 a showed the position of conduction and valence bands for the different sized PbS with various ligands. Comparing the 1.36eV-TBAI PbS and 1.36eV-EDT PbS, it is clear that EDT modification raises the band gap position relative to the vacuum. As observed by Chuang et al.⁴³, this blocks the flow of electrons and enhances the hole extraction at the cathode. By decreasing the HTL PbS band-gap the conduction band becomes deeper and the valence band shallower, thus further strengthening the hole extracting properties of the EDT layer.

Fermi level position measured by Kelvin probe is presented in Figure 4-8 c-d and Table 4-4. It is clear that the 1.38 eV-EDT thin film has a deeper Fermi level (-4.84 eV) than 1.38eV-TBAI (-4.79 eV) layer. This indicates more p-type behaviour relative to the valence band position. When a smaller band gap 1.12 eV EDT layer is used, the Fermi level is further lowered to -4.87 eV indicating even more p-type layer considering that its valence band position changes to be shallower as shown in Figure 4-8 a.

When the absorber and HTL layers are combined as shown in Figure 4-8 d, the combined layers' Fermi level lies between the original isolated TBAI layers' and EDT layers' Fermi levels because of the Fermi level equilibrium between these two layers, as can be seen in Figure 4-8 d and Table 4-4. Thus, the optimised layers have a deeper Fermi level and also a more p-type character than the reference layers. As open circuit voltage is significantly influenced by the quasi-Fermi level differences between the ZnO

and PbS layers, the deeper Fermi level in the PbS layers leads to larger V_{oc} which is consistent with Figure 4-4 e.⁹¹

Combining the Fermi level and band edge structures analysis, the full device band structures can be seen in Figure 4-8 b. When comparing the 1.38eV-EDT and 1.12eV-EDT HTL layers, the latter showed better valence band offset and deeper Fermi level without losing the advantages of blocking electrons, therefore resulting in better HTLs here.

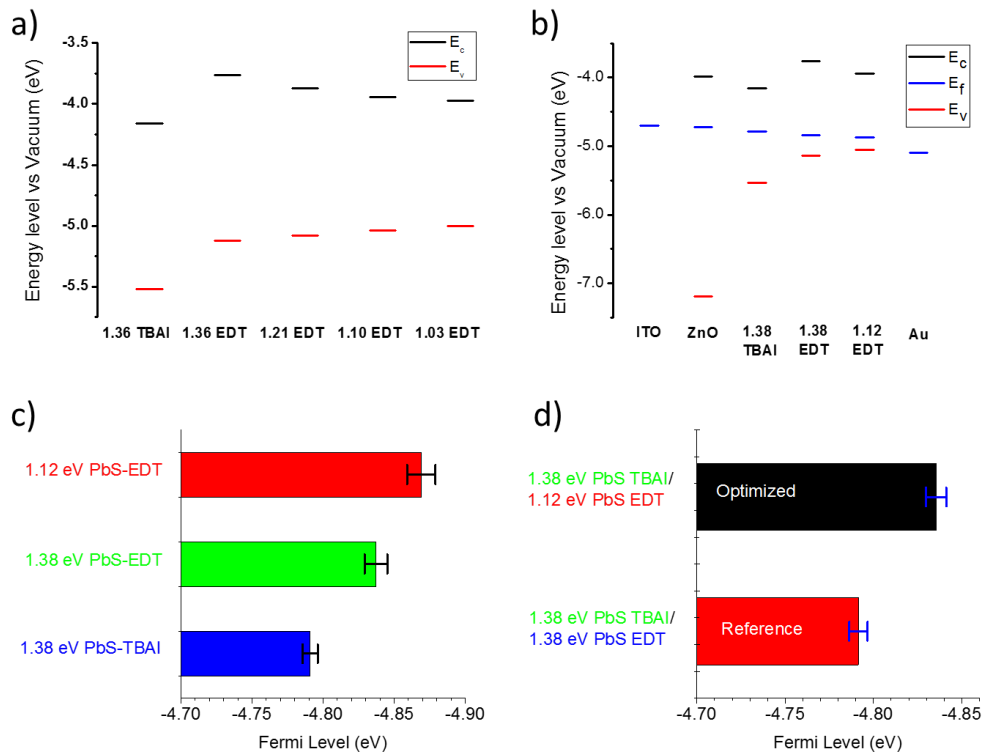


Figure 4-8 Band structures from cyclic voltammetry and Fermi level measurements using Kelvin probe on different films: a) band structures of different PbS films, b) isolated materials' band structures in the reference and optimised devices, c) Fermi levels of six-layer PbS films with only one ligand (TBAI: 174 nm, and EDT: 210 nm), and d) Fermi levels of 8 layer PbS films (244 nm) consisting of 6 TBAI layer (174 nm) and 2 EDT layer (70 nm). Kelvin probe tests were conducted by Mr Yujiro Tazawa. The error bars are based on statistics.

Table 4-4 the Fermi level results from Kelvin Probe tests: mean and standard deviation.

Kelvin probe tests were conducted by Mr Yujiro Tazawa. The error bars are based on statistics.

Films	Mean (eV)	STD (eV)
1.12eV PbS-EDT	-4.8691	0.009997
1.38eV PbS-EDT	-4.8372	0.007951
1.38eV PbS-TBAI	-4.7909	0.005278
1.38eV PbS-TBAI/1.12 eV PbS-EDT	-4.8355	0.005785
1.38eV PbS-TBAI/1.38eV PbS-EDT	-4.7915	0.005151

There is a trade-off between gaining valence band alignment advantages and losing conduction band alignment advantages as shown in Figure 4-8 a. Therefore, careful selection of band gap and Fermi level combination is required to optimise devices. Compared to the 1.37eV/1.20eV device, V_{oc} for the case of a smaller absorber band gap (1.30eV/1.20eV) is lower due to a small quasi Fermi level difference of PbS and ZnO layers (Figure 4-9 b-c). Comparing 1.52eV/1.20eV with 1.37eV/1.20eV, the V_{oc} is comparable, but FF and J_{sc} are reduced because of the poor conduction band alignment (Figure 4-9 a-b), leading to increased recombination (and hence slightly depressing V_{oc} too). Therefore, during the optimisation of absorbers' bandgap, the combination of 1.37eV/1.20eV reached a good balance of valence band and conduction band alignment. The diagrams of further optimisation on HTL layers were shown in Figure 4-10, and the best device 1.38eV/1.12eV was demonstrated.

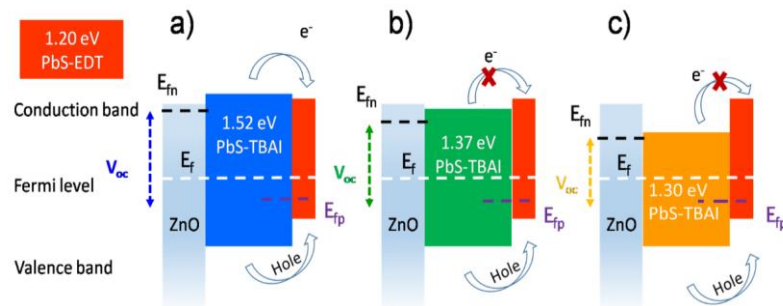


Figure 4-9 Band diagram of devices for absorbers' band gap optimisation: a) 1.52 eV/1.20 eV, b) 1.37 eV/1.20 eV, and c) 1.30 eV/1.20 eV.

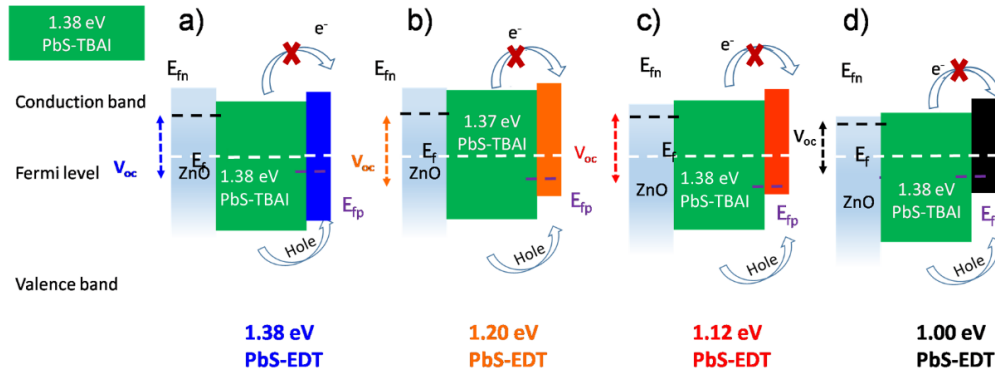


Figure 4-10 Band diagram of devices for HTL band gap optimisation: a) 1.38 eV/1.38 eV, b) 1.37 eV/1.20 eV, c) 1.38 eV/1.12 eV, and d) 1.38 eV/1.00 eV.

4.5 Optoelectronic characterisation

This better band alignment in the optimised device can also be implied by its longer carrier lifetime in open circuit voltage decay measurements. Under different light density, the optimised device's carrier lifetime is always longer than in the counterpart reference devices as shown in Figure 5 a. Under air mass (AM) 1.5, the optimised device's carrier lifetime is 4.6 μs , while that of the reference device is just 2.8 μs . The better band alignment structure lowers the barrier for carrier transport and hence reduces the probability of carrier recombination.

Furthermore, the incident light intensity dependence of short circuit current was studied to check the carrier extraction balance between holes and electrons (Figure 5 b).

$$J_{sc} \propto I^\alpha, \quad 4-1$$

If J_{sc} is observed to change linearly with incident light intensity, it indicates that the electron and hole extractions are balanced.^{87, 110} Deviation of α from 1 implies the formation of the space charge region.^{72, 110} For the optimised device and reference device, both α values are near 0.90, indicating that there is a small, but similar, space charge limiting effect in both cases. This quality similarity makes the electrical property comparison more meaningful.

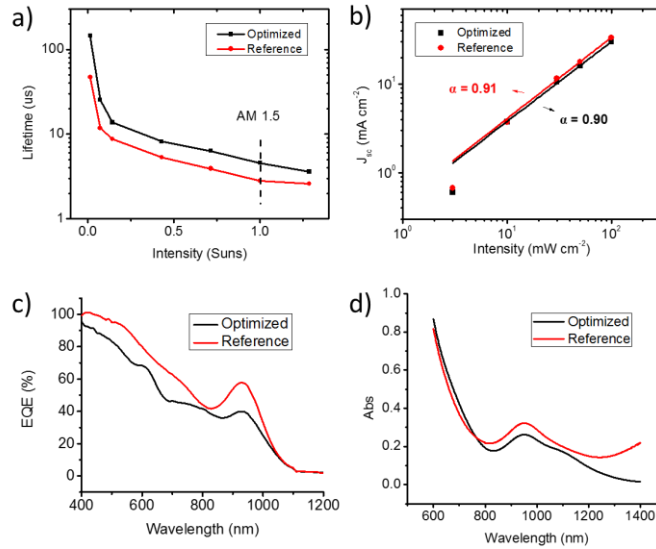


Figure 4-11 Optimised and reference devices' electrical performance comparison: a) carrier lifetime, b) light density dependence of J_{sc} , c) EQE, and d) UV-vis light absorption.

To investigate whether there is more light absorption contributing to the PCE enhancement, external quantum efficiency (EQE) and UV-visible absorption (UV-vis) measurements were conducted. In Figure 5c, it can be seen that the reference showed higher EQE than the optimised device, and the peaks in the same positions are found in both. The integrated J_{sc} from EQE (22.4 mA cm^{-2} for optimised devices; 26.3 mA cm^{-2} for reference devices) is slightly lower than that derived from I-V curves (25.3 mA cm^{-2} for optimised devices; 31.7 mA cm^{-2} for reference devices in Table 2). UV-vis curves also showed less absorption on the optimised device than reference. A small peak around 1100 nm corresponding to the small bandgap PbS was found in the optimised device's curve (Figure 5 d), but this contributes so little that it cannot be seen on EQE. When increasing EDT layer thickness, the PCE becomes lower (Figure 4-12), which is due to the high carrier recombination rates of the thick EDT layers. Although the band gap distribution in the optimised device is more aligned with the light absorption distribution across the solar cell, it seems the absorption depth for the infrared is beyond the active layer thickness. This further indicates that it is the optimal band alignment mainly responsible for the performance enhancement, rather than any additional absorption by smaller bandgap layers.

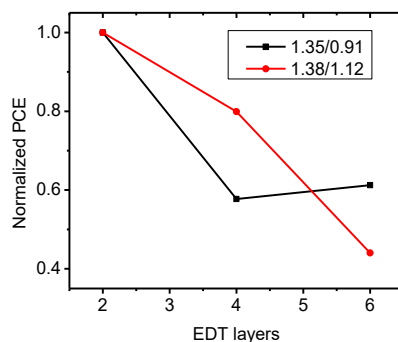


Figure 4-12 The influence of EDT layer thickness on optimised devices' performance in different QD combinations: PCE normalised to the value of 2-layer EDT.

4.6 Conclusion

The band gaps of Absorber and HTL layers of CQD solar cells have been optimised. It was found that a small band gap HTL layer with a more p-type-inducing ligand (EDT) resulted in the best devices (1.38eV/1.12eV) with the efficiency of $9.33 \pm 0.50\%$. The reason for higher efficiencies is mainly improved band alignment at the interface between the absorber and HTL, which results from an upshift of valence band position due to narrow bandgap CQDs and EDT ligands, and a lowering of the Fermi level due to oxidation. Improvements by further optimisation of bandgap combinations, layer thickness control, and ligand selection are expected to optimise the device further so that it has a more balanced hole and electron transport, as well as better light absorption which will be introduced in Chapter 5.

Chapter 5 DMF Free Passivation of PbS Quantum Dot Solar Cells Using CsI to Mitigate Surface Oxides

Abstract Lead sulphide (PbS) colloidal quantum dot photovoltaics (CQD PVs) is a promising technology to provide low-cost, flexible, and highly efficient solar cells. One main obstacle limiting their efficiency is surface defects, especially oxide species, which cause severe carrier recombination. Here we report a new method which uses CsI to passivate PbS QDs. This small inorganic molecule is alcohol dissolvable and passivates PbS CQDs well reducing the formation of oxide species dramatically. Besides Pb-I bonds, Cs-S bonds are also found on the surface, and we postulate that it will further improve passivation. We demonstrate PbS solar cells with broader depletion regions, pushing their optimal thickness higher, and hence the short-circuit current and efficiency are improved. A champion efficiency of 10.0% was obtained.

The Kelvin probe tests were done by Mr Yujiro Tazawa. TEM images were taken by Mr Daniel Gregory. PL was helped by Miss Zhanet Zaharieva. XPS was done by Dr Phil Holdway. Solar cell performances were verified by the Centre for Renewable Energy Systems Technology (CREST) in Loughborough University. All the other experiments and data analysis were done by me.

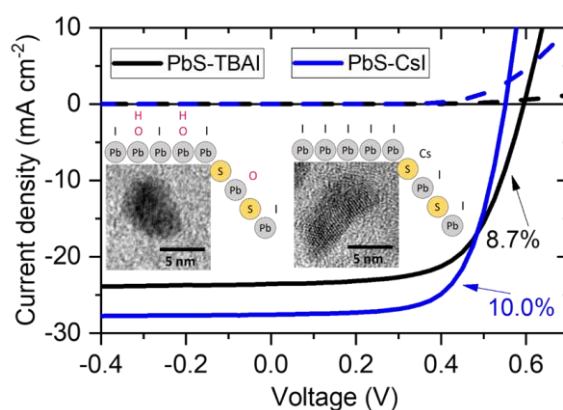


Figure 5-1 the table of content of CsI passivation on PbS CQDs. The device I-V curves under AM 1.5 of PbS-TBAI and PbS-CsI as the absorbers respectively. The inset showed a comparison of the surface passivation.

5.1 Introduction

CQD photovoltaics, as one of the emerging PV technologies, have the potential to provide low-cost, flexible, stable, and highly efficient solar cells. Despite record efficiencies up to 13.4%,^{4, 74} one obstacle towards further enhancement is surface defects present on the quantum dots, especially oxide species, for example, PbO, PbSO₄, Pb(OH)₂ etc. on PbS QDs,²² which can cause severe carrier recombination and shorten carrier diffusion lengths. Many advanced ligand exchange approaches have been reported to passivate them, thus to remove the trap states, for example by using tetrabutylammonium iodide (TBAI), 1-ethyl-3-methylimidazolium iodide (EMII), PbX₂ (I and/or Br), and perovskite.^{22, 43, 68, 121-123} However, the current ligand exchange methods, either failed to remove the defects efficiently because of the residual organic chains or required the use of toxic dimethylformamide (DMF) as the solvent. Caesium compounds have previously been used in QD PVs. For example, Zhang et al¹²³ introduced CsPbI₃ perovskite in DMF to coat PbS QDs, and Sanehira et al⁷⁴ reported CsPbI₃ QDs instead of PbS QDs for solar cell fabrications. Here we report a simple and feasible method using caesium iodide dissolved in methanol for the surface passivation. Its small inorganic molecules passivate the surface more efficiently compared to commonly used relatively long TBAI ligands, and Cs atoms are found capable of passivating the S atoms on the surface. These coincide with fewer oxide species, and hence fewer defects.

5.2 Experiments

5.2.1 CQDs synthesis

PbS CQDs and ZnO nanoparticles synthesis were conducted as discussed in Chapter 3.

5.2.2 Device fabrication

A pre-patterned ITO coated glass originally from Delta Technologies was cleaned by sonication sequentially in Decon-90, deionised water, acetone, and

isopropanol at 55 °C for 10 min. After the substrates were thoroughly dry, the solvent cleaning was followed by a UV ozone treatment for 15 min. ZnO solution was spin coated at 2000 rpm or 6000 rpm for 30 s straight after the cleaning. The substrates were then annealed at 100 °C for 10 min in the air.

50 mg/mL PbS CQD ink was spin coated at 3000 rpm for 20 s, which was then soaked in 15 mg/mL TBAI/methanol or 12 mg/mL CsI/methanol solution for 30 s before two iterations of methanol washing. This process was repeated several times until the desired thickness was reached. Another two layers of EDT-functionalised CQDs were subsequently spin coated at 2000 rpm as the HTLs. Two drops of 2% EDT-acetonitrile solution was dropped on the PbS film while it was spinning, followed by five drops of acetonitrile for rinsing. The films were placed into a shadow mask for Au evaporation defining an electrode width of 1 mm. The systems were held under vacuum for 2 h or overnight at 10^{-5} torr before starting evaporation. A deposition rate of 0.1 nm/s was conducted for Au until a thickness of 100 nm was reached.

5.3 Results and discussions

5.3.1 Better I-V performances

CsI-passivated PbS solar cells (marked as PbS-CsI) were fabricated in the same way as their TBAI-passivated counterparts (marked as PbS-TBAI) which are used as references in this work. An apparent current increase and voltage decrease are observed in Figure 5-2 a-b for PbS-CsI devices compared to PbS-TBAI ones of the same number of layers (350 nm vs 245 nm). A higher FF and PCE were also found in CsI devices (Figure 5-2 c-d). An increment of the absorber thickness usually comes with a drop of the charge collection efficiency so as FF, because the charge will be lost if their lifetime is less than the transit time, especially for PbS CQD PVs where the dominant drift-driven collection is bias dependent. A higher FF implies that the device thickness can be further increased. Thus, an optimisation of PbS-CsI thickness was conducted, as shown in Figure 5-2 and the best one is found to be 430 nm (Figure 5-2 a-d, marked as

CsI-optimised), as FF and PCE began to fall with three layers. In Figure 5-2, with the same number of layers of PbS, PbS-CsI showed a higher efficiency (9.6%) than PbS-TBAI (8.7%). With the optimised thickness, the efficiency was further enhanced to 10.0%. The reverse saturated current measured under dark conditions is an indicator of leak current and shunt resistance. Smaller current, higher shunt resistance, lower carrier recombination rate. From Figure 5-2 f, PbS-CsI and PbS-CsI-optimised devices have the same reverse saturated current as PbS-TBAI, indicating that there is no more recombination even with greater thickness. The much higher current density under the forward bias compared to PbS-TBAI implied that the carrier transport was much improved in PbS-CsI films.

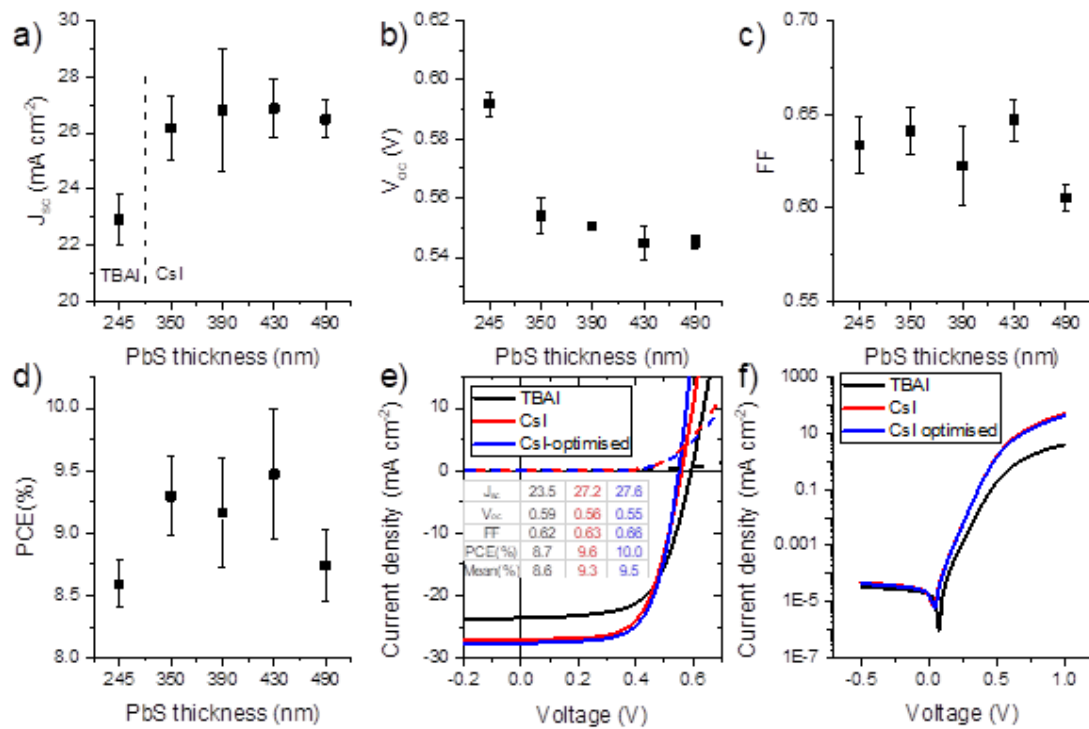


Figure 5-2 the I-V results of the TBAI and different thickness CsI devices: a) J_{sc} , b) V_{oc} , c) FF, and d) PCE. The I-V curves e) and f) dark current curves for PbS-TBAI, PbS-CsI and PbS-CsI-optimised devices. The error bars are based on statistics.

A slight hysteresis was observed on PbS-CsI-optimised devices, compared to PbS-TBAI devices (Figure 5-3 a). The photovoltaic performance of PbS-CsI-optimised devices was verified independently by the Centre for Renewable Energy Systems

Technology (CREST) in Loughborough University (Figure 5-3 b). The air I-V curves in Oxford and in CREST showed similar performances, while the performance in N₂ is better than in the air which is due that N₂ helps doped ZnO films.¹⁵ The J_{sc}, V_{oc}, and MPP performance of PbS-CsI-optimised devices were also certified by CREST, which were shown in Figure 5-4.

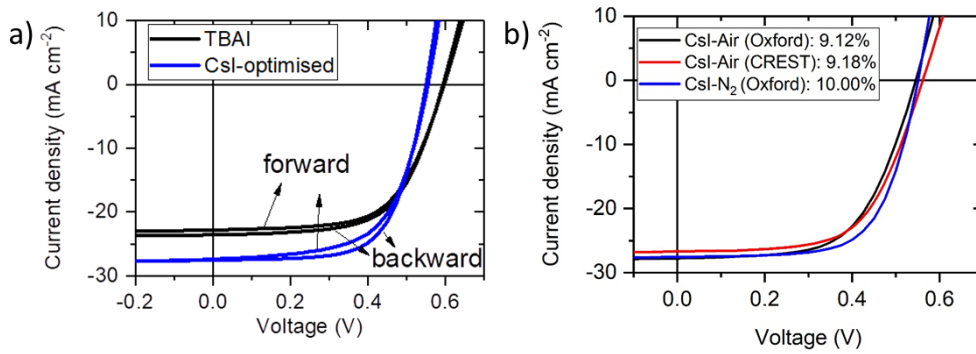


Figure 5-3 a) The forward and backward scanning I-V curves of PbS-TBAI and PbS-CsI-optimised devices. b) The I-V curves of PbS-CsI-optimised devices tested in Oxford and certificated in the Centre for Renewable Energy Systems Technology (CREST) of Loughborough University. The efficiency of the device in the air are 9.18% by CREST) and 9.12% by Oxford respectively, which proves the credibility of our results, and the efficiency in N₂ is 10.00% (Oxford).

EQE was conducted to check the spectral responses. As can be seen in Figure 5-5 a, CsI-optimised devices have obvious advantages in the range of 600-750 nm, compared to TBAI devices, which explains the higher current. From **Error! Reference source not found.** b, it can be seen that there is a redshift for the peak between 500-800 nm when increasing the thickness of PbS-CsI, which implies optical enhancement via constructive interference in the absorber layer.¹²⁴⁻¹²⁶ However, further increasing thickness will reduce the EQE at longer wavelengths between 800-1100 nm, because IR absorption mainly happens at the back of the cells and the carriers are getting harder to transport across the thicker devices. The calculated J_{sc} based on EQE is 21.9 mA cm⁻² and 24.1 mA cm⁻² respectively for PbS-TBAI and PbS-CsI-optimised devices, comparable to their I-V average results 22.9 mA cm⁻² and 26.9 mA cm⁻² respectively.

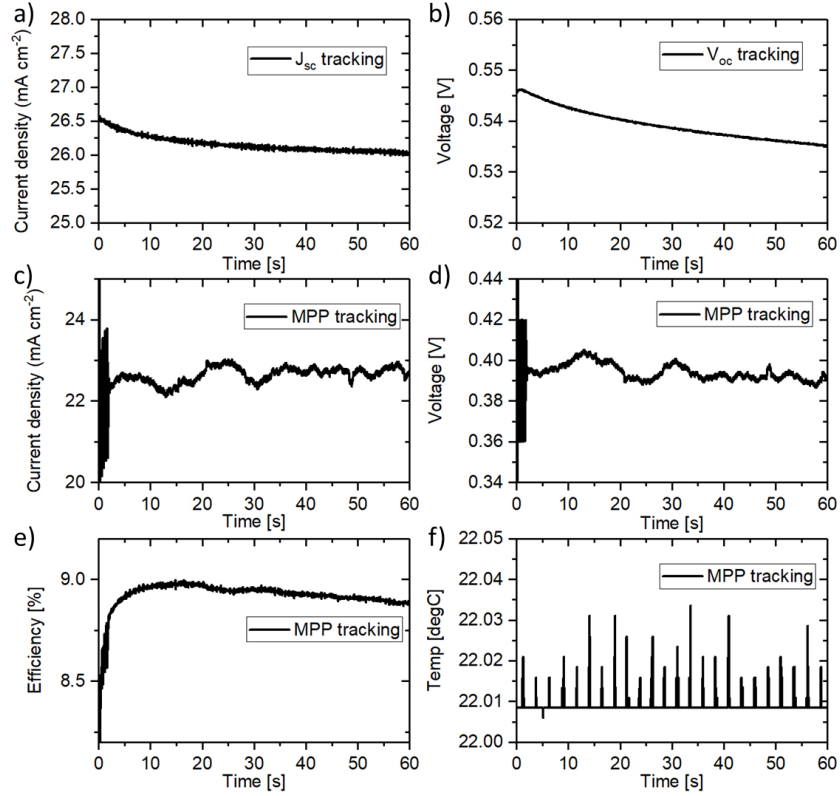


Figure 5-4 the J_{sc} tracking (a), V_{oc} tracking (b), and Maximum power point (MPP) tracking of the PbS-CsI-optimised devices: J_{MPP} tracking (c), V_{MPP} tracking (d), PCE_{MPP} tracking (e), and the temperature tracking (f). All the data was acquired in the air in CREST in Loughborough University.

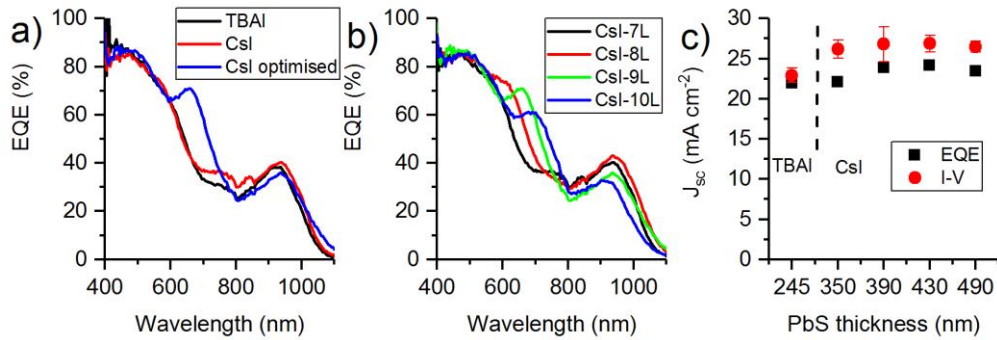


Figure 5-5 a) EQE of PbS-TBAI, -CsI, and -CsI-optimised devices. b) EQE of different thickness of PbS-CsI. c) the J_{sc} calculated from EQE and I-V curves for the TBAI and different CsI devices. The error bars are based on statistics.

5.3.2 Full ligand exchange

To understand the effect of the treatments at the PbS surface. Fourier-transform infrared (FTIR) spectroscopy for both TBAI and CsI films was used. As shown in Figure

5-6 a, the COO^- peaks around $1400\text{--}1600\text{ cm}^{-1}$ disappeared for PbS-Csl, while there is a small residue peak for PbS-TBAI, indicating that the oleic acid (OA) ligands are entirely removed on PbS-Csl. CH_2 chain peaks around $2800\text{--}2900\text{ cm}^{-1}$ in TBAI represents the tetrabutylammonium moieties. The peak at around 2300 cm^{-1} , which appeared in all three samples, is due to the carbon dioxide in the air. The UV-vis absorption spectrum in Figure 5-6 b showed that after ligand exchange the band gap of PbS was reduced from 1.39 eV to 1.35 eV on PbS-TBAI, and to 1.33 eV on PbS-Csl, indicated by its redshift of the excitonic peaks. Considering the quantum confinement effect, this implies a closer dot-to-dot distance in the order PbS-OA, PbS-TBAI, and PbS-Csl, consistent with the decreasing molecular size of the ligands. As with absorbance, the photoluminescence showed a redshift after ligand exchange as shown in Figure 5-6 c. Besides, the full-width-half-maximum (FWHM) of the PL peaks for PbS-TBAI and PbS-Csl is 124 nm and 111 nm respectively. The narrower PL peak in PbS-Csl implies it has fewer trap states in the band gap and better surface passivation of PbS.¹²³

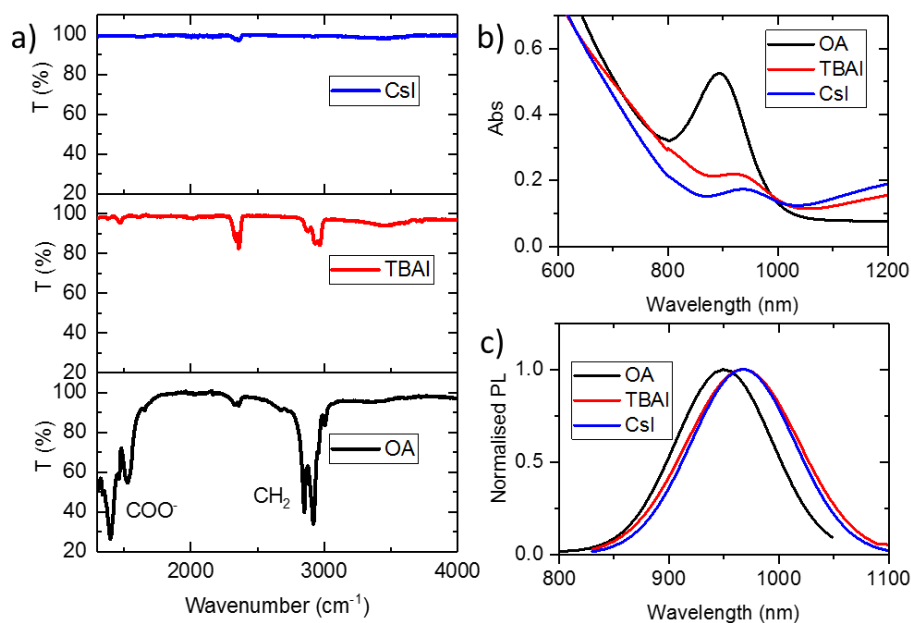


Figure 5-6 a) FTIR, b) Uv-vis, and c) normalised PL results of PbS-OA, PbS-TBAI, and PbS-Csl films. The FWHM of PbS-OA, PbS-TBAI and PbS-Csl is 103 nm , 124 nm and 111 nm respectively. PL measurements were helped by Miss Zhanet Zaharieva.

TEM was performed for PbS-OA, PbS-TBAI, and PbS-Csl samples respectively. In Figure 5-7 a-c, the PbS-OA before any ligand exchange showed a narrow size distribution centred on 2.81 nm. After ligand exchange with TBAI (Figure 5-7 d-f), the average size increased to 3.95 nm, while after the ligand exchange with Csl (Figure 5-7 g-i), it continued to increase to 4.14 nm. The larger size of PbS-Csl is due to the aggregation of QDs as shown of the big dot in Figure 5-7 h, where the dots fused together along (200) surfaces because of the short chain of Csl ligand. The size increase after ligand exchange is consistent with the band gap decrease, indicating a relaxation of the quantum confinement effect.

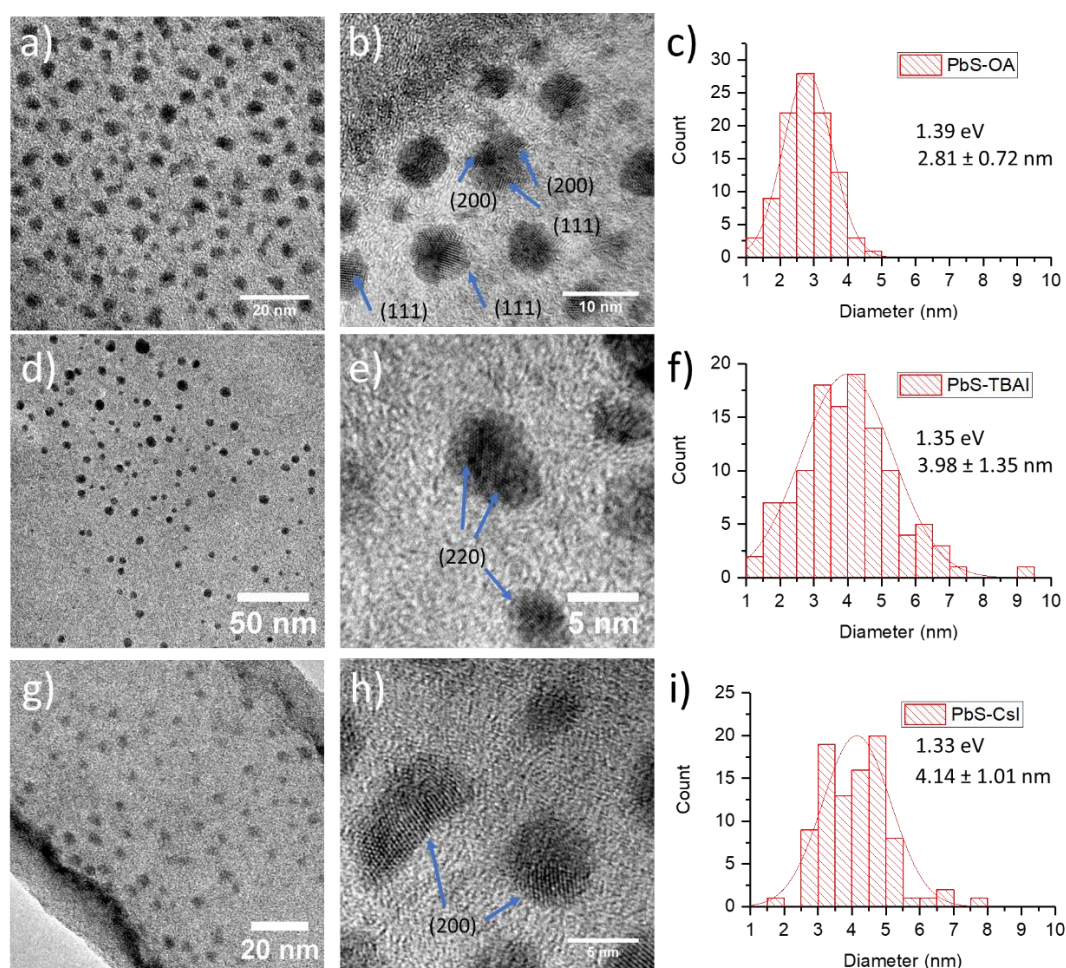


Figure 5-7 the TEM images and the histograms of diameter for PbS-OA (a-c), PbS-TBAI (d-f), and PbS-Csl (g-i) samples. TEM images were taken by Mr Daniel Gregory. The error bars are based on statistics.

5.3.3 Fewer oxide defects

X-ray photoemission spectroscopy (XPS) was further employed to characterise the PbS CQDs. The element ratio with respect to Pb atoms is summarised in Table 5-1. The O 1s spectrum in Figure 5-8 a showed a distinct decrease of oxide species after the ligand exchange with TBAI and CsI, which is consistent with the FTIR results in Figure 5-6 a that the COO^- ligands are thoroughly removed. By comparing the O 1s peak intensity of PbS-TBAI and PbS-CsI (Figure 5-8 b), it can be seen clearly that oxide species on PbS-CsI is much less than on PbS-TBAI. The O/Pb ratio was 0.45 on PbS-TBAI, while it is reduced to just 0.12 on PbS-CsI. After peak fitting, three peaks were obtained within O 1s, representing each of Pb-O bond on PbS (001) surface, Pb-OH bond on PbS (111) surface, and COO^- or CO_2 bond.^{11, 121} All three peaks on PbS-CsI were smaller than on PbS-TBAI. According to Table 5-1, there are almost no lead oxide species left on PbS-CsI, considering Pb-O and Pb-OH to Pb ratios are both just 0.02. Therefore, CsI ligand exchange resulted in a full removal of the oxides on PbS CQDs' surface.

Noticeably peak 1 (Pb-O) on PbS-TBAI is at 529.2 eV, while it is 530.3 eV on PbS-CsI. This binding energy difference for Pb-O on PbS (001) implies another bond's existence on PbS (001) surface, which is likely due to a Cs-S bond. To confirm this, S 2s peak was investigated in Figure 5-8 c. A higher binding energy of S 2s means higher valency (e.g. S^{6+}), and a lower binding energy denotes lower valency of (e.g. S^{2-}). PbS-TBAI has very similar binding energy as PbS-OA (225.1 eV vs 224.9 eV), indicating that they have the same metal-S bond (Pb-S). PbS-CsI, however, showed a much higher binding energy of 226.3 eV, which indicates a higher valency of S in PbS-CsI because a Cs-S bond has higher S valency than Pb-S bond. Considering Cs/Pb of 0.04 on PbS-CsI (Figure 5-8 d) and no S atoms on PbS (111) surface, Cs-S bonds on PbS (001) surface were confirmed.

Table 5-1 the elements ratio to Pb by XPS for different PbS films. XPS data was obtained by Dr Phil Holdway and analysed by myself.

Samples	I 3d5	Pb 4f	S 2s	Cs 3d5	O 1s	O 1s①	O 1s②	O 1s③
PbS-OA		1	0.54		3.19	0.93	0.90	1.36
PbS-TBAI	0.68	1	0.75		0.45	0.07	0.22	0.16
PbS-CsI	0.69	1	0.72	0.04	0.12	0.02	0.02	0.08

The band structure of PbS-TBAI and PbS-CsI was also investigated by valence band XPS and Kelvin probe tests. Figure 5-8 showed the gap between the valence band edge and the Fermi level of PbS-TBAI (-0.56 eV) and PbS-CsI (-1.01 eV). Considering that the band gap is 1.35 eV and 1.33 eV respectively, PbS-TBAI is an intrinsic layer (slightly p-type), and PbS-CsI is a highly n-type doping layer. The Fermi level of PbS-CsI is even deeper (5.16 eV) than TBAI (5.05 eV), resulting in a much deeper overall band structure as shown in Figure 5-8 f. This deep band structure of PbS-CsI resulted in a band misalignment with ZnO layer, creating an interface barrier and decreased its voltage output,⁹⁵ which explained its lower V_{oc} compared to PbS-TBAI.

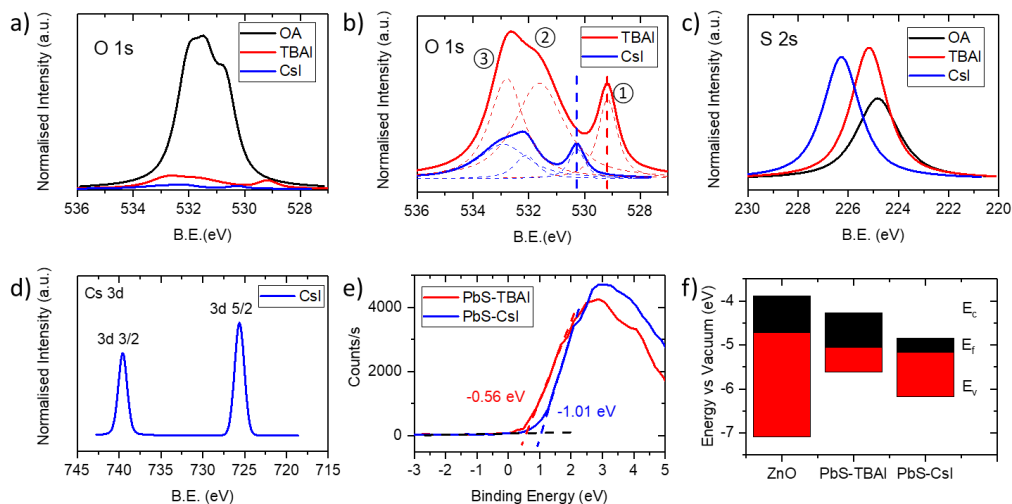


Figure 5-8 XPS results with the intensity normalised by Pb elements. a) O 1s. b) O 1s with peak fitting. c) S 2s. d) Cs 3d. e) valence band XPS. f) band structure from XPS, cyclic voltammetry, UV-vis, and Kelvin probe.

Table 5-2 the band edge energies, band gaps, and Fermi level energies: E_f by Kelvin probe, E_g by UV-vis, E_c of ZnO by CV and E_c of PbS by valence band XPS, and E_v by calculation based on E_g and E_c .

Samples	E_f	E_c	E_v	E_g
ZnO	-4.72	-3.89	-7.09	3.20
PbS-TBAI	-5.05	-4.27	-5.62	1.35
PbS-CsI	-5.16	-4.84	-6.17	1.33

5.3.4 Extended depletion width

The carrier concentration and the depletion region of CsI and TBAI devices were investigated by capacitance-voltage measurements. Figure 5-9 a shows the capacitance-voltage relations for PbS-TBAI, PbS-CsI, and PbS-CsI-optimised devices.

To simplify the calculation of carrier concentrations and depletion widths, a ZnO/PbS heterojunction was assumed with the PbS-CsI/TBAI and PbS-EDT layers considered as a whole. As with the fully depleted devices in this work (TBAI, CsI, CsI-optimised), the capacitance C at -0.5V equal to 1.71 nF, 1.59 nF, and 1.37 nF respectively. According to

$$C = \frac{A}{\frac{d_{ZnO}}{\epsilon_{ZnO}\epsilon_0} + \frac{d_{PbS}}{\epsilon_{PbS}\epsilon_0}}, \quad 5-1$$

Where A is the device area 0.025 cm^2 , d_{ZnO} is 150 nm, d_{PbS} are 245 (TBAI), 350 (CsI), and 430 nm (CsI-optimised) respectively, the permittivities of ZnO, PbS-TBAI/PbS-EDT and PbS-CsI/PbS-EDT were calculated to be 40.1, 26.7, and 34.7 respectively.¹²⁷

The Mott-Schottky analysis was conducted in Figure 5-9 b-c, and the results were presented in Table 5-3.

In heterojunction devices, the capacitance equals to

$$C = \sqrt{\frac{A^2 q \epsilon_0}{2 (V_{bi} - V) \left(\frac{1}{N_a \epsilon_p} + \frac{1}{N_d \epsilon_n} \right)}}, \quad 5-2$$

So

$$\frac{1}{C^2} = \frac{2(V_{bi} - V)}{A^2 q \epsilon_0} \left(\frac{1}{N_a \epsilon_p} + \frac{1}{N_d \epsilon_n} \right), \quad 5-3$$

Where V_{bi} is the built-in voltage, N_a and N_d are the carrier concentration of PbS and ZnO, and ϵ_p and ϵ_n are the permittivities of PbS and ZnO. The built-in voltages according to Mott-Schottky analysis are 0.67 V, 0.63 V, and 0.62 V for PbS-TBAI, PbS-CsI, and PbS-CsI-optimised devices, which fit well with the built-in voltages of 0.60 V, 0.58 V, and 0.56 V according to the light and dark curve intersections in Figure 5-2 e. Therefore, the carrier concentration of PbS, N_a , can be addressed with the assumption that the carrier concentration of ZnO, N_d , is $1E+17 \text{ cm}^{-3}$.²² The calculated acceptor carrier concentration (N_a) of the PbS layers is plotted against voltage in Figure 5-9 c. The PbS-TBAI/PbS-EDT has a carrier concentration of $2.92E+16 \text{ cm}^{-3}$, and the PbS-CsI/PbS-EDT in the PbS-CsI device and the PbS-CsI-optimised device has a concentration of $1.19E+16$ and $1.09E+16 \text{ cm}^{-3}$ respectively. This result is consistent with band energy analysis, where PbS-TBAI layers are slightly p-type and PbS-CsI layers are n-type. Therefore, when they get contacts with p-type PbS-EDT layers, PbS-CsI/PbS-EDT will have lower acceptor carrier concentration ($1.19E+16 \text{ cm}^{-3}$), compared to PbS-TBAI/PbS-EDT layers ($2.92E+16 \text{ cm}^{-3}$). When PbS-CsI got thicker, the value ($1.09E+16 \text{ cm}^{-3}$) was even lower.

The depletion width in the PbS layer is calculated according to the following equation:

$$w_p = \sqrt{\frac{2\epsilon_p \epsilon_n \epsilon_0 (V_{bi} - V) N_d}{q (N_a \epsilon_p + N_d \epsilon_n) N_a}}, \quad 5-4$$

Where w_p is the depletion width falling into the PbS layers (w_n is the depletion width falling into the ZnO layers). A donor carrier concentration (N_d) of $1E+17 \text{ cm}^{-3}$ for the ZnO layer was adopted from literature,^{22, 58} allowing the depletion width in the PbS layers to be calculated. Under 0 V bias, they are 238 nm, 430 nm, and 449 nm in PbS-TBAI, PbS-CsI, and PbS-CsI-optimised devices respectively, of which the PbS thicknesses are 245 nm, 350 nm, and 430 nm. The depletion width was enhanced 192

nm in PbS-CsI device compared to PbS-TBAI. After thickness optimisation, the depletion width in PbS-CsI-optimised devices is 211 nm wider than PbS-TBAI, which explains its much thicker optimal layers as well as its higher efficiency.

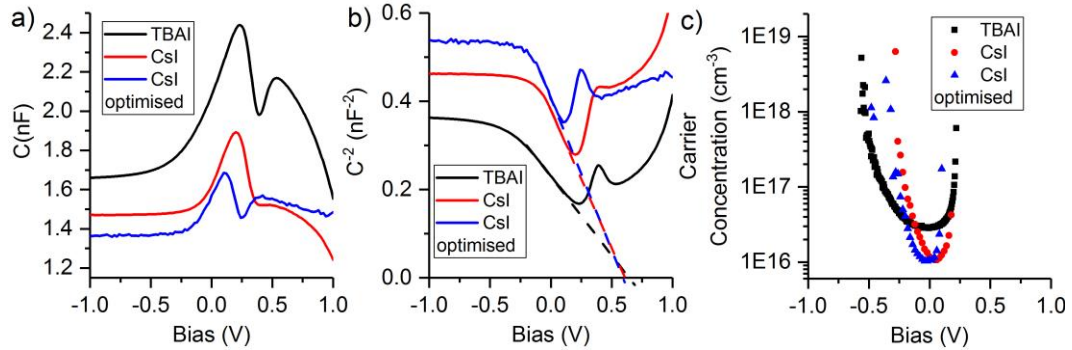


Figure 5-9 The capacitance-voltage measurements of the PbS-TBAI, PbS-CsI, and PbS-CsI-optimised devices. a) C-V. b) Mott-Schottky analysis. V_{bi} : 0.67V, 0.63 V, and 0.62V. c) the carrier concentration of the PbS layers in three devices.

Table 5-3 the parameters and results for Mott-Schottky analysis.

		TBAI	CsI	CsI optimised
Parameters	C (F)	1.71E-09	1.59E-09	1.37E-09
	Permittivity (F/m)	8.85E-12	8.85E-12	8.85E-12
	A (m ^{2})	2.50E-06	2.50E-06	2.50E-06
	d_{PbS} (m)	2.45E-07	3.50E-07	4.30E-07
	q (C)	1.60E-19	1.60E-19	1.60E-19
	N_d (cm $^{-3}$)	1.00E+17	1.00E+17	1.00E+17
Results	$d(1/C^2)/dV$ (1/(F ^{2} *V))	-3.46E+17	-6.04E+17	-6.54E+17
	Intercept(1/(F ^{2}))	2.31E+17	3.80E+17	4.08E+17
	$\epsilon_{(PbS)}$	27	35	35
	$\epsilon_{(ZnO)}$	40.1	40.1	40.1
	N_a (cm $^{-3}$)	2.92E+16	1.19E+16	1.09E+16
	V_{bi} (V)	0.67	0.63	0.62
	ω_p (nm) @ 0 V	238	430	449
	ω_n (nm) @ 0 V	69	51	49

5.4 Conclusion

In summary, here we introduced a new ligand passivation strategy by using inorganic CsI ligands in environmental friendly alcohol to passivate PbS CQDs' surface, based on which a maximum efficiency of 10% was achieved. Beside the contribution from the higher carrier transport by the CsI passivation strategy, the primary surface defects, oxide species, were reduced a lot compared to the commonly-used TABI ligands. A better passivation was also implied by its full removal of organic ligands, a narrower PL peak, and the additional Cs-S bond. A better passivation results in a lower p-type carrier concentration as well as a much larger depletion width, which illustrates the thicker optimal thickness and higher performance of the devices. Future work addressing the band misalignment at the ZnO/PbS interface is expected to improve the V_{oc} and efficiency further.

Chapter 6 High Voltage Output Microgroove-Structured Flexible PbS CQD Micro-Module Solar Cells: 9.2 V

Abstract Flexible photovoltaics are of great interest to provide high voltage and power wearable electronics. In this paper we describe the development of a microgroove-structured flexible lead sulphide based colloidal quantum dot (PbS CQD) micro-module solar cells with an open circuit voltage (V_{oc}) of 9.2 V. The device varies from planar solar cell devices in that the anode and cathode are deposited on the two walls of V-shape grooves textured in to polyethylene terephthalate (PET) substrates using glancing angle vacuum deposition. The grooves are around 100 μm wide, and 1, 5, 10, and 15 junctions are demonstrated. Despite the low currents generated due to large series resistance, the open circuit voltages correspond well to the number of junctions incorporated. To understand the physical operation of the groove devices three-dimensional (3D) characterisation techniques were used, including focused ion beam-scanning electron microscopy (FIB-SEM) across the grooves, light beam induced current (LBIC) scanning along the grooves, and layer-by-layer external quantum efficiency (LBL-EQE) measurements penetrating the grooves. With better groove CQD ink filling enhanced uniformities of coating, and optimised groove geometry, this microgroove-structured device has the potential to maximize the utilisation of light and supply much higher efficiencies in the future.

This work is a collaboration with PowerRoll Ltd, UK and the Agency for Science, Technology and Research (A*STAR), Singapore. The e-beam deposition was conducted by Dr Trevor McArdle from PowerRoll. FIB-SEM images were taken either by PowerRoll or Dr Jayce J. W. Cheng from A*STAR. All the other experiments and data analysis were done by me.

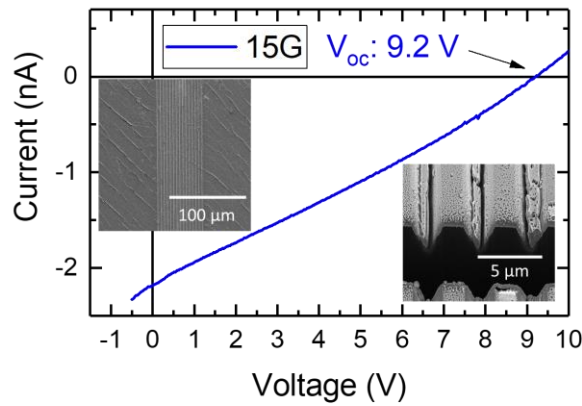


Figure 6-1 the table of content of the high voltage microgroove-structured PbS CQD micro-module solar cells. The I-V curve under AM 1.5 of a 15-groove device and its SEM image and cross-sectional FIB-SEM image.

6.1 Introduction

PbS CQD multiple junction solar cells have the potential to provide higher voltage and higher PCE, with abundant elements and solution process manufacture. With improved surface passivation and band engineering⁴³, the PCE of tandem PbS CQD solar cells have increased from 1.27% to 8.9%,^{53, 54, 80} with the highest V_{oc} at 1.13 V.⁸⁰ Monolithic structures need to be carefully designed in particular the interface between the photovoltaic junctions has to be transparent to light, highly conductive and minimise detrimental recombination processes. Recently microgroove-structured flexible substrates have been used to build multiple junction cells of CuInSe₂,¹²⁸ which removed the requirement to have a transparent interface layer and allow metal-metal connections between junctions.

However, it is expected to use cheaper materials and easier fabrication methods to achieve better performance, such as dip coating of solution-processed PbS CQDs.¹²⁹ Despite that spin coating is still the most common lab research method for solar cells, it is difficult to transfer spin coating to large-scale commercialisation. However, dip-coating, as an alternative not only for lab research but also for industrial manufacturing, has achieved comparable performance as spin-coating on planar devices.¹²⁹

In this work, microgroove-structured flexible micro-module PbS CQD solar cells (Figure 6-2 a) are reported for the first time with a high V_{oc} of 9.2 V. Using electron beam deposition metal electrodes and an n-type TiO_x are deposited on to the two walls of a V-shape grooves embossed on to a flexible PET substrate by varying the deposition angle (Figure 6-2 b). It is crucial to ensure that the top of the groove is connected to the corresponding counter electrode of the next junction while the bottom of the grooves is at open circuit. The last step is to solution deposit the CQD ink into the groove by either spin coating or dip coating the CQD ink. In this work, we optimise the ink deposition parameters using a lab-built automatic two-axis- dip coating system. Figure 6-2 C shows the top view and the side view of a device as produced. The line marked by the red arrow is the actual device which may contain a single groove or many. In the case of Figure 6-2 C, the device contains 15 grooves as can be seen in the optical microscopy image.

Successful devices for multiple grooves such as 5, 10, and 15 were achieved with the evidence of its linearly increased V_{oc} output. However, more grooves, poorer PCE. A single groove device showed a PCE of 0.094%, while with 15 grooves it decreased to 0.005%. The low efficiency is mainly due to its low current, the origin of which was then examined by the 3D characterisation of the groove devices with beam spot current scanning along the grooves, cross-sectional FIB-SEM across the grooves, and layer-by-layer EQE penetrating the grooves.

6.2 Experiments

6.2.1 PbS CQDs synthesis

PbS CQDs (1.40 eV) synthesis has been reported in Chapter 3. It was stored at 50 mg/mL in octane for spin coating and diluted to be 10 mg/mL for dip coating.

6.2.2 Device fabrications

Electrode e-beam deposition. Electrode e-beam deposition was mainly finished by Dr Trevor McArdle from PowerRoll Ltd. Grooves with width and depth both about 2 μm are pre-carved on flexible polyethylene terephthalate (PET) substrates.

Aluminium (and silver) was e-beam-deposited first on one wall of the grooves as the anode, which was followed by Ni (Mo) deposition with different deposition angles on the other wall as the cathode, creating an open circuit bottom and all grooves connected in series. Subsequently, TiO_x were e-beam-deposited on the Al (and Ag) wall as the n-type layer, which will be followed by merely spin coating or dip coating of PbS CQD inks into the grooves to finish the devices. Single groove devices were fabricated based on Al and Mo electrodes. In multiple-groove devices, the Al electrode was protected by another layer of Ag, and Mo was replaced by Ni.

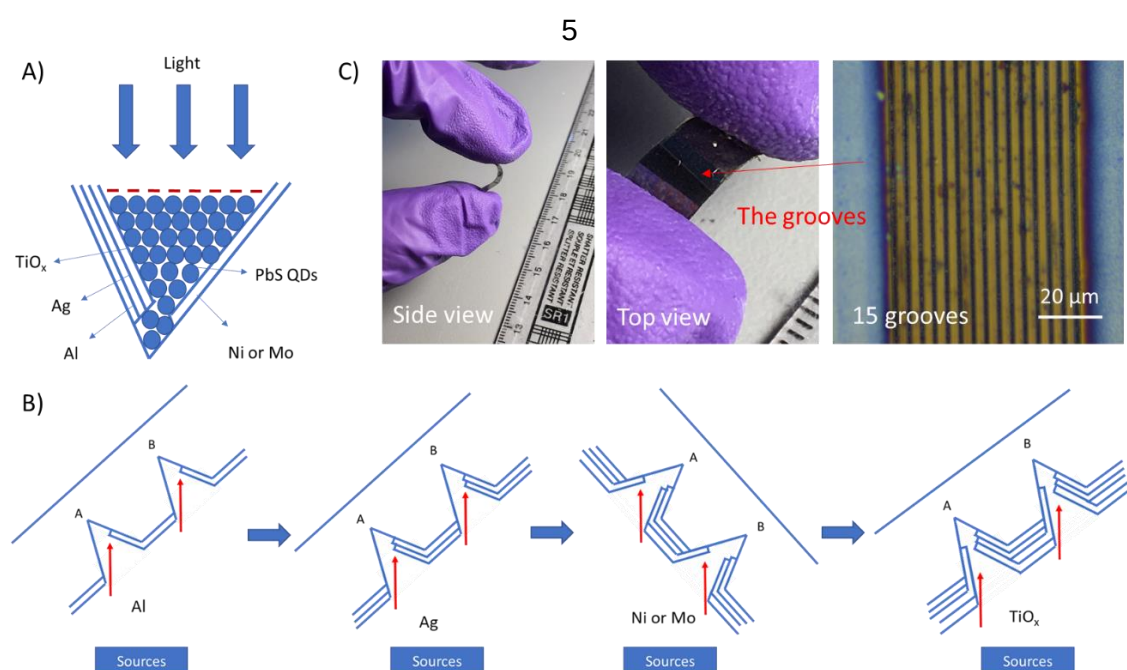


Figure 6-2 Flexible microgroove-structured micro-module PbS CQD photovoltaics. A) schematic of microgroove structured PbS CQD solar cells; **B)** the e-beam deposition process; **C)** the actual groove devices besides a ruler (mark-space 1 mm) and its optical image.

Spin coating process. With a 5-mm wide flexible substrate pasted on a glass slide, 50 mg/mL PbS ink was spin coated at a rate of 2000 rpm or 6000 rpm for 20 s. Subsequently, 15mg/mL TBAI in methanol was coated on the surface for 30 s before being washed away by methanol with spinning. The process is repeated several times until the desired thickness is achieved.

Dip coating process. The dip coating process was controlled and conducted automatically by a two-axis movement controller with a pre-designed program. With a 5-mm wide flexible substrate pasted on a glass slide, the slide was dipped into 10 mg/mL PbS CQD inks for 5s and then pulled out at a low rate of 2 cm/s. Excess PbS ink was removed by touching the slide bottom on a paper for three times. Then the dry film was soaked into 15 mg/mL TBAI/methanol solution for 30 s, which was followed by dipping the film into methanol three times for washing. The film was kept still for drying for 1 min before the next cycle. The process is repeated several times until the desired thickness was achieved.

6.2.3 Characterisations

I-V curves. I-V curves were measured using a Keithley 2400 source meter. An AM 1.5 solar spectrum illumination was produced by an ABET Sunlite solar simulator (model 11002). The power density of the light source was calibrated with a calibrated Si reference cell from ABET Technologies (model 15151). The length of the grooves, which was determined by a microscope, multiplying the groove width and the groove numbers will give the area of the grooves, which was used to calculate the solar cells' performance. Due that the grooves were not fully filled up, the active area is smaller, so that the PCEs are underestimated. The actual PCE is only provided when specifically explained.

Focused ion beam – Scanning electron microscopy (FIB-SEM). FIB-SEM images were taken either by PowerRoll or Dr Jayce J. W. Cheng from A*STAR. FIB cross-sections were milled on an FEI Helios 600 FIB-SEM. SEM images were taken either with or without any protective layers. When protection is needed, electron-beam and ion-beam platinum protective layers were deposited prior to milling. All the images were tilt corrected.

Light beam induced current (LBIC) scanning. LBIC scanning was conducted to research how the current varies along the grooves. With the current measured by a Keithley 6485 picoammeter, a fibre of an internal diameter of 400 μm was placed on the grooves as closely as possible, and the other end of the fibre was positioned under AM

1.5. The scanning is done by moving the fibre along the grooves with a step of 50 μm for 2 mm. The current was recorded for each point when it reached its maximum by fine adjustment of the fibre position across the grooves.

External quantum efficiency (EQE). EQE was tested with an Oriel 1/8 m monochromator coupled to a quartz tungsten halogen lamp. 410, 600, and 1000 nm filters were used to remove the second-order grating effects. The beam was chopped at a frequency of 220 Hz by a Bentham 218 chopper controller. Solar cell devices were connected to a Bentham 225 lock-in amplifier, and a Keithley 6485 picoammeter. A fibre of internal diameter 400 μm with one end under the beam was placed on the grooves where the device reached its maximum current at 500 nm. Calibrated photodiodes from Newport (818-UV and 918-IR) were used to measure the photon flux of the beam, and the actual photons on the grooves were calculated based on its area ratio to the beam size.

6.3 Results and discussions

6.3.1 Performances: Single and multiple groove devices

a. Single groove devices

To optimise single junction photovoltaic performance, layer-by-layer films were created by spin-coating at either 2000 rpm or 6000 rpm on a single groove substrates oleic acid capped PbS CQD and exchanging the oleic acid with tetrabutylammonium iodide (TBAI). Current-voltage (I-V) performance is shown in Figure 6-3 A-D. A noticeable difference was found between the low coating rate and the higher one. Higher coating rates lead to better photovoltaic performance which is thought to be due to creating thinner layers at higher speeds and hence improved ligand exchange (as shown in Figure 6-4). The J-V curves in Figure 6-3 E show that the highest PCE is 0.052% for 2000 rpm, while the highest PCE for 6000 rpm is improved to 0.094% mainly because of the enhancement of the current density from 0.56 mA cm^{-2} to 0.80 mA cm^{-2} . Comparing SEM images (Figure 6-3 F-G), it is found that the 6000 rpm one has better

coating quality than the 2000 rpm one, as there are more voids in the 2000 rpm sample compared to the 6000 rpm one, which further supports the hypothesis that higher speeds result in thinner denser CQD films.

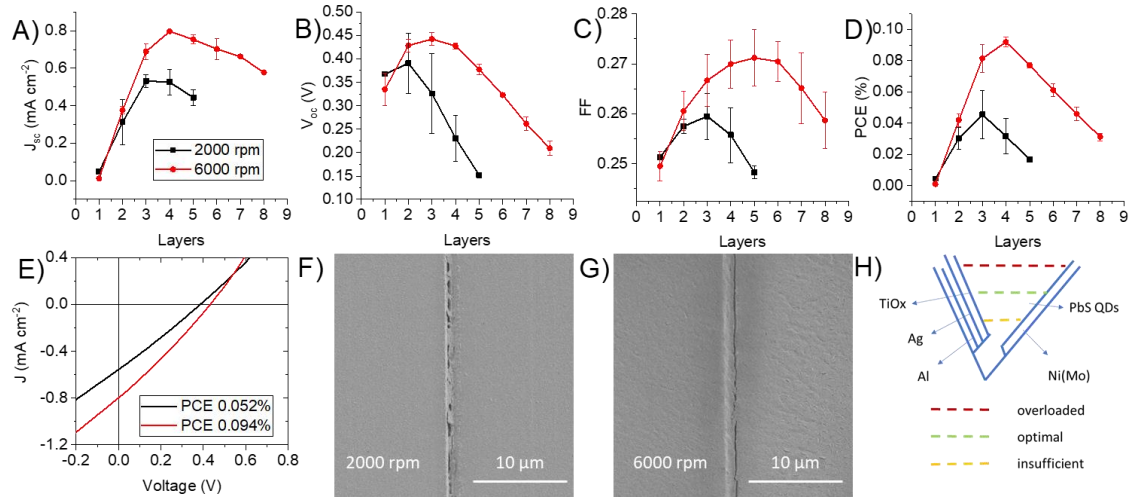


Figure 6-3 Single groove devices' performance. the I-V performances of different spin coating rates of PbS CQDs ink: A) J_{sc} ; B) V_{oc} ; C) fill factor; D) PCE; E) I-V curves; F) SEM images of 2000 rpm devices; G) SEM images of 6000 rpm devices; and H) a diagram explaining the volcano-shaped curves. As can be seen, there are more voids in the 2000 rpm device than the ones in the 6000 rpm device. SEM images taken by Dr Jayce Cheng.

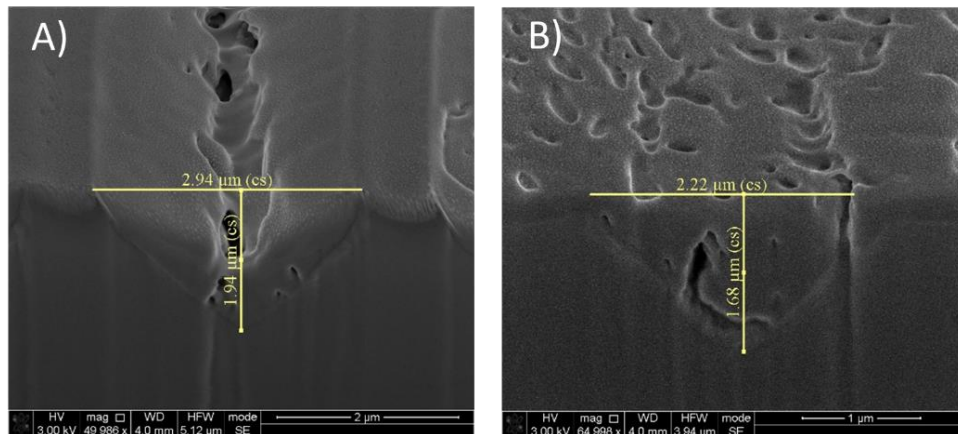


Figure 6-4 the FIB-SEM images of the devices of different coating rates at 1000 rpm (a) and 500 rpm (b) for six layers respectively: 500 rpm results in much thicker layers (1.94 μm) compared to the ones at 1000 rpm (1.68 μm). The thicker a layer, the less efficiently the ligand exchange. Corrected scales (cs) for tilt. FIB-SEM images taken by PowerRoll.

The device characteristic for the two spin-coat-speed samples is relayed in Figure 6-3 A-D. All showed volcano-shaped responses with more layers of coating

leading to a higher filling of the grooves up to a critical thickness (Figure 6-5 showed cross sections of the grooves when they are filled). At first, when the filling level is low at the yellow line level in Figure 6-3 H, the charge transport is efficient, but the active materials have an insufficient thickness to absorb the bulk of the solar spectrum. However, when it exceeds its optimal thickness to be the red line level, the distance between two electrodes are too wide to collect the carriers, because the groove width is about 2 μm , which is much beyond the typical diffusion length plus the depletion region width (in total 200-300 nm) in a PbS CQD solar cell. Therefore, the top layer contributes less but absorbs a lot of light. Thus, an optimal filling level (like that of the green line in Figure 6-3 H) is needed for each device, to provide the highest PCE.

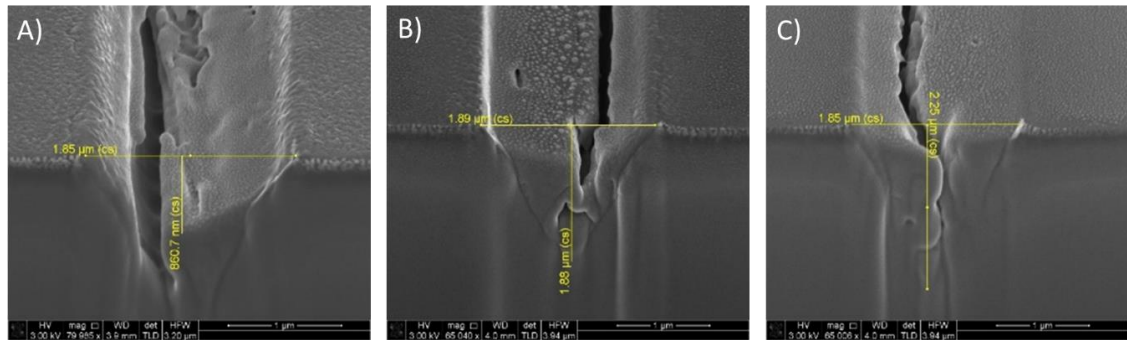


Figure 6-5 the FIB-SEM images for a) 3-, b) 6-, and c) 9-layers PbS-TBAI at 2000 rpm in the grooves: three layers of PbS-TABI at 2000 rpm filled half of the groove, with six layers filling about 85% and nine layers filling about 95%. Corrected scales (cs) for tilt. FIB-SEM images taken by PowerRoll.

b. Multiple groove devices: high voltage and low current

The multiple groove devices were fabricated by dip coating based on 5-groove (5G), 10-groove (10G), and 15-groove (15G) substrates respectively. With different filling up of the grooves, varying photovoltaic performances are obtained as shown in Table 6-1.

Table 6-1 the photovoltaic performances of 5G, 10G, and 15G devices with different dip coating layers. The highest voltage outputs for three different grooves are 2.79 V, 5.87 V, and 9.20 V respectively.

Devices	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE
5G-2L	0.0106	2.75	0.27	0.0078%
5G-3L	0.0237	2.79	0.25	0.0168%
5G-4L	0.0345	2.71	0.26	0.0242%
5G-5L	0.0426	2.48	0.23	0.0245%
5G-6L	0.0493	2.69	0.27	0.0356%
5G-7L	0.0477	2.54	0.25	0.0307%
10G-2L	0.0025	4.96	0.27	0.0034%
10G-3L	0.0059	5.65	0.26	0.0088%
10G-4L	0.0090	5.69	0.27	0.0136%
10G-5L	0.0107	4.90	0.29	0.0152%
10G-6L	0.0085	5.87	0.26	0.0131%
10G-7L	0.0091	5.63	0.26	0.0130%
10G-8L	0.0110	4.71	0.26	0.0135%
15G-2L	0.0013	7.93	0.27	0.0027%
15G-3L	0.0019	8.58	0.27	0.0044%
15G-4L	0.0020	8.92	0.28	0.0050%
15G-5L	0.0019	8.95	0.28	0.0048%
15G-6L	0.0013	9.20	0.27	0.0032%
15G-7L	0.0005	8.64	0.34	0.0013%

As can be seen in Figure 6-6 a, the highest V_{oc} outputs for 5G, 10G, and 15G are 2.79 V, 5.87 V, and 9.20 V respectively, which are about 5, 10, and 15 times of a single junction PbS solar cell around 0.60 V. This proves that successful micro-modules were achieved. As far as we know, 9.20 V is currently the highest tandem V_{oc} among the reported ones.^{53, 54, 80, 81, 83, 85, 86, 128} The I-V curves for highest PCEs were also shown in

Figure 6-6 a. The PCE decreased from 0.0356% on 5G, to 0.0152% on 10G, and to 0.0050% on 15G. The PCE decrease is consistent with the decrease of the current, from 23.5 nA of 5G to 10.5 nA of 10G, to 3.5 nA of 15G, which theoretically should stay the same no matter how many more grooves are added in series.

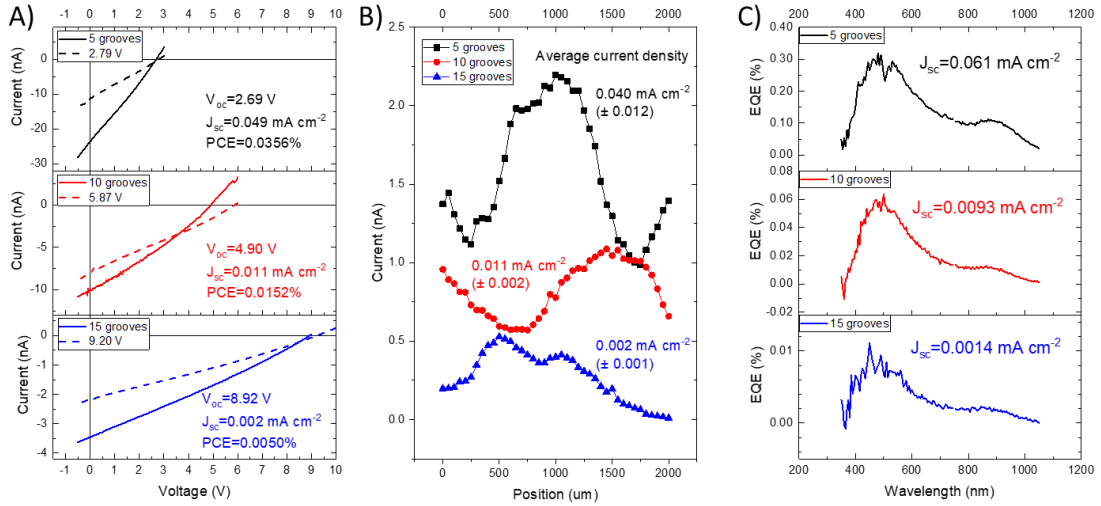


Figure 6-6 Multiple groove devices' performance. A) I-V curves under AM 1.5, solid: the highest PCE curves, dash: the highest V_{oc} curves; B) LBIC scanning along the grooves under AM 1.5 for the highest PCE devices; and C) EQE results of 5G, 10G, and 15G devices for the highest PCE devices. In the 5G (10G or 15G) tandem device, it was 5 (10 or 15) photons to be 1 electron. All three types of measurements showed the same order in terms of J_{sc} : 5G>10G>15G, and all the values showed proper consistency with each other.

6.3.2 3D characterisations

Successful devices for multiple grooves such as 5, 10, and 15 were achieved with the evidence of its linearly increased V_{oc} output. However, with more grooves, the PCE drops. The low efficiency is mainly due to its small current, the origin of which was then examined by the 3D characterisation of the groove devices with FIB-SEM across the grooves (x-axis), light beam induced current (LBIC) scanning along the grooves (y-axis), and layer-by-layer EQE penetrating the grooves (z-axis), the axis are defined in Figure 6-7 A.

a. X-axis: Cracking

The short-circuit current density of 1G, 5G, 10G, and 15G devices is 0.800, 0.049, 0.011, and 0.002 mA cm⁻² respectively, which are much lower compared to the theoretical limit for 1-, 5-, 10-, and 15-junction monolithic tandem devices' 40.89, 8.18, 4.09, and 2.73 mA cm⁻² assuming that all the photons with wavelengths smaller than 1050 nm are converted to be electrons. One of the main reasons for the low current density is due to the cracking in the grooves, which can be seen clearly in X-axis FIB-SEM images of a 15G device in Figure 6-7. The cracking is due to the volume shrink of the PbS active layers during the ligand exchange process, as the long chain oleic acid is replaced by the short ones. This cracking will, of course, cut off the carrier transport path to the anode and the cathode, causing serious recombination. Due to the impact of the centrifugal force during the spin coating process, the cracking will be more severe. Therefore, we moved to using dip coating as a mild method was considered (Figure 6-9) and proven beneficial to increase the PCE (Figure 6-8**Error! Reference source not found.**), which was applied to all the multiple groove devices.

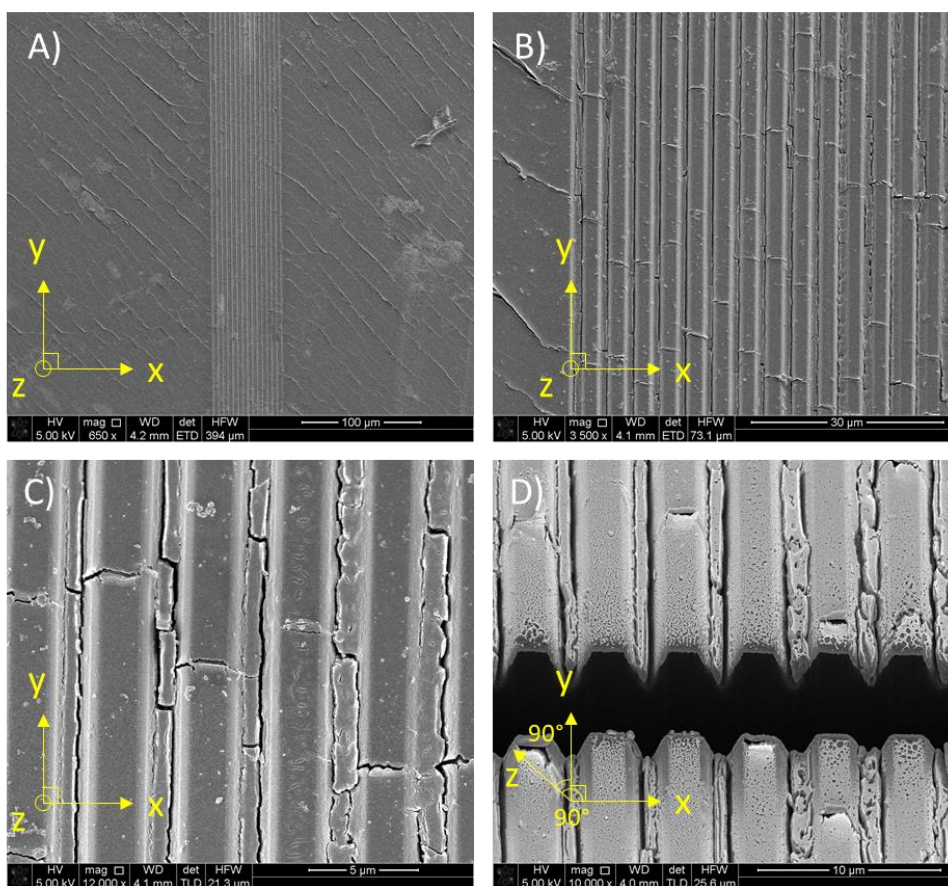


Figure 6-7 FIB-SEM images. (A-D) the FIB-SEM images of a 15G device under different magnifications without any protection layers. The x, y, and z-axis were defined in a). x: across the grooves. y: along the grooves. z: penetrating the grooves. The tilt degree for D is 63°. Scale bars corrected for tilt. FIB-SEM images taken by PowerRoll.

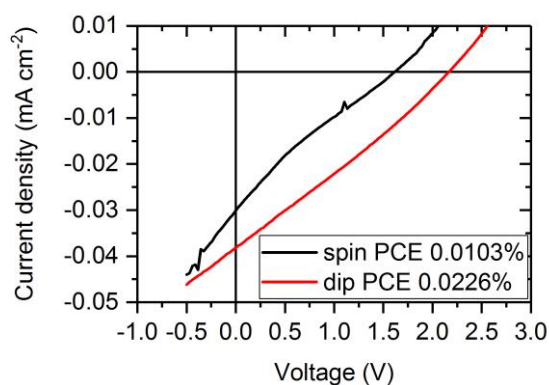


Figure 6-8 I-V curves of spin coating and dip coating on 4-groove substrates with Ag and Ni as the electrodes: dip coating showed higher PCE of 0.0226% compared to the spin-coated ones' 0.0103% for 4-groove devices.

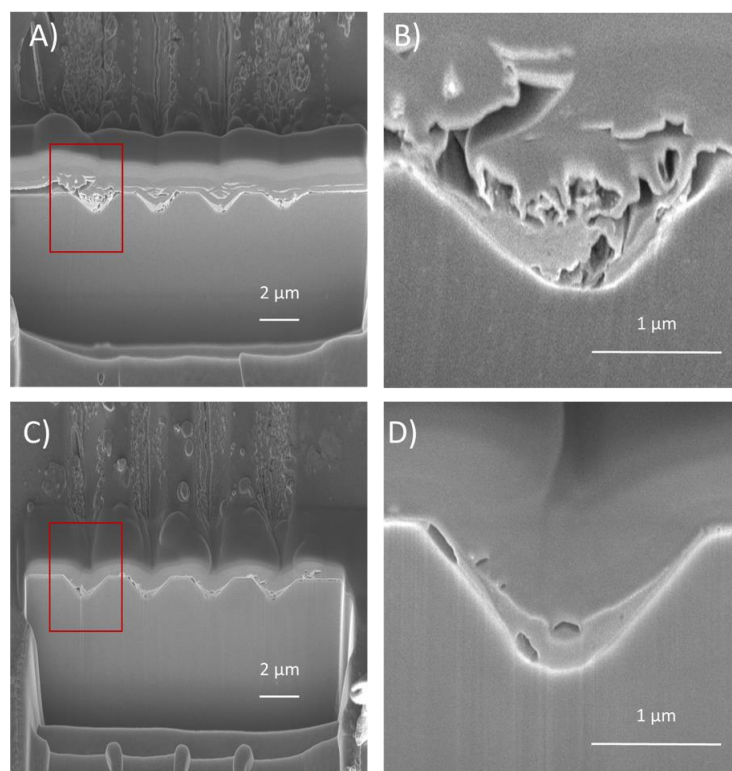


Figure 6-9 Cross-sectional FIB-SEM images of (A-B) spin-coated 4-groove devices, and (C-D) dip-coated 4-groove devices. The FIB-SEM images were taken with a carbon coating. FIB was done on JEOL JIB-4500 Multibeam, and SEM was done on Zeiss Gemini SEM 500. The cracks on spin-coated samples are more severe. Scale bars have been corrected for tilt. FIB-SEM images taken by PowerRoll.

b. Y-axis: Current loss origin with more grooves

The current decrease with more grooves can be either because of the solar cell quality fluctuations along the grooves or due to the connections across the grooves. To figure out how the current varies along the grooves, light beam induced current (LBIC) scanning along the Y axis was conducted using a 400 μm diameter fibre connected to an AM 1.5 Xenon lamp. The current variation along an arbitrary 2 mm of the groove was presented in Figure 6-6 b. It clearly showed that the 5G current is larger than 10G's, and 10G's is larger than 15G's. This independence from Y axis indicates that it is not the quality fluctuation along the grooves that results in lower overall current with more grooves, otherwise, at some points, the current of 5G, 10G, and 15G will have a lot of overlaps. Therefore, the current loss is mainly due to the incompatibility of many single

groove cells, as the tandem current is always the same as the worst groove's. To confirm the J_{sc} , EQE was compared among the three in Figure 6-6 c. The integral J_{sc} based on AM 1.5 were 0.061, 0.0093, and 0.0014 mA cm^{-2} for 5G, 10G, and 15G respectively. With all three methods above (Figure 6-6), the J_{sc} of all three devices showed good consistency.

c. Z axis: Vertical current contribution

The V shape grooves' width changes with depth, resulting in depth dependent external quantum efficiency. The configuration of the vertical current contribution along the Z axis will help design more efficient solar cells. A layer by layer EQE test was done on 15G devices with 2 layers, 3 layers, and 4 layers coating respectively (Figure 6-10 a). The J_{sc} calculated based on EQE for 2L ($J_{sc}2L$), 3L ($J_{sc}3L$), and 4L ($J_{sc}4L$) devices are 0.00222, 0.00278, and 0.00142 mA cm^{-2} . The highest current happens on 3L devices. When the 4th layer was applied, the current decreased to 0.00142 mA cm^{-2} .

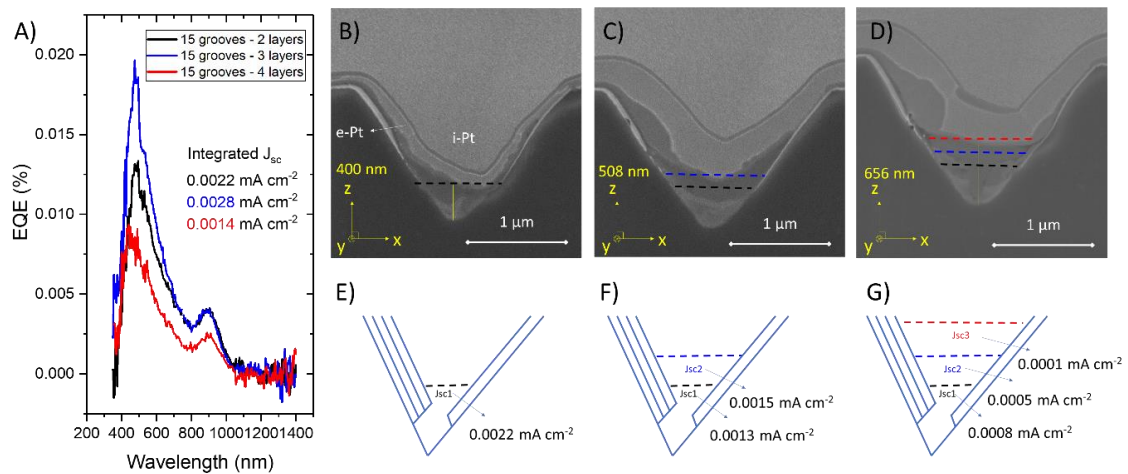


Figure 6-10 Vertical current contribution configuration. Layer-by-layer EQE curves for 15G devices with different layers of coating (A), and cross-sectional FIB-SEM images and vertical current contribution configuration in 15G-2L (B and E), 15G-3L (C and F), and 15G-4L (D and G) devices. Samples for FIB-SEM were coated with electron-deposited and ion-deposited Pt before the images were taken. Scale bars corrected for tilt. FIB-SEM images taken by Dr Jayce Cheng.

To figure out each layers' contribution, the light intensity at the 3L/4L and 2L/3L interfaces is calculated based on the absorbance coefficient and the above layer's thickness (Figure 6-11).

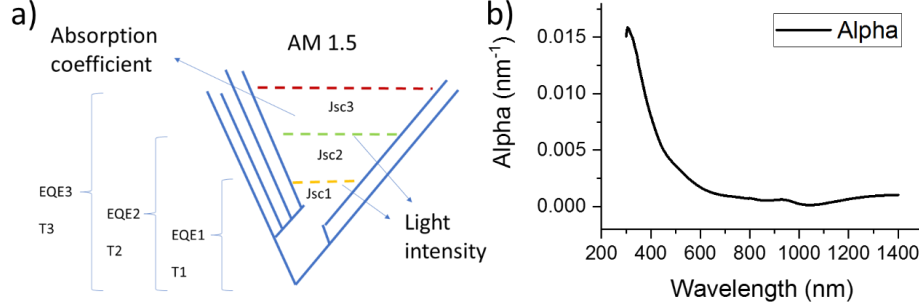


Figure 6-11 (a) The parameters needed to calculate the vertical current contribution for 15-2L, 15-3L, and 15-4L devices. (b) The absorption coefficient (alpha) of dip-coated PbS films. EQE1, EQE2, and EQE3 are the EQE of 15-2L, 15-3L, and 15-4L devices respectively. T1, T2, and T3 are the thickness of 15-2L, 15-3L, and 15-4L devices respectively. Jsc1, Jsc2, and Jsc3 are the current contributions of the first two layers, the third layers, and the fourth layer respectively.

In the 2L device (Figure 6-10 B and E), its current contribution:

$$J_{sc1} = J_{sc}(2L) \quad , \quad 6-1$$

where $J_{sc}(2L)$ is the J_{sc} calculated based on 15-2L device's EQE curve. J_{sc1} simply equals to the J_{sc} calculated directly from the EQE, $0.0022 \text{ mA cm}^{-2}$.

As to 3L devices (Figure 6-10 C and F), its current contribution:

$$J_{sc1} = \int EQE1(\lambda) * AM1.5(\lambda) * 10^{-\alpha(\lambda)*T2} d(\lambda) \quad ; \quad 6-2$$

$$J_{sc2} = J_{sc}(3L) - J_{sc1} \quad , \quad 6-3$$

where λ is the wavelength, α is the absorption coefficient, $J_{sc}(3L)$ is the J_{sc} calculated based on 15-3L device's EQE curve, EQE1 is the EQE of 15-2L, and T2 is the thickness of the 3rd layer of coating. J_{sc2} contributes $0.0015 \text{ mA cm}^{-2}$, while J_{sc1} contributes $0.0013 \text{ mA cm}^{-2}$, lower than the counterpart in 15G-2L.

In the 4L device (Figure 6-10 D and G), its current contribution

$$J_{sc1} = \int EQE1(\lambda) * AM1.5(\lambda) * 10^{-\alpha(\lambda)*(T2+T3)} d(\lambda) ; 6-4$$

$$J_{sc2} = \int EQE2(\lambda) * AM1.5(\lambda) * 10^{-\alpha(\lambda)*T3} d(\lambda) - J_{sc1} ; 6-5$$

$$J_{sc3} = J_{sc}(4L) - J_{sc1} - J_{sc2} , 6-6$$

Where $J_{sc}(4L)$ is the J_{sc} calculated based on 15-4L's EQE curve, EQE2 is the EQE of 15-3L, and $T3$ is the thickness of the 4th layer of coating. J_{sc1} and J_{sc2} contribution decrease to $0.0008 \text{ mA cm}^{-2}$ and $0.0005 \text{ mA cm}^{-2}$, which is due that the top J_{sc3} layer absorbs a lot of light while contributes almost nothing ($0.0001 \text{ mA cm}^{-2}$) because of its less efficient carrier extraction properties. Therefore, a better design of the groove geometry to fit the best parts of the configuration will lead to higher PCE.

6.4 Conclusions

In this work, we have developed a flexible microgroove-structured micro-module PbS CQD solar cells with open circuit voltages as high as 9.2 V using dip coating methods, which can be easily transferred to be large scale manufacturing. To understand the operation of the micro-module devices, the low efficiency of the devices is mainly limited by its poor current, which was characterised by three-dimensional methods, including x-axis cross-sectional FIB-SEM, y-axis light-beam-induced current scanning, and z-axis layer-by-layer EQE. The cracks along the grooves, and the incompatibility of different grooves, and the low EQE on the top the devices are the main reasons for the small currents. With the better filling of the grooves, enhanced uniformities of coating, and optimised groove geometry, a jump of the efficiency is expected.

Chapter 7 Conclusions and future work

In this thesis, we have explored three ways to enhance PbS CQD solar cells' performance, including band alignment engineering, quantum dot passivation, and smart device architecture design.

It is found that by using narrow band gap PbS-EDT layers as the HTLs, the extraction of the carrier is improved which is due to an improved interfacial band alignment proved by Kelvin probe and cyclic voltammetry. Smaller band gap PbS is found easier to be oxidised, or p-type doped, by oxygen. With the combination of TBAI and EDT as the absorber and HTLs' ligands, the best bandgap combination of 1.38eV/1.12eV was obtained through optimisation, with an efficiency of 9.33%. A favoured band alignment between electron transport layers and absorber layers are also needed to suppress carrier recombination at the interface. Surface modification to either ZnO or PbS absorber needs to be done to align the band structure well.

By using alcohol-dissolvable CsI as the ligand for PbS CQDs, a better surface passivation was achieved. Compared to commonly used TBAI, CsI resulted in much fewer oxide defects and additional Cs-S bonds, and narrow PL peaks also implied its better passivation. A much larger depletion region was consequently achieved so as a much larger optimal thickness of the devices. An efficiency of 10% was obtained. Oxide species removal improved the efficiency and the current density, while the V_{oc} was lowered down. This is because the deep band edges of PbS-CsI enlargers its band misalignment with ZnO. A doped ZnO or inserting a buffer layer will be beneficial.

A microgroove-structured flexible PbS CQD tandem solar cell is reported for the first time with a record V_{oc} of 9.2 V. This device was achieved by easy fabrications of automatic dip coating. The reasons for its poor efficiency was investigated by three-dimensional characterisations. Reducing the cracks, improving the combability, and optimising the groove geometry will lead to higher performances.

All the work in this thesis used solid-state ligand exchange for PbS CQD film depositions. However, a better passivation through liquid-state ligand exchange will passivate the QDs better, result in the denser packing of the films, and improve the efficiency further. Besides, it may also reduce the cracks in the microgroove-structured devices, dramatically enhance its carrier transport, increase its current density so as its efficiency. More work needs to be done in the future.

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